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WATER ENCYCLOPEDIA



Ground Water

Edited by
JAY H. LEHR
JACK KEELEY

GROUND WATER

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PREFACE

Throughout history, groundwater has played a major role in providing the resource needs of the world. It accounts for 97% of the world's freshwater and serves as the base flow for all streams, springs, and rivers. In the United States, one half of the population relies on groundwater for its drinking water and is the sole source of supply for 20 of the 100 largest cities. Well over 90% of rural America is totally dependent on groundwater. An inventory of the total groundwater resources in the United States can be visualized as being equal to the flow of the Mississippi River at Vicksburg for a period of 250 years.

One of the first groundwater scientists was a French engineer who was in charge of public drinking water in Dijon. In 1856, Henri Darcy conducted experiments and published mathematical expressions describing the flow of water through sand filters. His work remains one of the cornerstones of today's groundwater hydrologists. At about the same time, a Connecticut court ruled that the influences of groundwater movement are so secret, changeable, and uncontrollable that they could not be subject to regulations of law, nor to a system of rules, as had been done with surface streams.

In this volume of the *Water Encyclopedia*, we have attempted to erase the ignorance that existed in the early years of groundwater science by presenting the most current knowledge on the subject as provided by authors from around the globe. In addition to excellent articles from many American scholars, equally superb writings from such diverse countries as England, Nigeria, India, Iran, Thailand, and Greece are provided.

As the origins of the selected articles are diverse, so are the subjects of discussion. Along with straightforward descriptions of basic groundwater concepts (drawdown around pumping wells, hydraulic head, field capacity, and flow), the reader is introduced to more complex subjects (isotope technologies, aquifer tests, *in situ* remediation, tritium dating, modeling, and geophysical properties). There are also articles for more practical applications (well maintenance, subsurface drainage, nitrate contamination, tracer tests, well yields, and drilling technologies). Of course, for the more fanciful reader, we have selected articles that remind us of the way windmills sounded at night, the ancient use of qanats in Persia to provide sustainable groundwater resources, and the development of Darcy's Law.

In the end, we feel that the information provided will afford an educational home for readers approaching the *Water Encyclopedia* from a variety of needs as well as different levels of scientific acumen. We are also confident that many readers will simply be expanding their knowledge base by these sets of enjoyable reading.

Jay Lehr
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Naresh Singhal, *University of Auckland, Auckland, New Zealand,* Bacteria Role in the Phytoremediation of Heavy Metals, Sub-Surface Redox Chemistry: A Comparison of Equilibrium and Reaction-Based Approaches

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Q. Zhang, *(from Phytoremediation: Transformation and Control of Contaminants, Wiley 2003),* Phytoremediation of Methyl *Tertiary*-Butyl Ether

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ACID MINE DRAINAGE: SOURCES AND TREATMENT IN THE UNITED STATES

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Acid mine drainage (AMD) occurs when metal sulfides are exposed to oxidizing conditions. Leaching of reaction products into surface waters pollute over 20,000 km of streams in the United States alone. Mining companies must predict the potential of creating AMD by using overburden analyses. Where a potential exists, special handling of overburden materials and quick coverage of acid-producing materials in the backfill should be practiced. The addition of acid-neutralizing materials can reduce or eliminate AMD problems. Placing acid-producing materials under dry barriers can isolate these materials from air and water. Other AMD control technologies being researched include injection of alkaline materials (ashes and limestone) into abandoned underground mines and into buried acid material in mine backfills, remining of abandoned areas, and installation of alkaline recharge trenches. Chemicals used for treating AMD are $Ca(OH)_2$, CaO, NaOH, Na_2CO_3, and NH_3, with each having advantages under certain conditions. Under low-flow situations, all chemicals except $Ca(OH)_2$ are cost effective, whereas at high flow, $Ca(OH)_2$ and CaO are clearly the most cost effective. Floc, the metal hydroxide material collected after treatment, is disposed of in abandoned deep mines, refuse piles, or left in collection ponds. Wetlands remove metals from AMD through formation of oxyhydroxides and sulfides, exchange and organic complexation reactions, and direct plant uptake. Aerobic wetlands are used when water contains enough alkalinity to promote metal precipitation, and anaerobic wetlands are used when alkalinity must be generated by microbial sulfate reduction and limestone dissolution. Anoxic limestone drains are buried trenches of limestone that intercept AMD underground to generate alkalinity. Under anoxia, limestone should not be coated with Fe^{+3} hydroxides in the drain, which decreases the likelihood of clogging. Vertical flow wetlands pretreat oxygenated AMD with organic matter to remove oxygen and Fe^{+3}, and then the water is introduced into limestone underneath the organic matter. Open limestone channels use limestone in aerobic environments to treat AMD. Coating of limestone occurs, and the reduced limestone dissolution is designed into the treatment system. Alkaline leach beds, containing either limestone or slag, add alkalinity to acid water. At present, most passive systems offer short-term treatment and are more practical for installation on abandoned sites or watershed restoration projects where effluent limits do not apply and where some removal of acid and metals will benefit a stream.

Acid mine drainage (AMD) forms when sulfide minerals deep in the earth are exposed during coal and metal mining, highway construction, and other large-scale excavations. Upon exposure to water and oxygen, sulfide minerals oxidize to form acidic products, which then can be dissolved in water. The water containing these dissolved products often has a low pH, high amounts of dissolved metals such as iron (Fe) and aluminum (Al), and sulfate.

The metal concentrations in AMD depend on the type and quantity of sulfide minerals present, and the overall water quality from disturbed areas depends on the acid-producing (sulfide) and acid-neutralizing (carbonate) minerals contained in the disturbed rock. The carbonate content of overburden determines whether there is enough neutralization potential or base to counteract the acid produced from pyrite oxidation. Of the many types of acid-neutralizing compounds present in rocks, only carbonates (and some clays) occur in sufficient quantity to effectively neutralize acid-producing rocks. A balance between the acid-producing potential and neutralizing capacity of the disturbed overburden will indicate the ultimate acidity or alkalinity that might be expected in the material upon complete weathering.

Approximately 20,000 km of streams and rivers in the United States are degraded by AMD, but sulfide minerals occur throughout the world causing similar problems. About 90% of the AMD reaching streams originates in abandoned surface and deep mines. No company or individual claims responsibility for reclaiming abandoned mine lands and contaminated water flowing from these sites is not treated.

Control of AMD before land disturbance requires an understanding of three important factors: (1) overburden geochemistry, (2) method and precision of overburden handling and placement in the backfill during reclamation, and (3) the postmining hydrology of the site.

OVERBURDEN ANALYSES, HANDLING, AND PLACEMENT

Premining analysis of soils and overburden are required by law (1). Identifying the acid-producing or acid-neutralizing status of rock layers before disturbance aids in developing overburden handling and placement plans. Acid-base accounting provides a simple, relatively inexpensive, and consistent procedure to evaluate overburden chemistry. It balances potential acidity (based on total or pyritic sulfur content) against total neutralizers. Samples containing more acid-producing than acid-neutralizing materials are "deficient" and can cause AMD, whereas those rock samples with the reverse situation have "excess" neutralizing materials and will not cause AMD. Rock layers with equal proportions of each type of material should be subjected to leaching or weathering analyses (2). Kinetic tests such as humidity cells and leach columns are important because they examine the rate of acid-producing and neutralization reactions. This information from kinetic tests can supplement information given by acid-base accounting and help regulators in permitting decisions (3).

The prevailing approach to control AMD is to keep water away from pyritic material. Once overburden materials have been classified, an overburden handling and placement plan for the site can be designed.

Segregating and placing acid-producing materials above the water table is generally recommended (2,4). Where alkaline materials overwhelm acid-producing materials, no special handling is necessary. Where acid-producing materials cannot be neutralized by onsite alkaline materials, it is necessary to import a sufficient amount to neutralize the potential acidity or the disturbance activity may not be allowed.

Postmining Hydrology

The hydrology of a backfill and its effect on AMD are complex. Generally, the porosity and hydraulic conductivity of the materials in a backfill are greater than those of the consolidated rock overburden that existed before mining, and changes in flow patterns and rates should be expected after mining (5). Water does not move uniformly through the backfill by a consistent wetting front. As water moves into coarse materials in the backfill, it follows the path of least resistance and continues downward through voids or conduits until it encounters a barrier or other compacted layer. Therefore, the chemistry of the water from a backfill will reflect only the rock types encountered in the water flow path, and not the entire geochemistry of the total overburden (6).

Diverting surface water above the site to decrease the amount of water entering the mined area is highly recommended. If it cannot be diverted, incoming water can be treated with limestone to improve water quality. Under certain conditions, pyritic material can be placed where it will be rapidly and permanently inundated, thereby preventing oxidation. Inundation is only suggested where a water table may be reestablished, such as below drainage deep mines (see WET COVERS).

CONTROL OF AMD

Acid mine drainage control can be undertaken where AMD exists or is anticipated. Control methods treat the acid-producing rock directly and stop or retard the production of acidity. Treatment methods add chemicals directly to acidic water exiting the rock mass. Companies disturbing land in acid-producing areas must often treat AMD, and they face the prospect of long-term water treatment and its liabilities and expense. Cost-effective methods, which prevent the formation of AMD at its source, are preferable. Some control methods are most suited for abandoned mines, and others are only practical on active operations. Other methods can be used in either setting.

Land Reclamation

Backfilling (regrading the land back to contour) and revegetation together are effective methods of reducing acid loads from disturbed lands (7). Water flow from seeps can be reduced by diversion and reclamation, and on some sites where flow may not be reduced, water quality can change from acid to alkaline by proper handling of overburden. Diverting surface water or channeling surface waters to control volume, direction, and contact time can minimize the effects of AMD on receiving streams. Surface diversion involves construction of drainage ditches to move surface water quickly off the site before infiltration or by providing impervious channels to convey water across the disturbed area.

Alkaline Amendment to Active Disturbances

Certain alkaline amendments can control AMD from acid-producing materials (8–11). All alkaline amendment schemes rely on acid-base accounting or kinetic tests to identify the required alkalinity for neutralization of acidic materials. Special handling of overburden seeks to blend acid-producing and acid-neutralizing rocks in the disturbance/reclamation process to develop a neutral rock mass. The pit floor or material under coal is often rich in pyrite, so isolating it from groundwater may be necessary by building highwall drains (which move incoming groundwater away from the pit floor) or placing impermeable barriers on the pit floor. Acid-forming material can be compacted or capped within the spoil (12).

If insufficient alkalinity is available in the spoil, then external sources of alkalinity must be imported (13,14). Limestone is often the least expensive and most readily available source of alkalinity. It has a neutralization potential of between 75% and 100%, and it is safe and easy to handle. On the other hand, it has no cementing properties and cannot be used as a barrier. Fluidized bed combustion ashes generally have neutralizing amounts of between 20% and 40%, and they tend to harden into cement after wetting (15). Other power-generation ashes, like flue gas desulfurization products and scrubber sludges, may also have significant neutralization potential, which make them suitable alkaline amendment materials (16). Other materials, like kiln dust, produced by lime and cement kilns, or lime muds, grit, and dregs from pulp and paper industries contain neutralization products (10). Steel slags, when fresh, have neutralizing amounts from 45% to 90%. Slags are produced by several processes, so care is needed to ensure that candidate slags are not prone to leaching metal ions like Cr, Mn, and Ni. Phosphate rock has been used in some studies to control AMD. It may react with Fe released during pyrite oxidation to form insoluble coatings (17), but phosphate usually costs much more than other calcium-based amendments and is needed in about the same amounts (18).

Alkaline Recharge Trenches

Alkaline recharge trenches (19) are surface ditches or cells filled with alkaline material, which can minimize or eliminate acid seeps through an alkaline-loading process with infiltrating water. Alkaline recharge trenches were constructed on top of an 8-ha, acid-producing coal refuse disposal site, and after 3 years, the drainage water showed 25% to 90% acidity reductions with 70% to 95% reductions in Fe and sulfate (20). Pumping water into alkaline trenches greatly accelerates the movement of alkalinity into the backfill and can cause acid seeps to turn alkaline (21).

Dry Barriers

Dry barriers retard the movement of water and oxygen into areas containing acid-producing rock. These “water

control" technologies (4) include impervious membranes, dry seals, hydraulic mine seals, and grout curtains/walls. Surface barriers can achieve substantial reductions in water flow through piles, but generally they do not control AMD completely. Grouts can separate acid-producing rock and groundwater. Injection of grout barriers or curtains may significantly reduce the volume of groundwater moving through backfills. Gabr et al. (22) found that a 1.5-m-thick grout wall (installed by pumping a mixture of Class F fly ash and Portland cement grout into vertical boreholes near the highwall) reduced groundwater inflow from the highwall to the backfill by 80%, which results in some seeps drying up and others being substantially reduced in flow. At the Heath Steele Metal Mine in New Brunswick, a soil cover was designed to exclude oxygen and water from a tailings pile (23). It consisted of a 10-cm gravel layer for erosion control, 30-cm gravel/sand layer as an evaporation barrier, 60-cm compacted till (conductivity of 10^{-6} cm/sec), 30-cm sand, and pyritic waste rock. This barrier excluded 98% of precipitation, and oxygen concentrations in the waste rock dropped from 20% initially to around 1%. At the Upshur Mining Complex in West Virginia, Meek (12) reported covering a 20-ha spoil pile with a 39-mil PVC liner, and this treatment reduced acid loads by 70%.

Wet Covers

Disposal of sulfide tailings under a water cover, such as in a lake or fjord, is another way to prevent acid generation by excluding oxygen from sulfides. Wet covers also include flooding of aboveground tailings in ponds. Fraser and Robertson (24) studied four freshwater lakes used for subaqueous tailings disposal and found that the reactivity of tailings under water was low and that there were low concentrations of dissolved metals, thereby allowing biological communities to exist.

Alkaline Amendment to Abandoned Mines

Abandoned surface mines comprise huge volumes of spoil of unknown composition and hydrology. Abandoned underground mines are problematic because they are often partially caved and flooded, cannot be accessed, and have unreliable or nonexistent mine maps. Re-handling and mixing alkalinity into an already reclaimed backfill is generally prohibitively expensive.

Filling abandoned underground mine voids with nonpermeable materials is one of the best methods to prevent AMD. Underground mine voids are extensive (a 60-ha mine with a coal bed height of 1.5 m and a recovery rate of 65% would contain about 600,000 m^3 of voids), so fill material and the placement method must be cheap. Mixtures of Class F fly ash and 3–5% Portland cement control subsidence in mined-under residential areas and these slurries are generally injected through vertical boreholes at between 8- and 16-m centers. Pneumatic (air pressure) and slurry injection for placing fly ash in abandoned underground mines can extend the borehole spacing to about 30 m (25). On reclaimed surface mines still producing AMD, researchers in Pennsylvania saw small improvements in water quality after injecting coal combustion residues into buried pods of pyritic materials.

Remining and Reclamation

"Remining" means returning to abandoned surface or underground mines for further coal removal. Where AMD occurs, remining reduces acid loads by (1) decreasing infiltration rates, (2) covering acid-producing materials, and (3) removing the remaining coal, which is the source of most of the pyrite. Hawkins (26) found contaminant loads of 57 discharges from remined sites in Pennsylvania to be reduced after remining and reclamation. Short-term loads were sometimes increased during the first six months after remining and reclamation, but reduction in loads after six months resulted from decreased flow rather than large changes in concentrations. Ten remining sites in Pennsylvania and West Virginia were reclaimed to current standards (which included eliminating highwalls, covering refuse, and revegetating the entire area), and all sites had improved water quality (15).

CHEMICAL TREATMENT OF AMD

If AMD problems develop during mining or after reclamation, a plan to treat the discharge must be developed. A water treatment system consists of an inflow pipe or ditch, a storage tank or bin holding the treatment chemical, a valve to control its application rate, a settling pond to capture precipitated metal oxyhydroxides, and a discharge point. At the discharge point, water samples are analyzed to monitor whether specified parameters are being attained. Water discharge permits (NPDES) on surface mines usually require monitoring of pH, total suspended solids, and Fe and Mn concentrations. The type and size of a chemical treatment system is based on flow rate, pH, oxidation status, and concentrations of metals in the AMD. The receiving stream's designated use and seasonal fluctuations in flow rate are also important. After evaluating these variables over a period of time, the operator can consider the economics of different chemicals.

Six chemicals treat AMD (Table 1). Each is more or less appropriate for a specific condition. The best choice depends on both technical (acidity levels, flow, and the types and concentrations of metals) and economic factors (chemical prices, labor, machinery and equipment, treatment duration, and interest rates). Enough alkalinity must be added to raise pH to between 6 and 9 so insoluble metal hydroxides will form and settle out. Treatment of AMD with high Fe (ferric) concentrations often affords coprecipitation of other metals with the Fe hydroxide, thereby removing them from AMD at a lower pH. Limestone has been used for decades to raise pH and precipitate metals in AMD. It has the lowest material cost and is the safest and easiest to handle of the AMD chemicals. Unfortunately, it is limited because of its low solubility and tendency to develop an external coating, or armor, of $Fe(OH)_3$ when added to AMD. Fine-ground limestone may be dumped in streams directly or the limestone may be pulverized by water-powered rotating drums and metered into the stream. Limestone has also treated AMD in anaerobic (anoxic limestone drains) and aerobic environments (open limestone channels).

Table 1. Chemical Compounds Used in AMD Treatment

Common Name	Chemical Name	Formula	Conversion Factor[a]	Neutralization Efficiency[b]	2000 Cost[c] $ per Mg or L	
					Bulk	<Bulk
Limestone	Calcium carbonate	$CaCO_3$	1.00	30%	$11	$16
Hydrated Lime	Calcium hydroxide	$Ca(OH)_2$	0.74	90%	$66	$110
Pebble Quicklime	Calcium oxide	CaO	0.56	90%	$88	$264
Soda Ash	Sodium carbonate	Na_2CO_3	1.06	60%	$220	$350
Caustic Soda (solid)	Sodium hydroxide	NaOH	0.80	100%	$750	$970
20% Liquid Caustic	Sodium hydroxide	NaOH	784	100%	$0.06	$0.16
50% Liquid Caustic	Sodium hydroxide	NaOH	256	100%	$0.29	$0.33
Ammonia	Anhydrous ammonia	NH_3	0.34	100%	$330	$750

[a]The conversion factor may be multiplied by the estimated milligrams acid/yr to get milligrams of chemical needed for neutralization per year. For liquid caustic, the conversion factor gives liters needed for neutralization.
[b]Neutralization efficiency estimates the relative effectiveness of the chemical in neutralizing AMD acidity. For example, if 100 Mg of acid/yr was the amount of acid to be neutralized, then it can be estimated that 82 Mg of hydrated lime would be needed to neutralize the acidity in the water (100(0.74)/0.90).
[c]Price of chemical depends on the quantity being delivered. Bulk means delivery of chemical in a large truck, whereas < Bulk means purchased in small quantities. Liquid caustic prices are for liters. Others in milligrams.

Lime

Hydrated lime is common for treating AMD. As a powder, it tends to be hydrophobic, and extensive mechanical mixing is required for dissolution. Hydrated lime is particularly useful and cost effective in large-flow, high-acidity situations where a lime treatment plant with a mixer/aerator is constructed to help dispense and mix the chemical with the water (27). Hydrated lime has limited effectiveness if a very high pH (>9) is required to remove ions such as Mn. Unfortunately, increasing the lime rate increases the volume of unreacted lime that enters the floc-settling pond.

Pebble quicklime (CaO) is used with the Aquafix Water Treatment System using a water wheel concept (28). A water wheel is turned based on water flow, which causes a screw feeder to dispense the chemical. This system was initially used for small and/or periodic flows of high acidity because CaO is very reactive, but water wheels have been attached to large silos for high-flow/high-acidity situations. Tests show an average of 75% cost savings over NaOH systems and about 20% to 40% savings over NH_3 systems.

Soda Ash

Soda ash (Na_2CO_3) generally treats AMD in remote areas with low flow and low amounts of acidity and metals. This choice is usually based on convenience rather than on chemical cost. Soda ash comes as solid briquettes and is gravity fed into water through bins. The number of briquettes used per day is determined by the rate of flow and quality of the water. One problem is that the briquettes absorb moisture, expand, and stick to the corners of the bin and will not drop into the stream. For short-term treatment, some operators use a much simpler system that employs a wooden box or barrel with holes that allows water inflow and outflow. The operator simply fills the barrel with briquettes on a regular basis and places the barrel in the flowing water. This system offers less control of the amount of chemical used.

Caustic Soda

Caustic soda (i.e., lye, NaOH) is often used in remote low-flow, high-acidity situations, or if Mn concentrations in the AMD are high. The system can be gravity fed by dripping liquid NaOH directly into the AMD. Caustic is very soluble, disperses rapidly, and raises the pH quickly. Caustic should be applied at the surface of ponds because the chemical is denser than water. The major drawbacks of using liquid NaOH for AMD treatment are high cost and dangers in handling.

Ammonia

Ammonia compounds (NH_3 or NH_4OH) are extremely hazardous. NH_3 is compressed and stored as a liquid but returns to the gaseous state when released. Ammonia is extremely soluble, reacts rapidly, and can raise the pH of receiving water to 9.2. At pH 9.2, it buffers the solution to further pH increases, and therefore very high amounts of NH_3 must be added to go beyond 9.2. Injection of NH_3 into AMD is one of the quickest ways to raise water pH, and it should be injected near the bottom of the pond or water inlet because NH_3 is less dense than water. NH_3 is cheap, and a cost reduction of 50% to 70% is usually realized when NH_3 is substituted for NaOH (29). Major disadvantages of using NH_3 include (1) the hazards; (2) uncertainty concerning nitrification, denitrification, and acidification downstream; and (3) consequences of excessive application rates, which cause toxic conditions to aquatic life.

Costs of Treating AMD

Costs were estimated for five treatment chemicals under four sets of flow and acid concentration conditions [Table 1 from Skousen et al. (30)]. Na_2CO_3 had the highest labor requirements (10 hours per week) because the dispensers must be filled by hand and inspected frequently. Caustic had the highest reagent cost per mole of acid-neutralizing capacity, and Na_2CO_3 had the second highest. Hydrated lime treatment systems had the highest installation costs of the five chemicals because of the need to construct a lime treatment plant and install a pond aerator. However, the cost of $Ca(OH)_2$ was very low, and the combination of high installation costs and low reagent cost made $Ca(OH)_2$ systems particularly appropriate for long-term treatment of high-flow/high-acidity conditions.

For a 5-year treatment, NH_3 had the lowest annual cost for the low-flow/low-acid situation. Pebble quicklime had about the same cost as the NH_3 system, but slightly higher installation costs. Caustic was third because of its high labor and reagent costs, and Na_2CO_3 was fourth because of high labor costs. Hydrated lime was the most expensive because of its high installation costs. At high-flow/high-acidity, the $Ca(OH)_2$ and CaO systems were clearly the cheapest treatment systems (annual costs of about $250,000 less than NH_3, the next best alternative).

After chemical treatment, the treated water flows into sedimentation ponds so metals in the water can precipitate. All AMD treatment chemicals cause the formation of metal hydroxide sludge or floc. Sufficient residence time of the water (dictated by pond size and depth) is important for adequate metal precipitation. The amount of metal floc generated depends on water quality and quantity, which in turn determines how often the ponds must be cleaned. Knowing the chemical and AMD being treated will provide an estimate of the stability of metal compounds in the floc. Floc disposal options include (1) leaving it submerged indefinitely, (2) pumping or hauling it to abandoned deep mines or to pits dug on surface mines, and (3) dumping it into refuse piles. Pumping flocs onto land and letting them age and dry is a good strategy for disposal, because they become crystalline and behave like soil material.

Each AMD is unique, requiring site-specific treatment. Each AMD source should be tested with various chemicals by titration tests to evaluate the most effective chemical for precipitation of the metals. The costs of each AMD treatment system based on neutralization (in terms of the reagent cost, capital investment, and maintenance of the dispensing system) and floc disposal should be evaluated to determine the most cost-effective system.

PASSIVE TREATMENT OF AMD

Active chemical treatment of AMD is often an expensive, long-term proposition. Passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of natural chemical and biological processes to cleanse contaminated mine waters. Passive technologies include constructed wetlands, anoxic limestone drains, vertical flow wetlands (also known as SAPS), open limestone channels, and alkaline leach beds (Fig. 1). In low-flow and low-acidity situations, passive systems can be reliably implemented as a single permanent solution for many AMD problems.

Constructed Wetlands

Wetlands are of two basic types: aerobic and anaerobic. Metals are retained within wetlands by (1) formation of metal oxides and oxyhydroxides, (2) formation of metal sulfides, (3) organic complexation reactions, (4) exchange with other cations on negatively charged sites, and (5) direct uptake by living plants. Other beneficial reactions in wetlands include generation of alkalinity caused by microbial mineralization of dead organic matter, microbial dissimilatory reduction of Fe oxyhydroxides and SO_4, and dissolution of carbonates.

Aerobic wetlands consist of relatively shallow ponds (<30 cm) with wetland vegetation. Aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn oxyhydroxides. Successful metal removal depends on dissolved metal concentrations, dissolved oxygen content, pH and net acidity of the mine water, the presence of active microbial biomass, and detention time of the water in the wetland. The pH and net acidity/alkalinity of the water are particularly important because pH influences both the solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis. Therefore, aerobic wetlands are best used in conjunction with water that contains net alkalinity to neutralize metal acidity.

Anaerobic wetlands consisting of deep ponds (>30 cm) with substrates of soil, peat moss, spent mushroom compost, sawdust, straw/manure, hay bales, or other organic mixtures, often underlain or admixed with limestone. Anaerobic wetlands are most successful when used to treat small flows of acidic water. Anaerobic wetlands use chemical and microbial reduction reactions to precipitate metals and neutralize acidity. The water infiltrates through a thick permeable organic subsurface that becomes anaerobic because of high biological oxygen demand. Other chemical mechanisms that occur *in situ* include metal exchanges, formation and precipitation of metal sulfides, microbial-generated alkalinity, and formation of carbonate alkalinity (because of limestone dissolution). As anaerobic wetlands produce alkalinity, they can be used in net acidic and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are critical to long-term AMD treatment. Under high acid loads (>300 mg/L), pH-sensitive microbial activities are eventually overwhelmed. At present, the sizing value for Fe removal in these wetlands is 10 gs per day per meter squared (31).

Sorption onto organic materials (such as peat and sawdust) can initially remove 50% to 80% of the metals in AMD (32), but the exchange capacity declines with time. Over the long term, metal hydroxide precipitation is the predominant form of metal retention in a wetland. Wieder (33) reported up to 70% of the Fe in a wetland to be composed of Fe^{+3} oxyhydroxides, whereas the other 30% is reduced and combined with sulfides (34).

Sulfate reducing bacteria (SRB) reactors have been used to generate alkalinity by optimizing anaerobic conditions. Good success has been noted for several systems receiving high and low flows (35,36).

Anoxic Limestone Drains

Anoxic limestone drains are buried cells or trenches of limestone into which anoxic water is introduced. The limestone raises pH and adds alkalinity. Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe^{+2} does not precipitate as $Fe(OH)_2$ at pH 6.0. Faulkner and Skousen (37) reported both successes and failures among 11 anoxic drains in WV. Failures resulted when ferric iron and Al precipitate as hydroxides in the limestone causing plugging and coating.

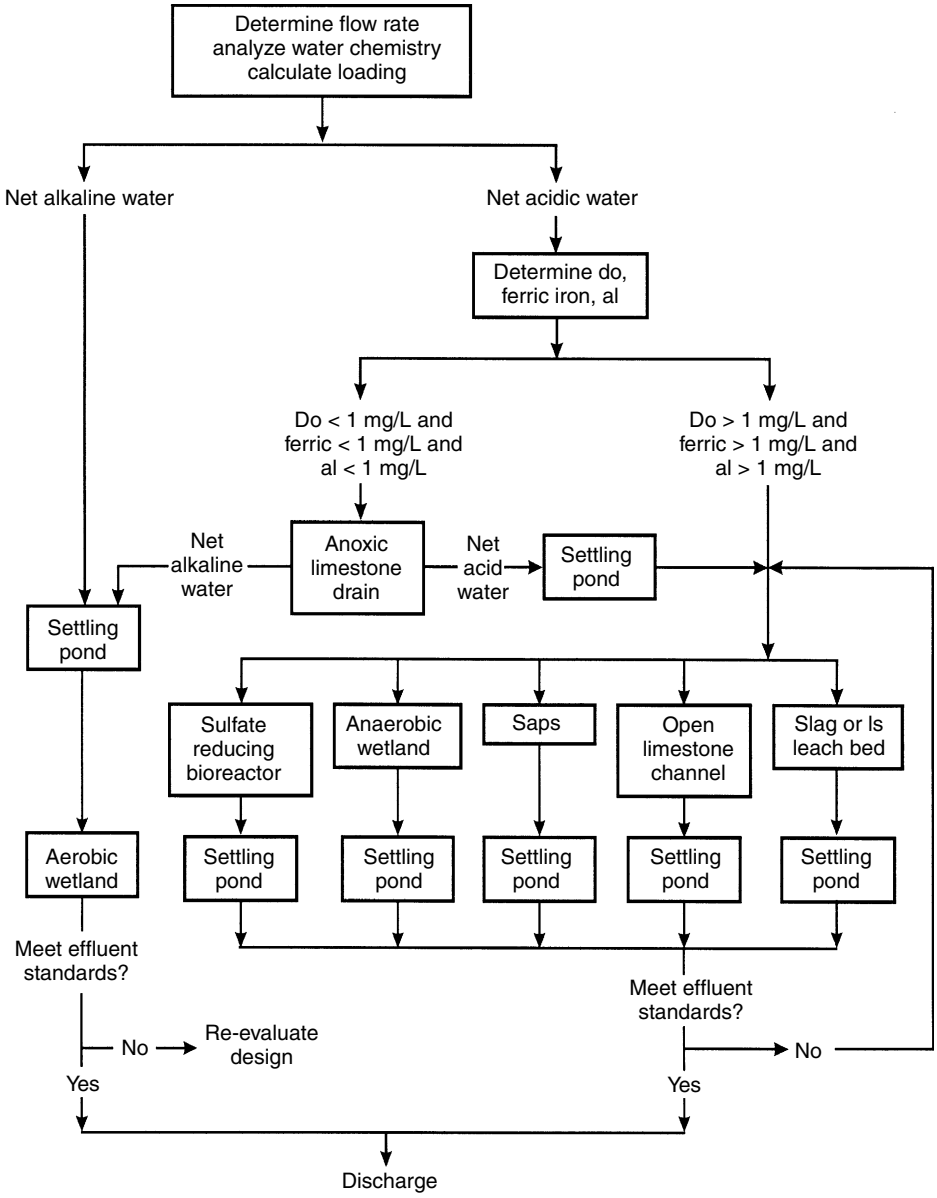


Figure 1. Diagram of possible passive treatment systems to treat mine water based on water flow and chemistry.

Longevity of treatment is a major concern for anoxic drains, especially in terms of water flow through the limestone. Selection of the appropriate water and environmental conditions is critical for long-term alkalinity generation in an anoxic drain. Eventual clogging of the limestone pore spaces with precipitated Al and Fe hydroxides, and gypsum is predicted (38). For optimum performance, no Fe^{+3}, dissolved oxygen, or Al should be present in the AMD. Like wetlands, anoxic limestone drains may be a solution for AMD treatment for specific water conditions or for a finite period after which the system must be replenished or replaced.

Vertical Flow Wetlands

In these modified wetlands [called SAPS by Kepler and McCleary (39)], 1 to 3 m of acid water is ponded over an organic compost of 0.2 to 0.3 m, underlain by 0.5 to 1 m of limestone. Below the limestone are drainage pipes that convey the water into an aerobic pond where metals are precipitated. The hydraulic head drives ponded water through the anaerobic organic compost, where oxygen stripping as well as Fe and sulfate reduction can occur before water entry into the limestone. Water with high metal loads can be successively cycled through additional wetlands. Iron and Al clogging of limestone and pipes can be removed by flushing the system (40). Much work is being done on these wetlands presently, and refinements are being made for better water treatment.

Open Limestone Channels

Open limestone channels are another means of introducing alkalinity to acid water (41). We usually assume that armored limestone ceases to dissolve, but Ziemkiewicz et al. (42) found armored limestone to be 50% to 90% effective in neutralizing acid compared with unarmored limestone. Seven open channels in the field reduced acidity

in AMD by 4% to 62% compared with a 2% acid reduction in a sandstone channel. Open limestone channels show promise for neutralizing AMD in watershed restoration projects and AML reclamation projects where there can be only a one-time installation cost, little to no maintenance is required, and water exiting the system does not have to meet water quality standards. Long channels of limestone can convey acid water to a stream or other discharge point. Cross sections of channels can be designed with calculated amounts of limestone (which will become armored) to treat the water. Open limestone channels work best on steep slopes (>20%), where flow velocities keep metal hydroxides in suspension, thereby limiting plugging. If constructed correctly, open limestone channels should be maintenance free and provide AMD treatment for decades.

Alkaline Leach Beds

Limestone, when placed in an open pond or leach bed, will dissolve slowly over time and continually add alkalinity to water unless the limestone gets coated with metal hydroxides, thereby reducing its dissolution rate (41). Therefore, limestone treatment in aerobic systems works best in low-pH, metal-free water, and can add alkalinity to streams before encountering acid water downstream (42). As limestone generally reacts relatively slowly under field conditions, steel slag, a byproduct of steel making and composed of hydrated amorphous silica and calcium compounds, can be used as an alkaline material to add alkalinity to water. Steel slags have high neutralization potentials (from about 50–70%), can generate exceptionally high levels of alkalinity in water, and do not armor (43). Steel slag fines can be used in leach beds. Effluents from slag leach beds attain high pH (>10) and have alkalinity concentrations in the thousands of milligrams/liter. Slag leach beds may receive AMD directly, or effluent from "fresh water" beds may be combined with an AMD source downstream to treat acid indirectly.

SUMMARY

Acid mine drainage occurs when metal sulfides are oxidized. Leaching of reaction products into surface waters pollute over 20,000 km of streams in the United States alone. Companies must predict AMD before mining by using overburden analyses. On sites where a potential exists, special handling of overburden materials and quick coverage of acid-producing materials in the backfill should be practiced. Alkaline addition with materials such as kiln dust and FBC ash can reduce or completely eliminate AMD problems. Other control techniques include dry barriers, wet barriers, injection of alkaline materials into underground mines, remining of abandoned areas, and alkaline recharge trenches. Five chemicals typically treat AMD, and each has characteristics that make it suitable for specific applications. Companies must select a chemical that treats the water adequately and cost-effectively. Passive systems are low maintenance systems that are implemented on abandoned mine land and stream restoration projects. Certain systems are more suited to specific water quality and show good success where the acid levels do not overwhelm the system.

BIBLIOGRAPHY

1. Sobek, A., Skousen, J., and Fisher, S. (2000). Chemical and physical properties of overburdens and minesoils. In: *Reclamation of Drastically Disturbed Lands*, 2nd Edn. American Society of Agronomy, Madison, WI.
2. Skousen, J.G., Sencindiver, J.C., and Smith, R.M. (1987). *A Review of Procedures for Surface Mining and Reclamation in Areas with Acid-Producing Materials*. EWRC 871, West Virginia University, Morgantown, WV.
3. Geidel, G., Caruccio, F.T., Hornberger, R., and Brady, K. (2000). Guidelines and recommendations for use of kinetic tests for coal mining (AMD) prediction in the eastern U.S. In: *Prediction of Water Quality at Surface Coal Mines*. National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.
4. Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., and Hellier, W. (1998). *Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage*. National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.
5. Caruccio, F.T. and Geidel, G. (1989). Water management strategies in abating acid mine drainage—Is water diversion really beneficial? In: *1989 Multinational Conference on Mine Planning and Design*. 16–17 Sept. 1989, University of Kentucky, Lexington, KY.
6. Ziemkiewicz, P.F. and Skousen, J.G. (1992). Prevention of acid mine drainage by alkaline addition. *Green Lands* **22**(2): 42–51.
7. Faulkner, B.B. and Skousen, J.G. (1995). Effects of land reclamation and passive treatment systems on improving water quality. *Green Lands* **25**: 34–40.
8. Brady, K., Smith, M.W., Beam, R.L., and Cravotta, C.A. (1990). Effectiveness of the use of alkaline materials at surface coal mines in preventing or abating acid mine drainage: Part 2. Mine site case studies. In: *Proceedings, 1990 Mining and Reclamation Conference*. J. Skousen et al. (Eds.). 23–26 April 1990, West Virginia University, Morgantown, WV.
9. Perry, E.F. and Brady, K.B. (1995). Influence of neutralization potential on surface mine drainage quality in Pennsylvania. In: *Proceedings, Sixteenth Annual Surface Mine Drainage Task Force Symposium*. 4–5 April 1995, West Virginia University, Morgantown, WV.
10. Rich, D.H. and Hutchison, K.R. (1994). Coal refuse disposal using engineering design and lime chemistry. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
11. Rose, A.W., Phelps, L.B., Parizek, R.R., and Evans, D.R. (1995). Effectiveness of lime kiln flue dust in preventing acid mine drainage at the Kauffman surface coal mine, Clearfield County, Pennsylvania. In: *Proceedings, 1995 National Meeting of the American Society for Surface Mining and Reclamation*. 3–8 June 1995, Gillette, WY.
12. Meek, F.A. (1994). Evaluation of acid prevention techniques used in surface mining. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.
13. Skousen, J. and Larew, G. (1994). Alkaline overburden addition to acid-producing materials to prevent acid mine drainage. In: *International Land Reclamation and Mine*

Drainage Conference. 24–29 April 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.

14. Wiram, V.P. and Naumann, H.E. (1995). Alkaline additions to the backfill: A key mining/reclamation component to acid mine drainage prevention. In: *Proceedings, Sixteenth Annual Surface Mine Drainage Task Force Symposium*. 4–5 April 1995, West Virginia University, Morgantown, WV.
15. Skousen, J., Bhumbla, D., Gorman, J., and Sencindiver, J. (1997). Hydraulic conductivity of ash mixtures and metal release upon leaching. In: *1997 National Meeting of the American Society for Surface Mining and Reclamation*. 10–15 May 1997, Austin, TX.
16. Stehouwer, R., Sutton, P., Fowler, R., and Dick, W. (1995). Minespoil amendment with dry flue gas desulfurization by-products: element solubility and mobility. *J. Environ. Qual.* **24**: 165–174.
17. Evangelou, V.P. (1995). *Pyrite Oxidation and its Control*. CRC Press, Boca Raton, FL.
18. Ziemkiewicz, P.F. and Meek, F.A. (1994). Long term behavior of acid forming rock: results of 11-year field studies. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.
19. Caruccio, F.T., Geidel, G., and Williams, R. (1984). Induced alkaline recharge zones to mitigate acid seeps. In: *Proceedings, National Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation*. 7–10 Dec. 1984, Univ. of Kentucky, Lexington, KY.
20. Nawrot, J.R., Conley, P.S., and Sandusky, J.E. (1994). Concentrated alkaline recharge pools for acid seep abatement: principles, design, construction and performance. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
21. Ziemkiewicz, P.F., Donovan, J., Frazier, J., Daly, M., Black, C., and Werner, E. (2000). Experimental injection of alkaline lime slurry for *in situ* remediation of an acidic surface mine aquifer. In: *Proceedings, Twenty-first West Virginia Surface Mine Drainage Task Force Symp.* April 4–5, 2000, Morgantown, WV.
22. Gabr, M.A., Bowders, J.J., and Runner, M.S. (1994). Assessment of acid mine drainage remediation schemes on groundwater flow regimes at a reclaimed mine site. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.
23. Bell, A.V., Riley, M.D., and Yanful, E.G. (1994). Evaluation of a composite soil cover to control acid waste rock pile drainage. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.
24. Fraser, W.W. and Robertson, J.D. (1994). Subaqueous disposal of reactive mine waste: an overview and update of case studies-MEND/Canada. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
25. Burnett, J.M., Burnett, M., Ziemkiewicz, P., and Black, D.C. (1995). Pneumatic backfilling of coal combustion residues in underground mines. In: *Proceedings, Sixteenth Annual Surface Mine Drainage Task Force Symposium*. 4–5 April 1995, West Virginia University, Morgantown, WV.
26. Hawkins, J.W. (1994). Assessment of contaminant load changes caused by remining abandoned coal mines. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
27. Skousen, J. and Ziemkiewicz, P. (1996). *Acid Mine Drainage Control and Treatment*, 2nd Edn. National Research Center for Coal and Energy, National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.
28. Jenkins, M. and Skousen, J. (2001). Acid mine drainage treatment costs with calcium oxide and the Aquafix Machine. *Green Lands* **31**: 46–51.
29. Skousen, J., Politan, K., Hilton, T., and Meek, A. (1990). Acid mine drainage treatment systems: chemicals and costs. *Green Lands* **20**(4): 31–37.
30. Skousen, J.G., Sexstone, A., and Ziemkiewicz, P. (2000). Acid mine drainage control and treatment. In: *Reclamation of Drastically Disturbed Lands*, 2nd Edn. American Society of Agronomy, Madison, WI.
31. Hedin, R.S. and Nairn, R.W. (1992). Passive treatment of coal mine drainage. *Course Notes for Workshop*. U.S. Bureau of Mines, Pittsburgh, PA.
32. Brodie, G.A., Hammer, D.A., and Tomljanovich, D.A. (1988). An evaluation of substrate types in constructed wetlands acid drainage treatment systems. In: *Mine Drainage and Surface Mine Reclamation*. 19–21 April 1988, Vol. 1, Info. Circular 9183, U.S. Bureau of Mines, Pittsburgh, PA.
33. Wieder, R.K. (1993). Ion input/output budgets for wetlands constructed for acid coal mine drainage treatment. *Water, Air, and Soil Pollution* **71**: 231–270.
34. Wieder, R.K. (1992). The Kentucky wetlands project: A field study to evaluate man-made wetlands for acid coal mine drainage treatment. Final Report to the U.S. Office of Surface Mining, Villanova Univ., Villanova, PA.
35. Canty, M. (2000). Innovative *in situ* treatment of acid mine drainage using sulfate-reducing bacteria. In: *Proceedings, Fifth International Conference on Acid Rock Drainage*. Society for Mining, Metallurgy, and Exploration, Inc., Denver, CO.
36. Gusek, J., Mann, C., Wildeman, T., and Murphy, D. (2000). Operational results of a 1200 gpm passive bioreactor for metal mine drainage, Missouri. In: *Proceedings, Fifth International Conference on Acid Rock Drainage*. Society for Mining, Metallurgy, and Exploration, Inc., Denver, CO.
37. Faulkner, B.B. and Skousen, J.G. (1994). *Treatment of Acid Mine Drainage by Passive Treatment Systems*. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
38. Nairn, R.W., Hedin, R.S., and Watzlaf, G.R. (1991). A preliminary review of the use of anoxic limestone drains in the passive treatment of acid mine drainage. In: *Proceedings, Twelfth Annual West Virginia Surface Mine Drainage Task Force Symposium*. 3–4 April 1991, West Virginia University, Morgantown, WV.
39. Kepler, D.A. and McCleary, E. (1997). Passive aluminum treatment successes. In: *Proceedings, Eighteenth Annual West Virginia Surface Mine Drainage Task Force Symposium*. 15–16 April 1997, West Virginia University, Morgantown, WV.
40. Kepler, D.A. and McCleary, E. (1994). Successive alkalinity-producing systems (SAPS) for the treatment of acidic mine drainage. In: *International Land Reclamation and Mine Drainage Conference*. 24–29 April 1994, USDI, Bureau of Mines SP 06A-94, Pittsburgh, PA.
41. Ziemkiewicz, P.F., Skousen, J., and Lovett, R. (1994). Open limestone channels for treating acid mine drainage: a new look at an old idea. *Green Lands* **24**(4): 36–41.

42. Ziemkiewicz, P.F. et al. (1997). Acid mine drainage treatment with armored limestone in open limestone channels. *J. Environ. Qual.* **26**: 718–726.
43. Ziemkiewicz, P.F., Skousen, J., and Simmons, J. (2001). Cost benefit analysis of passive treatment systems. In: *Proceedings, 22nd West Virginia Surface Mine Drainage Task Force Symposium*. 3–4 April, Morgantown, WV.
44. Ziemkiewicz, P.F. and Skousen, J. (1998). The use of steel slag in acid mine drainage treatment and control. In: *Proceedings, 19th West Virginia Surface Mine Drainage Task Force Symposium*. 7–8 April, Morgantown, WV.

READING LIST

Rich, D.H. and Hutchison, K.R. (1990). Neutralization and stabilization of combined refuse using lime kiln dust at High Power Mountain. In: *Proceedings, 1990 Mining and Reclamation Conference*. 23–26 April 1990, West Virginia University, Morgantown, WV.

Skousen, J.G., Hedin, R., and Faulkner, B.B. (1997). Water quality changes and costs of remining in Pennsylvania and West Virginia. In: *1997 National Meeting of the American Society for Surface Mining and Reclamation*. 10–15 May 1997, Austin, TX.

AQUIFERS

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GENERAL DEFINITION

An aquifer is a geologic formation or geologic unit from which significant amounts of groundwater can be pumped for domestic, municipal, or agricultural uses. The four major types of rock formations that serve as aquifers are unconsolidated sand and gravel, sandstone, carbonate rocks, and fractured volcanic rocks. Aquifers may also occur in other geologic formations, particularly in fractured zones of igneous, metamorphic, or sedimentary rocks.

ORIGIN OF THE WORD

The word aquifer was probably adopted around the early twentieth century from the French word aquifère, which originates from the two Latin words aqua (water) and ferre (to carry, to bear). Hence, literally translated from Latin, aquifer means 'that which carries water.'

FURTHER DEFINITIONS

There is no strict definition of the hydrogeologic attributes or volumetric extent necessary to make a geologic formation or geologic unit an aquifer. Rather, the term aquifer is used for local formations that have relatively higher permeability than surrounding formations. Geologic units that form an aquifer in one setting may therefore not be considered to constitute an aquifer in other settings. For example, a small intermontane valley aquifer that consists of very shallow, sandy loam deposits a few feet thick may supply enough water to maintain a pumping rate of 0.5–2 gallons per minute, enough for domestic water supply wells and some stock supply wells. This may be significantly more water than would be provided by the hardrock formations underlying and bounding such a shallow aquifer. In contrast, the same sandy loam deposits of the same thickness would not be considered an aquifer if they were part of an unconsolidated sedimentary sequence in a larger alluvial basin, where gravel and sand aquifers yield from 50 to more than 1,000 gallons per minute.

ROLE OF AN AQUIFER IN THE HYDROLOGIC CYCLE

Aquifers are part of the hydrologic cycle. They receive water through

- recharge from precipitation,
- recharge from irrigation return water,
- seepage from rivers and streams,
- lateral transfer of water from neighboring aquifer basins, and
- leakage from aquifer formations situated either above or below the aquifer.

Water that collects in aquifers from those sources over periods of years, decades, centuries, and even millennia is discharged back to the surface through (Fig. 1)

- springs,
- subsurface discharge into rivers and streams,
- lateral outflow to downgradient aquifers,
- vertical leakage to overlying or underlying aquifers, and
- man-made wells.

LIMITATION TO FORMATIONS WITH APPROPRIATE WATER QUALITY

The term aquifer is applied to formations that produce low to moderate salinity water (appropriate for domestic, municipal, or agricultural uses). Geologic formations containing exclusively brackish or saline groundwater (even if they are made of highly permeable material) are typically not referred to as aquifers unless the salinity was induced through human activity (e.g., in seawater intrusion, which is the advance of saline seawater into an overpumped aquifer).

AQUIFER SIZE

Aquifers can be vastly different in size: a small local aquifer in a mountainous setting may be only a few feet thick and extend over an area of a few acres to tens of acres. Other aquifers span entire regions. For example, the Ogallala aquifer in the western-central United States underlies most of the High Plains region, which extends

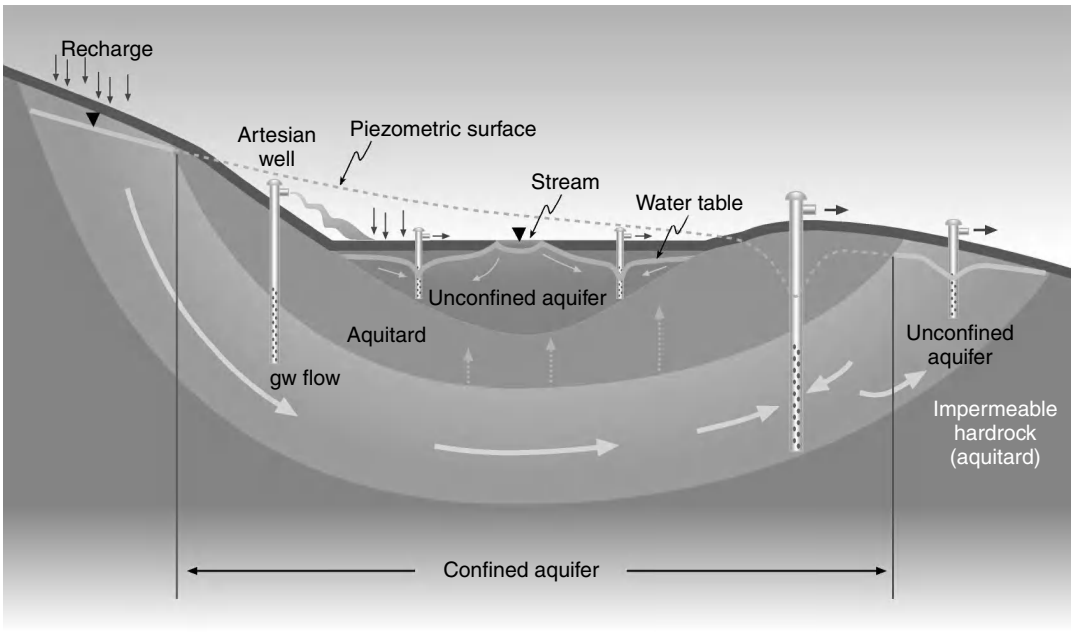


Figure 1. Schematic representation of uncontinued aquifers, confined aquifers, aquitards, and aquicludes. Blade vertical arrows indicate recharge. Black horizontal arrows indicate pumping. Light colored arrows indicate the direction of groundwater movement.

eastward from the Rocky Mountains through parts of Texas, Oklahoma, Colorado, Kansas, and Nebraska. The aquifer consists of alluvial sediments, predominantly sands and gravel. It is an important production aquifer.

An aquifer is characterized by its geologic extent (regional extent and thickness), the type of geologic formations that makes up the aquifer, the hydraulic conductivity, the transmissivity (which is defined as the product of hydraulic conductivity and aquifer thickness), the specific yield (the drainable porosity), the specific storage (the amount of water and rock compressed by hydrostatic pressure in a confined aquifer, see below), and the specific capacity (specific capacity is the amount of water pumped from a well per foot of water level drawdown created by pumping). The hydraulic conductivity of aquifers typically ranges from 1 m/day to more than 100 m/day. The specific capacity of wells located in aquifers may range from less than 0.1 gpm/ft (small, low-yielding aquifers suitable for domestic water supplies) to more than 100 gpm/ft (large production aquifers suitable for municipal and irrigation pumping).

AQUIFER CHARACTERIZATION

The amount of water that can be pumped from an aquifer depends primarily on four parameters: the hydraulic conductivity (also called the permeability) of the aquifer, the thickness of the aquifer, the specific yield or specific storage of the aquifer (related mostly to its porosity), and the amount of competition for water between wells. All four of these may change from location to location. The amount of pumping wells and the rate at which wells are pumping may be different from area to area; the thickness of the aquifer naturally changes with the thickness of the geologic formation. With respect to hydraulic conductivity, porosity, and specific yield or specific storage, hydrogeologists have found that small variations that occur in the geologic composition of aquifer formations often result in large localized changes in hydraulic conductivity. This latter phenomenon is referred to as "natural aquifer heterogeneity." As a result of all this variability, each well within the same aquifer will have a different specific capacity. Sometimes, the specific capacity of wells can vary quite significantly from well to well, especially in fractured rock aquifers, but also in unconsolidated aquifers with sand and gravel.

Hydraulic conductivity, thickness, and specific yield or specific storage of an aquifer are determined indirectly by using literature values available for specific geologic formations, by using computer models in conjunction with local observations of groundwater fluxes or groundwater table fluctuations, or directly by performing an aquifer test (pumping test).

AQUIFERS, AQUITARDS, AND AQUICLUDES

Aquifers are the major hydrogeologic units within the hydrogeologic framework of a region from which groundwater is or can be extracted. The description of local or regional hydrogeology centers around the description of aquifers, that is, of those geologic formations with the highest significance—locally or regionally—with respect to (potential) groundwater production. Geologic formations that bound aquifers are referred to as aquicludes or aquitards. Aquicludes are, for all practical purposes, impermeable. Important aquicludes are thick, continuous clay formations and unfractured igneous rocks. Aquitards are geologic formations that have a lower

hydraulic conductivity than adjacent (aquifer) formations and therefore act as a partial barrier to groundwater flow between overlying aquifers. Aquitards can consist of material similar to aquifers, but either the amount of fine sediments is much larger (in unconsolidated formations) relative to the aquifer formation, or the degree of fracturing and size of fractures is smaller than that in the aquifer formation (in hardrock formations).

CONFINED AND UNCONFINED AQUIFERS

Aquifers can be either unconfined or confined, depending on the existence of an overlying aquitard or aquiclude. In an unconfined aquifer, there is no overlying aquitard or aquiclude. Recharge to the aquifer from the land surface or from and to streams is not restricted. The water table moves freely up and down, depending on the water stored, added to, or removed from the unconfined aquifer. The water level in a borehole drilled into an unconfined aquifer will be the same as the water level in the aquifer (if we ignore the effects of the capillary fringe).

In a confined aquifer, on the other hand, water is "sandwiched" between two aquitards or between an aquitard and an aquiclude above and below the aquifer. Water in a confined aquifer is under hydrostatic pressure created by the weight of the overlying geologic formations and the water pressure created by the higher water levels in the usually remote recharge area of a confined aquifer. Due to the pressure in a confined aquifer, the water level in a borehole drilled into a confined aquifer will rise significantly above the top of the aquifer. An artesian well occurs where the pressure is so large that the water level in a well drilled into the confined aquifer rises above the land surface. A confined aquifer does not have a water table—it is completely filled with groundwater. The water level in wells drilled into a confined aquifer, instead, corresponds to the hydrostatic pressure head or potentiometric surface of the aquifer, which is located higher than the upper boundary of the aquifer itself. If the hydrostatic pressure head falls below the top of the confined aquifer, it becomes unconfined.

An aquifer that is confined by an aquitard rather than an aquiclude is referred to as a "leaky aquifer" or a "semiconfined aquifer." The aquitard is not always a contiguous layer of less permeable material. Local accumulations of multiple, smaller clay lenses and other clay-rich or otherwise impermeable layers dispersed within a more permeable formation may render the entire formation an aquitard. The actual low permeable lenses are not contiguous, but the overall effect of their presence within such a heterogeneous formation on the regional aquifer below is identical to that of a continuous aquitard formation.

PERCHED WATER TABLE

Occasionally, water collects above an impermeable or low permeability layer within the unsaturated (aerated) zone and forms a "perched" water table. By definition, a "perched" water table is a saturated groundwater zone separated from the aquifer below by a zone that is unsaturated or aerated. This should not be confused with an unconfined shallow aquifer that is separated from a deeper confined aquifer through thick but saturated layers of clay.

ARTIFICIAL RECHARGE OF UNCONFINED AQUIFER

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INTRODUCTION

Groundwater plays a major role in augmenting water supply to meet the ever-increasing domestic, agricultural, and industrial demands. Increasing dependence of water supply on groundwater resources is resulting in increasing use of aquifers as a source of fresh water supply and subsurface reservoir for storing excess surface water. Aquifers are the geological formations that can store water as well as allow the flow of significant amount of water through their pores under ordinary field conditions. If the aquifer is bounded by two impermeable formations from top and bottom, it is called a confined aquifer. If the upper boundary of the aquifer is the water table, it is called an unconfined aquifer. The advantage of unconfined aquifers over confined aquifers to serve as a subsurface reservoir is that the storage of groundwater in large quantity is possible only in unconfined aquifer, which is because the storativity of the unconfined aquifer is linked to the porosity and not to the elastic properties of the water and solid matrix, as in case of the confined aquifer (1). Also, the vast surface area of the unconfined aquifer above the water table is available to receive the surface applied recharge, whereas in case of the confined aquifer, only a small open area exposed near to the ground surface or leaky portion of the aquifer boundary is available to receive the recharge (Fig. 1). This article deals with the artificial recharging of unconfined aquifer and related problems.

Natural replenishment of aquifers occurs very slowly. Therefore, withdrawal of groundwater at a rate greater than the natural replenishment rate causes declining of groundwater level, which may lead to decreased water supply, contamination of fresh water by intrusion of pollutant water from nearby sources, seawater intrusion into the aquifer of coastal areas, etc. To increase the natural replenishment, artificial recharging of the aquifer is becoming increasingly important in groundwater management. The artificial recharge may be defined as an augmentation of surface water into aquifers by some artificially planned operations. The source of water for recharge may be direct precipitation, imported water, or reclaimed wastewater. The purpose of artificial recharging

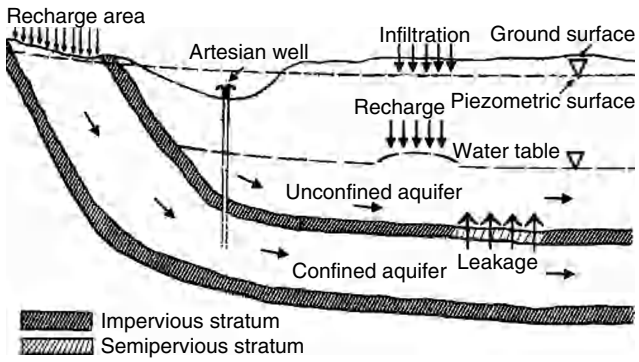


Figure 1. Aquifer types.

of groundwater systems has been to reduce, stop, or even reverse the declining trend of groundwater level; to protect fresh groundwater in coastal aquifers against saline water intrusion from the ocean; and store surface water, including flood or other surplus water, imported water, and reclaimed wastewater for future use.

RECHARGE METHODS

A variety of direct surface, direct subsurface, and indirect recharge techniques have been developed to recharge groundwater systems. The choice of a technique depends on the source of water, quality of the water, the type of aquifer, topographical condition, etc. The most widely practiced methods are direct surface techniques, which include surface flooding in basins, ponds, lakes, ditches, trenches, and furrow systems; stream and channel modification; and bunds (2–5). Trenches are constructed mostly in foothill regions to arrest the runoff and put it into the aquifers for storage. Stream channel modification involves alteration in the course of stream flow to detain stream flow and increasing the stream bed area for recharging purposes. Construction of check dams across the stream flow is one technique of stream channel modification. It enhances artificial recharge in two ways. Above the dam, impoundments enhance recharge by increasing the recharge area and detaining water for a longer period by reducing the rate of water flow. Below the dam, recharge is enhanced through exposure of a larger area than the original area of stream channel flow. Bunds, which are small earthen barriers, are constructed in agricultural lands with slopes to facilitate impounding of runoff for a longer duration, thereby increasing recharge. In indirect subsurface recharge techniques, water is injected directly into an aquifer through (a) natural openings in the aquifers, (b) pits or shafts, and (c) wells. In contrast to the direct surface techniques, groundwater recharge by indirect subsurface techniques is practiced mostly for recharging the confined aquifer and where the topography or existing land use, such as in urban areas, makes recharge by surface flooding impractical. Indirect recharge techniques involve special cases in which potable water supply is provided by river bank or sand dune filtration of generally polluted river water (6,7).

In many cases, excess recharging leads to the growth of water table near the ground surface and causes several types of environmental problems, such as water logging, soil salinity, etc. In these situations, proper management of groundwater resources is needed to overcome the shortage of water supply on one hand and to prevent the environmental problems on the other hand. In order to address the management problem, one must be able to predict the response of the aquifer system to any proposed operational policy of groundwater resources development such as artificial recharging. Such problems are referred to as forecasting problems. Their solution will provide the new state of the groundwater system. Once the new state is known, one can check whether the related recharge scheme is feasible. Then one can compare responses of different proposed recharge schemes in order to select the best scheme that can meet the preset objectives of groundwater resources development without disturbing the regional water balance and without creating any kind of environmental problems. The forecasting problems are effectively tackled by application of modeling techniques. A model is the simplified representation of a complex real physical system and the processes taking place in it. It can be physical (for example, a laboratory sand pack model), electrical analog, or mathematical. Development and applications of mathematical models are much easier than the other two types of models. Therefore, mathematical models are mostly in use today for solving groundwater management problems.

MATHEMATICAL MODELING

Modeling begins with a conceptual understanding of the physical problem (in this case, groundwater flow in the unconfined aquifer). The next step is translating the physical problem into a mathematical framework resulting in equation forms that describe the groundwater flow. Mathematical models may be deterministic, statistical, or some combination of the two. Deterministic models retain a good measure of physical insight while permitting any number of problems of the same class to be tackled with the same model. Here, discussion will be confined to deterministic models.

Formulations of groundwater flow equations are based on the conservation principles dealing with mass and momentum. These principles require that the net quantity of mass (or momentum) entering or leaving a specified volume of aquifer during a given time interval be equal to the change in the amount of mass (or moment) stored in the volume. Groundwater flow equations are formulated by combining the equation of motion in the form of Darcy's law, which follows principle of conservation of momentum with the mass balance equations, also known as continuity equations, which follows the principle of conservation of mass. Some mathematical models commonly used for solving the forecasting problem in the presence of recharge are discussed below:

2-D groundwater flow in an inhomogeneous anisotropic unconfined aquifer with a horizontal base is described by the following equation (1,8):

$$\frac{\partial}{\partial x}\left(K_x h \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y h \frac{\partial h}{\partial y}\right) + N(x, y, t) = S_y \frac{\partial h}{\partial t} \qquad (1)$$

in which h is the variable water table height measured from the horizontal base of the aquifer, K_x and K_y are the hydraulic conductivities in x and y directions, respectively, S_y is the specific yield, t is time of observation, and $N(x, y, t)$ is the sum of all recharge rates from distributed sources (recharge basins, ponds, streams, etc.) and withdrawal rates from distributed sinks (wells, leakage boundaries, etc.) and is represented by

$$N(x,y,t) = \begin{cases} \sum_{i=1}^{n} N_i(t) & \text{for } x_{i1} \le x \le x_{i2}, y_{i1} \le y \le y_{i2} \\ o & \text{elsewhere} \end{cases} \quad (2)$$

where n is the total number of basins, $N_i(t)$ is the time-varying recharge (or pumping) rate for the ith basin (or well, respectively), and x_{i1}, x_{i2}, y_{i1}, and y_{i2} are the coordinates of ith basin (or well). $N_i(t)$ is positive for recharge to the aquifer and negative for pumping.

For an inhomogeneous isotropic aquifer, Eq. (1) becomes

$$\frac{\partial}{\partial x}\left(K\,h\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K\,h\frac{\partial h}{\partial y}\right) + N(x,y,t) = S_y\frac{\partial h}{\partial t} \quad (3)$$

Equations (1 and 3) are nonlinear second-order partial differential equation. The nonlinearity is because of the presence of h as a coefficient of partial derivatives on the left-hand side. Solving these equations because of nonlinearity is possible only by numerical methods, such as finite difference, finite element, and boundary elements (1,9,10). These equations need to be linearized for their analytical solution.

For homogenous isotropic aquifers (K = constant), Eq. (3) can be written in the following two forms:

$$K\left[\frac{\partial}{\partial x}\left(h\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(h\frac{\partial h}{\partial y}\right)\right] + N(x,y,t) = S_y\frac{\partial h}{\partial t} \quad (4)$$

$$\frac{\partial^2 h^2}{\partial x^2} + \frac{\partial^2 h^2}{\partial y^2} + \frac{2N(x,y,t)}{K} = \frac{S_y}{Kh}\frac{\partial h^2}{\partial t} \quad (5)$$

Two procedures of lineraization are commonly used to facilitate analytical solutions of Eqs. (4 and 5). According to the first procedure, i.e., the Baumann procedure of lineraization, if the variation in h is much less than the initial height of the water table h_0, then the coefficient h appearing on the left-hand side of Eq. (4) can be replaced by h_0 (11). Then Eq. (4) can be rewritten as

$$T\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2}\right) + N(x,y,t) = S_y\frac{\partial h}{\partial t} \quad (6)$$

where $T = Kh_0$ (known as transmissivity). Now, Eq. (6) is linear in h. Sometimes the mean depth of saturation is also used in place of h_0.

In the second procedure, i.e., the Hantush procedure of linearization, h appearing in the denominator on the right-hand side of Eq. (5) is replaced by the weighted mean of the depth of saturation $\overline{h}$, a constant of linearization that is approximated by $0.5[h_0 + h(t_e)]$, and t_e is the period at the end of which $\overline{h}$ is to be approximated (12). Then, Eq. (5) becomes

$$\frac{\partial^2 h^2}{\partial x^2} + \frac{\partial^2 h^2}{\partial y^2} + \frac{2N(x,y,t)}{K} = \frac{S_y}{K\overline{h}}\frac{\partial h^2}{\partial t} \quad (7)$$

Now, Eq. (7) becomes linear in h^2. By substituting a new variable H, defined as $H = h^2 - {h_0}^2$, into Eq. (7) gives

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} + \frac{2N(x,y,t)}{K} = \frac{S_y}{K\overline{h}}\frac{\partial H}{\partial t} \quad (8)$$

GROUNDWATER FLOW EQUATIONS FOR SLOPING AQUIFER

2-D groundwater flow in a sloping unconfined aquifer is described by (13,14)

$$\frac{\partial^2 s}{\partial x^2} + \frac{\partial^2 s}{\partial y^2} - 2a\frac{\partial s}{\partial x} + \frac{2N(t)}{K} = \frac{1}{\Re}\frac{\partial s}{\partial t} \quad (9)$$

where $s = h^2$, $a = \theta/2D$, θ = slope of the base, D = the mean depth of saturation, $\Re = KD/S_y$, x, y = space coordinates, t = time of observation, and $N(t)$ = time varying rate of recharge.

One-dimensional groundwater flow equations can be obtained by substituting zero for the derivative of y in the above equations. These equations are used to predict the water table fluctuations in response to artificial recharge from strip basins, canals, channels, etc.

GROUNDWATER FLOW EQUATIONS IN CYLINDRICAL COORDINATES

These types of equations are used to describe groundwater flow induced by recharging through circular-shaped recharge basins/wells and is given by (15,16).

$$S\frac{\partial h}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(rq) + N(r) \quad (10)$$

where q is defined by Darcy's law as

$$q = -Kh\left(\frac{\partial h}{\partial r}\right) \quad (11)$$

The groundwater flow equations presented here are in the form of partial differential equations having an infinite numbers of solutions. To obtain a unique solution for a particular problem, more information about the aquifer's parameters, geometry of the flow domain and recharge basins, duration and rate of recharge rate, and initial and boundary conditions are needed. These values can be deduced from field as well as experimental methods (1,17,18).

Initial Conditions

Initial conditions describe distribution of h at all points of the flow domain at the beginning of the investigation, that is, at $t = 0$, which is expressed as

$$h = \psi(x, y, 0) \quad (12)$$

where ψ is a known value of h for all points of the flow domain.

Boundary Conditions

These conditions describe the nature of interaction of the flow system with its surroundings. Three types of boundary conditions are generally encountered in groundwater flow problems.

- Dirichlet boundary condition—In this case, h is prescribed for all points of the boundary for the entire period of investigation, which is expressed as

$$h = \psi\ (x, y, t) \tag{13}$$

  where $\psi\ (x, y, t)$ are known values of h at all points on the boundary.
- Neumann boundary condition—This type of boundary condition prescribes the flux across the boundary of the flow system and can be expressed as

$$q = \psi_1\ (x, y, t) \tag{14}$$

  where $\psi_1\ (x, y, t)$ are known values at the boundary. A special case of this boundary condition is the no flow boundary condition in which flux is zero. This condition occurs at impermeable surface or at the groundwater divide, a surface across which no flow takes place.
- Cauchy boundary condition—This boundary condition is encountered at the semipervious boundary layer between the aquifer and an open water body such as a river. As a result of the resistance to the flow offered by the semipervious boundary that lies between the aquifer and the river, the water level in the river differs from that in the aquifer on the other side of the semipervious boundary. In this case, the flux is defined by

$$q = K' \frac{h - h_0}{b} \tag{15}$$

  where h is the head at $x = 0$, h_0 is the water level in the river, and b and K' are the thickness and hydraulic conductivity of the semipervious boundary, respectively.

The purpose of solving a groundwater flow equation is to obtain the values of $h(x, y, t)$. Generally, two types of methods, namely analytical methods and numerical methods, are used for this purpose. Numerical methods are used to solve the nonlinear groundwater flow equation to tackle the real field problems, and analytical methods are used to solve the linearized form of groundwater flow equations. Analytical methods commonly used for the solution of groundwater problems include Fourier transforms, Laplace transforms, integral balance methods, method of separation of variables, approximate analytic methods, etc. Details about these methods can be found in many books (19–25). Most of the analytical solutions developed earlier for this purpose were based on the assumption of constant recharge. Warner et al. (26) have reviewed the performance of some such analytical solutions (27–31). However, the rate of recharge largely depends on the infiltration rate, which initially decreases because of swelling and dispersion of soil particles. After some time, the infiltration rate increases because of the release of air entrapped into soil pores and reaches to a maximum value. Then, it starts decreasing because of clogging of soil pores beneath the bottom of the basin. Recharge rate also follows a more or less similar pattern of variation with some time lag and less intensity. When it falls below a prescribed low value, the recharge operation is discontinued for some time. After drying and, if necessary, scrapping of the silted base of the basin, a high recharge rate closer to its initial value is rejuvenated in the next phase of recharge operation (1,32–34). Zomorodi (35) has also shown that the analytical solution of Dagan (36), which is based on the assumption of constant recharge rate, fails to predict the recession of the water table caused by decrease in the recharge rate. Therefore, it would be more appropriate to consider recharge rate as time-dependent to simulate the actual field conditions. Some solutions have been developed for the time-varying recharge cases in which the decreasing rate of recharge has been represented by two linear elements (37–39) or by exponential function (14,16,40–44). However, approximation of time-varying recharge by two linear elements or exponential function is possible only for one recharge cycle. However, recharge is applied intermittently for more than one cycle separated by dry periods. Manglik et al. (45), Rai et al. (46), Manglik and Rai (48), and Rai and Manglik (49) used a general scheme of recharge approximation for any number of recharge cycles. In this scheme, time-varying recharge is approximated by a number of linear elements of different lengths and slopes depending on the nature of variation of recharge rate. Later on, this scheme was modified to represent rates of recharge from any number of basins. In mathematical form, this scheme can be represented by

$$N_i(t) = \begin{cases} r_{ij}t + c_{ij} & t_j \le t \le t_{j+1}[j = 1, 2, \cdots, k-1] \\ r_{ik}t + c_{ik} & t \ge t_k \qquad [j = k] \end{cases} \tag{16}$$

where r_{ij} and c_{ij} are the slope and intercept of the jth line element of the recharge rate for the ith basin and k is the number of elements. The advantage of this scheme of recharge approximation is that any type of variation in the recharge rate for any number of recharge cycles from any number of recharge basins of different dimensions located anywhere within the flow domain can be approximated with the help of the required number of linear elements of different lengths and slopes depending on the nature of variation of recharge rate. By using this recharge scheme, several analytical solutions to describe water table fluctuation in different flow systems representing different physical conditions have been developed (50–53). The following analytical solution given by Manglik and Rai (50) is considered as an example to demonstrate the application of these solutions in prediction of water table fluctuation in the presence of time-varying recharge and

pumping,

$$h^2(x,y,t) = h_0^2 + \frac{8a}{K\pi^2}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{1}{mn}\sin\left(\frac{m\pi\, x}{A}\right)\sin\left(\frac{n\pi\, y}{B}\right) \sum_{i=1}^{N}\left[\cos\frac{m\pi\, x_{i2}}{A} - \cos\frac{m\pi\, x_{i1}}{A}\right] \left[\cos\frac{n\pi\, y_{i2}}{B} - \sin\frac{n\pi\, y_{i1}}{B}\right]\left[\sum_{j=1}^{k-1} R_{ij} + R_{ik}\right] \quad (17)$$

in which A and B are the length and width of the aquifer, $a = K\overline{h}/S_y$, and m and n are integers representing number of Fourier coefficients. $\lambda = \frac{a\,\pi^2}{4}\left[\frac{m^2}{A^2} + \frac{n^2}{B^2}\right]$

$$R_{ij} = \frac{r_{ij}}{\lambda}[t_{j+1}\exp\{-\lambda(t-t_{j+1})\} - t_j\exp\{-\lambda(t-t_j)\}] - \left(\frac{r_{ij}}{\lambda^2} - \frac{c_{ij}}{\lambda}\right)[\exp\{-\lambda(t-t_{j+1})\} - \exp\{-\lambda(t-t_j)\}]$$

$$R_{ik} = \frac{r_{ik}}{\lambda}[t - t_k\exp\{-\lambda(t-t_k)\}] - \left(\frac{r_{ik}}{\lambda^2} - \frac{c_{ik}}{\lambda}\right)[1 - \exp\{-\lambda(t-t_k)\}]$$

This solution is obtained by solving Eq. (8) with recharge/pumping rates defined by Eq. (16) and subjected to the horizontal water table as an initial condition and Dirichlet boundary condition. In order to demonstrate the application of Eq. (17) in the prediction of water table fluctuation, we consider an example in which an unconfined aquifer of 10×10 km^2 dimension is having two recharge basins of dimension 60×40 m^2 and 50×50 m^2 centered at (4470 m, 4500 m) and (5875 m, 5530 m), respectively, and two wells each of 10×10 cm^2 dimension centered at (5000 m, 4500 m) and (5000 m, 5500 m), respectively. The pattern of time-varying recharge rate and pumping rate are shown in Fig. 2. The recharge operation for both the basins consists of two wet periods and one dry period, each of 20 days duration. During the first wet period, the rate of recharge decreases from its initial value of 0.8 m d^{-1} to a lower value of 0.7 m d^{-1} after 2 days. It again increases and attains maximum value of 0.9 m d^{-1} on the fourth day. After that, it starts decreasing and reduces to zero on twentieth day. The second cycle of recharge operation begins on the fortieth day and continues until the sixtieth day. The nature of variation of recharge rate for the second cycle is considered similar to the first cycle. Pumping of groundwater at a rate of 10^5 m d^{-1} from each well is considered for two periods. The first period is from the tenth to the twentieth day, and the second period is from the fortieth to the fiftieth day after a gap of 20 days. Numerical values of other controlling parameters are $h_0 = 20$ m, $K = 8$ m d^{-1}, and $S_y = 0.20$. Two water table profiles computed for $t = 45$ days along a line parallel to the x-axis at $y = 4500$ m are shown in Fig. 3. These profiles pass through the center of one recharge basin and one well centered at (4470 m, 4500m) and (5000 m, 4500 m). The profile represented by the dotted curve is in response to recharge only. Hence, it shows only growth of groundwater mound. The profile represented by continuous curve shows growth as well

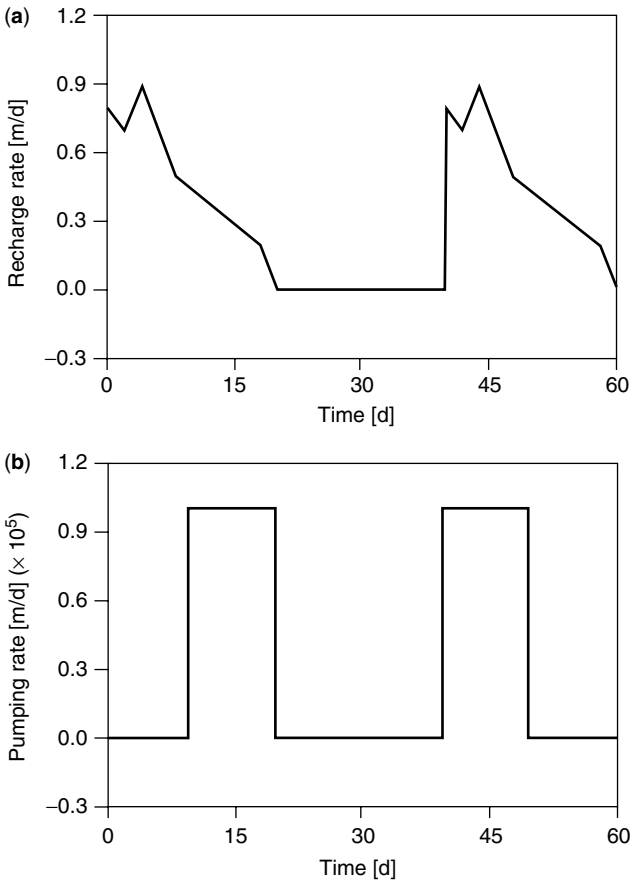


Figure 2. Nature of time-varying (**a**) recharge, and (**b**) pumping rates.

as depression of the water table at the respective site of recharging and pumping. This example demonstrates the capabilities of prediction of water table variations in response to time-varying recharge and withdrawal.

Accurate estimation of the varying recharge rate is a major problem in groundwater resources management. If the time history of water table variation at a site of an observation well is known, then analytical

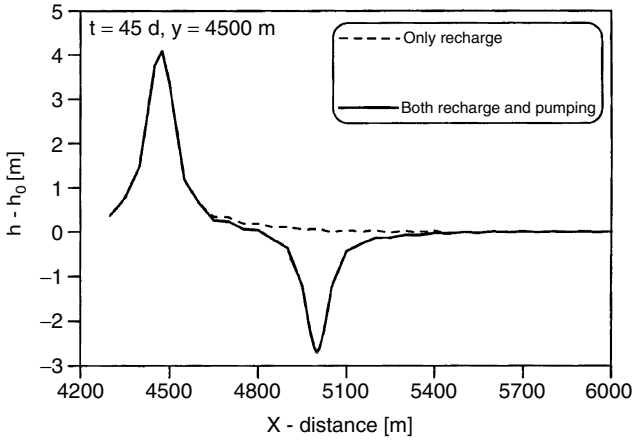


Figure 3. Water table profiles in the presence of only recharge (dashed curve), and both recharge and pumping (solid curve).

solutions can be used for the estimation of varying recharge rate by making a judicious selection of recharge rate using trial and error method, such that the computed water table variation matches well with the observed one. Although the application of analytical solutions is restricted to the relatively homogeneous isotropic aquifer system having boundaries of simple geometrical shapes, their application is fast and simple in comparison with that of the numerical methods. Analytical solutions are also useful for other purposes, such as analysis of the effects of various controlling parameters, such as aquifers properties, initial and boundary conditions, intensity and duration of recharge rate, shape, size, and location of a recharge basin, etc., on the response of the aquifer system. Such information is very essential for the judicious selection of a suitable recharge scheme out of many proposed schemes to achieve the preset objectives of groundwater resource management.

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BIBLIOGRAPHY

1. Bear, J. (1979). *Hydraulics of Groundwater*. McGraw-Hill, New York, p. 567.
2. Asano, T. (1985). Overview: Artificial recharge of groundwater. In: *Artificial Recharge of Groundwater*. T. Asano (Ed.). Butterworth Publ., New York, pp. 3–19.
3. Oaksford, E.T. (1985). Artificial recharge: methods, hydraulics and monitoring. In: *Artificial Recharge of Groundwater*. T. Asano (Ed.). Butterworth Publ., New York, pp. 69–127.
4. Singh, R. (2002). Building community leaders for groundwater resources management—working on people's priorities. In: *Proceedings of Intl. Conference on Sustainable Development and Management of Groundwater Resources in Semi-Arid Region with Special Reference to Hard Rocks*. M. Thanagarajan, S. N. Rai, and V. S. Singh (Eds.). Oxford & IBH Publ. Co., New Delhi, India, pp. 526–533.
5. Katyal, J.C., Singh, R.P., Sharma, S., Das, S.K., Padmanabhan, M.V., and Mishra, P.K. (1995). *Field Manual on Watershed Management*. Central Research Institute for Dryland Agricultural, Hyderabad, India, pp. 1–87.
6. Wilderer, P.A., Forstner, U., and Kuntschik, O.R. (1985). The role of river bank filtration along the Rhine river for municipal and industrial water supply. In: *Artificial Recharge of Groundwater*. T. Asano (Ed.). Butterworth Publ., New York, pp. 509–528.
7. Piet, G.J. and Zoedeman, B.C.J. (1985). Bank and dune infiltration of surface water in the Netherlands. In: *Artificial Recharge of Groundwater*. T. Asano (Ed.). Butterworth Publ., New York, pp. 529–540.
8. Rai, S.N. (2002). Groundwater flow modeling. In: *Dynamics of Earth's Fluid Systems*. S.N. Rai, D.V. Ramana, and A. Manglik (Eds.). A. A. Balkema Publ., Holland, pp. 49–62.
9. Pinder, G.F. and Gray, W.G. (1977). *Finite Element Simulation in Surface and Subsurface Hydrology*. Academic Press, New York, p. 295.
10. Cabral, J.J.S.P., Wrobel, L.C., and Brebbia, C. (1990). Boundary element analysis of unconfined flow in porous media using B-splines. In: *Proceedings of the 8th Intl. Conference on 'Computational methods in water resources, Part B*. Venice, pp. 405–411.
11. Rao, N.H. and Sarma, P.B.S. (1980). Growth of groundwater mound in response to recharge. *Groundwater*. **18**: 587–595.
12. Marino, M.A. (1967). Hele-Shaw model study of the growth and decay of groundwater ridges. *J. Geophys. Res.* **72**: 1195–1205.
13. Baumann, P. (1965). Technical development in groundwater recharge. In: *Advances in Hydroscience*. Vol. 2. V.T. Chow (Ed.). Academic Press, New York, pp. 209–279.
14. Ramana, D.V., Rai, S.N., and Singh, R.N. (1995). Water table fluctuation due to transient recharge in a 2-D aquifer system with inclined base. *Water. Resour. Manag.* **9**: 127–138.
15. Mercer, J.W. and Faust, C.R. (1980). Groundwater modeling; Mathematical models. *Groundwater*. **16**: 212–227.
16. Rai, S.N., Ramana, D.V., and Singh, R.N. (1998). On the prediction of ground water mound formation in response to transient recharge from a circular basin. *Water. Resour. Manag.* **12**: 271–284.
17. Todd, D.K. (1980). *Groundwater Hydrology*, 2nd Edn. John Wiley & Sons, New York, p. 535.
18. Rushtun, K.R. (2003). *Groundwater Hydrology: Conceptual and Computational Models*. John Wiley & Sons, New York, p. 407.
19. Carslaw, M.S. and Jaeger, J.C. (1959). *Conduction of Heat in Solids*. Oxford Univ. Press, Oxford, UK, p. 510.
20. Polubarinova-Kochina, P.Ya. (1962). *Theory of Groundwater Movement*. Princeton University Press, Princeton, NJ, p. 613.
21. Abramowidz, M. and Stegun, I.A. (1970). *Handbook of Mathematical Functions*. Dover, New York, p. 1046.
22. Ozisik, M.N. (1980). *Heat Conduction*. John Wiley & Sons, New York, p. 687.
23. Sneddon, I.N. (1974). *The Use of Integral Transforms*. Tata McGraw Hill, New Delhi, India.
24. Lee, T-C. (1999). *Applied Mathematics in Hydrogeology*. Lewis, Boca Raton, FL, p. 382.
25. Bruggeman, G.A. (1999). *Analytical Solution of Geohydrological Problems*. Elsevier, New York, p. 959.
26. Warner, J.W., Molden, D., Chehata, M., and Sunada, D.K. (1989). Mathematical analysis of artificial recharge from basins. *Water Resour. Bull.* **25**(2): 401–411.
27. Baumann, P. (1952). Groundwater movement controlled through spreading. *Amer. Soc. Civ. Eng. Trans.* **117**: 1024–1074.
28. Hantush, M.S. (1967). Growth and decay of groundwater mounds in response to uniform percolation. *Water Resour. Res.* **3**(1): 227–234.
29. Glover, R.E. (1961). *Mathematical Derivations as Pertain to Groundwater Recharge*. Agricultural Research Service, USDA, Ft. Collins, CO, p. 81.
30. Hunt, B.W. (1971). Vertical recharge of unconfined aquifers. *J. Hydraul. Div. ASCE.* **97**(HY7): 1017–1030.
31. Rao, N.H. and Sarma, P.B.S. (1981). Groundwater recharge from rectangular areas. *Groundwater*. **19**: 271–274.
32. Singh, V.P. (1989). *Hydrologic Systems—Watershed Modelling*. Vol. 2. Prentice Hall, Englewood Cliffs, NJ, p. 320.
33. Detay, M. (1995). Rational groundwater reservoir management, the role of artificial recharge. In: *Artificial Recharge of Groundwater II*. A.I. Johnson and R.D.G. Pyne (Eds.). ASCE, New York, pp. 231–240.

34. Mousavi, S.F. and Rezai, V. (1999). Evaluation of scraping treatment to restore infiltration capacity of three artificial recharge projects in central Iran. *Hydrogeol. J.* **7**: 490–500.
35. Zomorodi, K. (1991). Evaluation of response of a water table to a variable recharge rate. *Hydrol. Sci. J.* **36**: 67–78.
36. Dagan, G. (1966). *Linearized Solutions of Free-Surface Groundwater Flow with Uniform Recharge*. Technion Publication No. 84, Technion, Israel Institute of Technology, Tel Aviv, Israel.
37. Rai, S.N. and Singh, R.N. (1979). Variation of water table induced by time varying recharge. *Geophys. Res. Bull.* **17**(2): 97–109.
38. Rai, S.N. and Singh, R.N. (1980). Dynamic Response of an unconfined aquifer system subjected to transient recharge. *Geophy. Res. Bull.* **18**(2): 49–56.
39. Rai, S.N. and Singh, R.N. (1981). A mathematical model of water table fluctuations in a semi-infinite aquifer induced by localised transient recharge. *Water Resour. Res.* **17**(4): 1028–1032.
40. Abdulrazzak, M.J. and Morel-Seytoux, H.J. (1983). Recharge from an ephemeral stream following wetting front arrival to water table. *Water Resour. Res.* **19**: 194–200.
41. Rai, S.N., Manglik, A., and Singh, R.N. (1994). Water table fluctuation in response to transient recharge from a rectangular basin. *Water Resour. Manag.* **8**(1): 1–10.
42. Rai, S.N. and Singh, R.N. (1995). An analytical solution for water table fluctuation in a finite aquifer due to transient recharge from a strip basin. *Water Resour. Manag.* **9**(1): 27–37.
43. Rai, S.N. and Singh, R.N. (1996). On the prediction of ground water mound formation due to transient recharge from a rectangular area. *Water. Resour. Manag.* **10**: 189–198.
44. Rai, S.N. and Singh, R.N. (1998). Evolution of the water table in a finite aquifer due to transient recharge from two parallel strip basins. *Water. Resour. Manag.* **12**: 199–208.
45. Manglik, A., Rai, S.N., and Singh, R.N. (1997). Response of an unconfined aquifer induced by time varying recharge from a rectangular basin. *Water Resour. Manag.* **11**(3): 185–196.
46. Rai, S.N., Ramana, D.V., and Manglik, A. (1997). Modeling of water table fluctuation in finite aquifer system in response to transient recharge. In: *Proceeding of Intl. Symposium of Emerging Trend in Hydrology*. D. C. Singhal et al. (Eds.). pp. 243–250.
47. Rai, S.N., Ramana, D.V., Thiagarajan, S., and Manglik, A. (2001). Modelling of groundwater mound formation due to transient recharge. *Hydrological Processes* **15**(8): 1507–1514.
48. Manglik, A. and Rai, S.N. (1998). Two-dimensional modelling of water table fluctuations due to time-varying recharge from rectangular basin. *Water Resour. Manag.* **12**: 467–475.
49. Rai, S.N. and Manglik, A. (1999). Modelling of water table variation in response to time varying recharge from multiple basins using the linearized Boussinesq equation. *J. Hydrol.* **220**: 141–148.
50. Manglik, A. and Rai, S.N. (2000). Modelling of water table fluctuation in response to time varying recharge and withdrawal. *Water Resour. Manag.* **14**(5): 339–347.
51. Rai, S.N. and Manglik, A. (2000). Water table variation due to time varying recharge and withdrawal. In: *Groundwater: Past Achievement and Future Challenges*. Oliver Silio et al. (Eds.). Proc. of XXX IAH Congress, Minneapolis, MN, pp. 259–262.
52. Rai, S.N. and Manglik, A. (2001). Modelling of water table fluctuations due to time-varying recharge from canal seepage. In: *New Approaches Characterizing Groundwater Flow*. K.-P. Seiler and S. Wohnlich (Eds.). Balkema Pub., The Hague, The Netherlands, pp. 775–778.
53. Manglik, A., Rai, S.N., and Singh, V.S. (2004). Modeling of aquifer response to time varying recharge and pumping from multiple basins and wells. *J. Hydrol.* **292**: 23–29.

GROUNDWATER AND ARSENIC: CHEMICAL BEHAVIOR AND TREATMENT

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INTRODUCTION

Arsenic is not an abundant element in the earth's crust; the average crustal concentration of arsenic is 1.8 mg/Kg (1) to 5 mg/Kg (2). Arsenic ranks as the 52nd element in abundance, between tin and molybdenum (1). However, through geogenic processing of crustal materials, arsenic can be concentrated in soils to a typical range of 2 to 20 mg/Kg (3) to 1 to 50 mg/Kg (2), with concentrations as high as 70 mg/Kg being unremarkable (3). Human activity generates anthropogenic arsenic, which makes it the third most common regulated inorganic contaminant found at U.S. Superfund sites.

Arsenical copper was in use by 4000 BC, and the toxic effects of arsenic were documented by early Greek writers. More recently, arsenic has been linked to skin, bladder, and other cancers (4). The U.S. Environmental Protection Agency (USEPA) lowered the arsenic standard in drinking water from 50 μg/L to 10 μg/L, effective January 23, 2006.

Modern usage of arsenic includes formulation of pesticides and herbicides, decolorization of glass, paint manufacturing, the production of semiconductors, and the treatment/preservation of wood. Pressure treated lumber was commonly treated for decades using copper-chromium-arsenate (CCA). This product, also called "green wood," has been used for foundation lumber and more recently as wood for outdoor children's play structures and picnic tables. The CCA wood is being phased out for toxicity concerns and environmental reasons. Many of the pressure treatment lumber facilities have significant soil and groundwater contaminated with arsenic as well as chromium.

CHEMICAL CHARACTER

Although arsenic occurs in more than 20 minerals, only a few are commonly found in ore deposits (5). Arsenic may occur as a semimetallic element (As^0), arsenate (As^{5+}), arsenite (As^{3+}), or arsine (As^{3-}). The biogeochemistry of arsenic involves adsorption, biotransformation, REDOX reactions, and precipitation-dissolution processes (6,7).

The chemical character of arsenic is labile and readily changes oxidation state or chemical form through chemical or biological reactions that are common in the environment. Therefore, rather than solubility equilibrium controlling the mobility of arsenic, it is usually controlled by REDOX conditions, pH, biological activity, and adsorption/desorption reactions. Arsenic in groundwater most often occurs from geogenic sources, although anthropogenic arsenic pollution does occur. Geogenic arsenic is almost exclusively an arsenite or arsenate. The most oxidized pentavalent form, arsenic, forms oxyanions ($H_3ASO_4^-$, $H_2ASO_4^-$, H2ASO4-, $HASO_4^{2-}$, ASO_3^-). These arsenic oxyanions are isomorphous with oxyanions of phosphorous, substituting for phosphate in both marine organisms and phosphate deposits (4). Arsenite is the trivalent form that also forms a series of oxyanions that change specific configuration and charge with pH. Of critical importance with regard to the controls of the mobility of arsenite is the fact that at a pH of 9.5 or lower, the arsenite oxyanion is not charged. This result obviates all ionic interactions of the species.

Common arsenic minerals are arsenopyrite (FeAsS), enargite (Cu,AsS), proustite (Ag,AsS), and lollingite ($FeAs_2$). Late-stage magmatic crystallization (pyrometasomatic and hydrothermal stages) contributes to arsenic-rich sulfides. In sedimentary rocks, arsenic is commonly found adsorbed onto fine-grained sedimentary rocks, such as iron and manganese oxides (4). According to the U.S. Geological Survey, arsenic concentrations in sedimentary iron-ores range from 65 to 650 mg/Kg (8). Arsenic is also associated with sedimentary pyrite at concentrations of 100 to 77,000 mg/Kg (6).

Anthropogenic arsenic may have any form including organic arsine species. Groundwater in acidic to intermediate volcanic rocks, or in sediments derived from those rocks, will often have arsenic concentrations exceeding 50 μg/L.

Figure 1 illustrates the difference in molecular structure between arsenate and arsenite. The double bond oxygen in the arsenate molecule influences its ability to become ionized through the of hydrogen ions. The process is termed dissociation. A negative charge develops on the arsenate molecule when dissociation occurs. The double bond oxygen increases the capacity to delocalize that charge, which cases the loss of hydrogen ions. The propensity for ionization is expressed by the constant of dissociation, pKa. The pKa value, which is a negative log, shows a greater degree of dissociation with a smaller value.

For arsenate and arsenite, pKa values are as follows:

Arsenate- H_3ASO_4 $pK_1 = 2.19$ $pK_2 = 6.94$

$pK_3 = 11.5$

Arsenite- H_3ASO_3 $pK_1 = 9.20$ $pK_2 = 14.22^*$

$pK_3 = 19.22^*$

The pH at which these ionization steps occur is significantly different between arsenate and arsenite, as illustrated in Fig. 2 (10,11). Figure 2 also shows the control of REDOX potential (Eh) on the arsenate/arsenite transition. This Eh/pH relationship is key in understanding arsenic mobility in groundwater and the effectiveness of arsenic water treatment systems.

*These pKa values are extrapolated from the strength of oxygen acid rules (9).

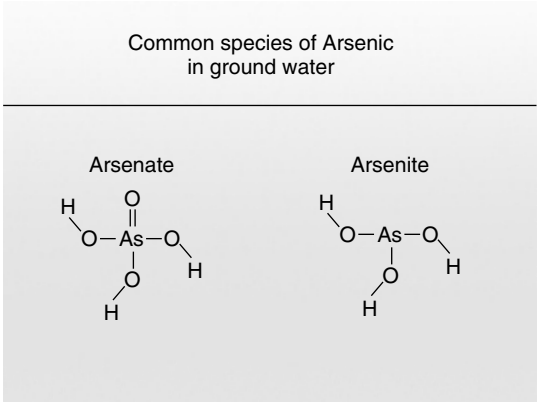


Figure 1. Difference in molecular configuration of arsenate and arsenite.

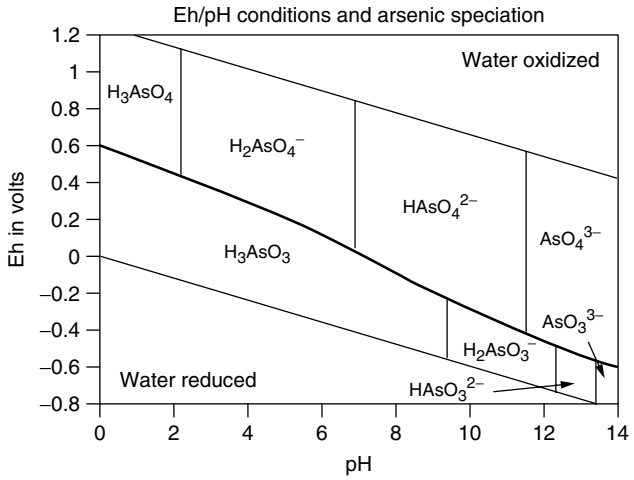


Figure 2. Control of arsenic speciation by Eh and pH conditions.

Arsenic Immobilization

The previous section described the conditions under which arsenic can become an ionized species. The most commonly recognized adsorption reactions are based on ion exchange between charged adsorption sites and charged soluble ions. However, London Van der Waals bonding is another mechanism that is also responsible for adsorption. This type of bonding is the result of complex interactions among the electron clouds of molecules, molecular polarity, and attractive forces of an atomic nucleus for electrons beyond its own electron cloud. Consequently, some degree of immobilization can occur with soluble species that are not ionized. Arsenic immobilization through ionic adsorption can be controlled within normal oxidizing Eh/pH conditions. London Van der Waals bonding is complex to the point of unpredictability except for arsenic

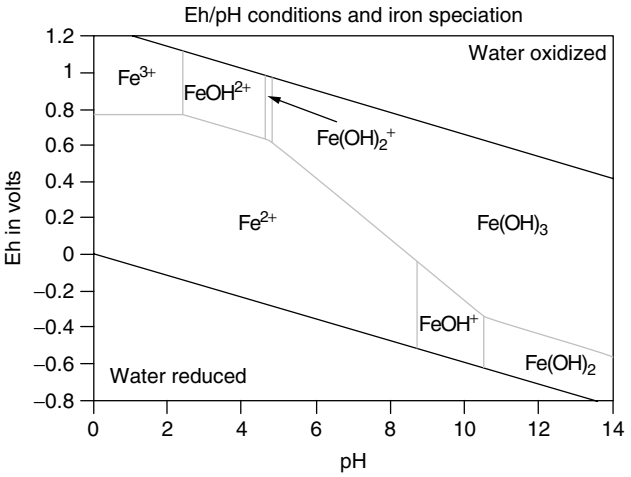


Figure 3. Iron speciation as controlled by Eh/pH conditions.

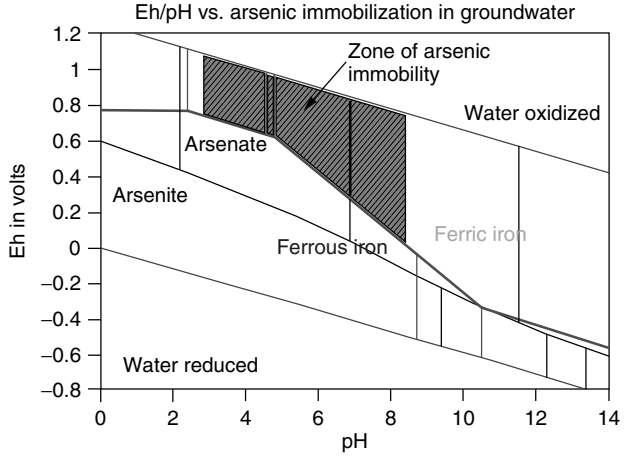


Figure 4. Arsenic mobility in groundwater as controlled by the effect of Eh/pH conditions on the speciation of arsenic and iron.

mobility at extreme Eh/pH conditions that can be obtained in industrial settings, but not in groundwater.

Components of soil that participates in both types of adsorptive reactions include clays, carbonaceous material, and oxides of iron, aluminum, and manganese. In the most shallow soils, the organic fractions typically dominate, whereas at greater depths, iron oxyhydroxides play the principal adsorptive role.

The typical iron content of soil ranges from 0.5% and 5%. Not only is iron common, but as with arsenic, it is also labile and readily reflects changes in surrounding Eh/pH conditions. This relationship for iron is illustrated in Fig. 3 (12).

Ferric hydroxide acts as an amphoteric ion exchanger. Depending on pH conditions, the ferric hydroxide has the capacity for cation or anion exchange. Given the average iron concentration in soil and soluble arsenic concentrations in groundwater at 50 μg/L, ferric hydroxides in sediment can potentially adsorb 0.5 to 5 pounds of arsenic per cubic yard of aquifer matrix, which may then act as a significant potential reservoir for arsenic release under changing Eh/pH conditions.

ARSENIC IN GROUNDWATER

Arsenic concentrations up to 12,000 μg/L have been reported for the St. Peter aquifer in eastern Wisconsin (4). In this case, the oxidation of arsenic sulfides in a sulfide cement horizon (SCH) within the aquifer is a source of the high arsenic concentrations.

Figure 4 superimposes the Eh/pH relationship for the arsenic and iron systems; it illustrates the conditions under which arsenic will be immobilized in a groundwater system. Of equal importance, it illustrates how arsenic adsorbed to ferric hydroxides in sediment can be released at exposure to groundwater that is chemically reducing. Two effects would be at work: Arsenate is reduced to arsenite that will not remain ionically bound to the geologic substrate, and ferric iron is reduced to ferrous, which is soluble under normal pH conditions. Outside the immobilized zone, arsenic mobility is variable. London Van der Waals bonding of arsenite is in effect, but it is not sufficient to assure complete immobilization.

WATER TREATMENT SYSTEMS

Introduction

Following is a brief review of various technologies used for the removal of arsenic from drinking water and industrial wastewater. Table 1 summarizes the effectiveness of each and gives the source for the information.

Arsenite Oxidation

As previously described, the ionization chemistry of arsenic in groundwater precludes the removal of arsenite by ion exchange within normal pH ranges. Other technologies including coprecipitation, electrodialysis, and reverse osmosis are also affected by arsenite's dissociation profile. One solution to this problem is an oxidation step to form arsenate. Figure 5 illustrates the Eh/pH range required for this process. Oxidation, particularly of drinking water, may be problematic. Chemical residues of the oxidant, byproducts from oxidation of other organic or inorganic species, reagent costs, and operational issues are all factors. Oxygen would be ideal, as it is thermodynamically capable of this oxidizing step. The kinetics for oxidizing arsenic compounds in groundwater are exceedingly slow (22). It is possible to use gas diffusion technologies that slowly release dissolved oxygen into aquifers and that have demonstrated the capacity to convert anaerobic groundwater systems into aerobic systems within 3 to 6 months (23). This process will convert soluble ferrous iron to insoluble ferric iron oxides capable of attracting arsenate to their surfaces. The oxidation of arsenite is complex and may take additional time or the presence of other abiotic or biological (24) stimulants. In Bangladesh, *in situ* concentrations of arsenic less than 0.1 mg/L were readily removed by the oxygenation of groundwater; concentrations greater than that had only 50% removal (25).

Other chemicals can affect arsenite oxidation including free chlorine, hypochlorite, ozone, permanganate, and hydrogen peroxide with ferrous iron.

Table 1. Effectiveness of Arsenic Water Treatment Methods

Treatmenttechnology	Initial Arsenic Concentration	Final Arsenic Concentration*	Reference
Iron Coprecipitation	Oxidized Arsenic 56 mg/L	10 μg/L	(13)
	Arsenate 350 μg/L	6 μg/L	(14)
	Arsenite 350 μg/L	140 μg/L	(14)
	Arsenate 560 μg/L	10 μg/L	(15)
	Arsenate 300 μg/L	6 μg/L	(16)
	Arsenite 300 μg/L	138 μg/L	(16)
Alum Coprecipitation	Arsenate 350 μg/L	74 μg/L	(14)
	Arsenite 350 μg/L	263 μg/L	(14)
	Arsenate 300 μg/L	30 μg/L	(16)
	Arsenite 300 μg/L	249 μg/L	(16)
Lime Precipitation	Arsenate 500 mg/L	4 mg/L	(17)
	Arsenite 500 mg/L	2 mg/L	(17)
	Arsenate 2 mg/L	20 μg/L	(17)
	Arsenite 2 mg/L	160 μg/L	(17)
Activated Alumina	Arsenate 100 μg/L	4 μg/L	(18)
	Arsenite 100 μg/L	Ineffective	(18)
	Arsenate 57 μg/L	ND at pH 6.0	(19)
	Arsenite 31 μg/L	Ineffective	(19)
Ion Exchange	Arsenate 100 mg/L	<800 μg/L	Vance
	Arsenate 68 mg/L	12.2 to 0 mg/L	(20)
Reverse Osmosis	Arsenite 37 μg/L	7 μg/L	(19)
	Arsenate 51 μg/L	1.5 μg/L	(19)
Electrodialysis	Arsenite 188 μg/L	136 μg/L	(19)
Sulfide Precipitation	Arsenate 132 mg/L	26 mg/L	(21)
Activated Carbon	Arsenite 500 μg/L	300 μg/L	(21)

*The current limit for drinking water is 50 μg/L.

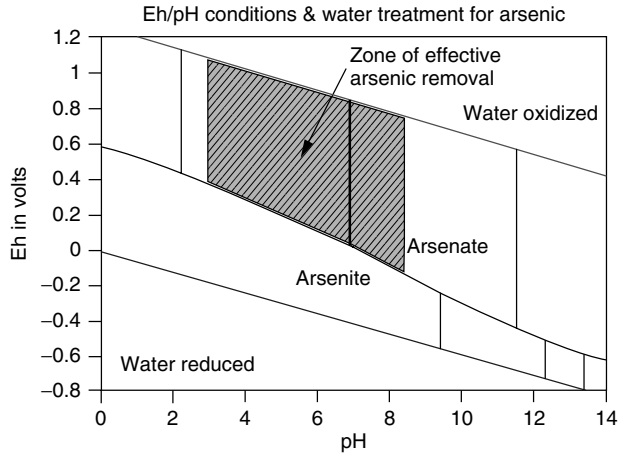


Figure 5. Eh/pH range required for effective treatment of soluble arsenic.

Iron Coprecipitation

Coprecipitation of arsenate with ferric iron is recognized as overall the most effective and practical existing method of arsenic removal. Ferric iron coprecipitation is particularly useful in the mining industry, where large amounts of ferric iron and arsenic can be byproducts of production or refining. Adding ferric iron salts for the treatment of drinking water is usually necessary. Figure 4 shows that arsenate is readily removed by iron coprecipitation and the Eh/pH conditions that must be maintained to effect that removal. Because of London Van der Waals bonding, ferric iron coprecipitation of arsenite is also moderately effective, with 50% removal at a pH of 7.0 (26).

The use of iron hydroxides for the coprecipitation of arsenic in industrial wastewater (in which arsenic is in the mg/L range) requires iron dosage four to eight times higher than that of the soluble arsenic; a greater iron dosage yields no further benefit (27).

Alum Coprecipitation

Suspended aluminum salts (alum) can remove arsenate via mechanisms similar to those for ferric hydroxides. However, it is less effective over a narrower pH range for arsenate removal and is ineffective for removal of arsenite (16).

Lime Precipitation

In testing by Nishimura and Tozawa (17), removal of arsenic with lime precipitation was feasible, but not necessarily practical. High concentrations of arsenic were removed to concentrations of 2 and 4 mg/L for arsenate and arsenite, respectively. Removal to lower levels required a second treatment step in which initial arsenic concentrations of 2 mg/L were lowered to 20 μg/L for arsenate and 160 μg/L for arsenite. However, to achieve these removal efficiencies, the lime dosage was between 5 and 15 g/L.

Activated Alumina

Activated alumina can be effective for the removal of arsenate under moderately acidic pH conditions

(5.5 to 6.0). High levels of competing anions such as sulfate significantly reduce the effectiveness of activated alumina (18). The use of activated alumina for complete arsenite removal is ineffective because of the nonionic character of arsenite in that pH range (see Fig. 1). Some initial arsenite removal is observed because of London Van der Waals bonding, but compared with arsenate adsorption, this capacity is rapidly exhausted.

Ion Exchange

Ion exchange has the potential for soluble arsenic removal. Anion exchange resins are available in two basic forms, weak base and strong base. Many weak-base anion exchangers are capable of significant adsorption because of London Van der Waals bonding in addition to ion exchange, which gives them a higher level of adsorptive capacity for nonionic arsenite. The author has evaluated anion exchange resins for arsenate removal. The most effective activation was in the hydroxyl form. Chloride and acetate were also tested. Weak base resins had higher loading capacities than did strong base (6% vs. 4.8%), but they did not have adequate removal efficiencies (75% vs. 99+% for the strong base resin). Anion exchange resins are also prone to chromatographimg because of the presence of competing anions in the treated water. However, ion exchange is an area of intense research where the development of anionic chelating exchange resins or ion exchange polymers may dramatically improve the technology for arsenic treatment.

Reverse Osmosis

Reverse osmosis (RO) has been shown to have a removal efficiency greater than 97%. Electrodialysis was only 73% effective. When used to treat 100% arsenite, removal was only 28% (19).

Other

Rosehart (21) evaluated a series of removal technologies including activated carbon and sulfide precipitation. Neither performed at a level adequate for use in the treatment of drinking water.

CONCLUSIONS

The behavior of arsenic in groundwater and industrial wastewater is dominated by REDOX and pH conditions. Under a limited range of specific Eh/pH conditions, the ability to predict total immobility of arsenic in groundwater and in water treatment systems exists (see Figs. 4 and 5). Except for those conditions, arsenic will be partially mobile, the magnitude of which is difficult to predict.

Implications of this behavior include:

- Arsenic treatment without control of Eh/pH is likely to be ineffective.
- The injection of water in a reduced oxidation state into sediments with adsorbed arsenic may cause a dramatic mobilization of arsenic into the groundwater.
- If ferric iron sludges used for the coprecipitation of arsenic are disposed under improper Eh/pH conditions, arsenic will remobilize. *In situ* remediation via recovery or stabilization of arsenic contaminated groundwater should be focused on Eh control through chemical or biological methods

Site-specific arsenic chemistry including source, mobility, migration, fate, and transport is complex. Any *in situ* treatment of groundwater containing arsenic should be evaluated carefully with laboratory bench tests, computer groundwater modeling, and field pilot tests before full-scale remediation is attempted.

BIBLIOGRAPHY

1. Demayo, A. (1985). Elements in the Earth's crust. In: *CRC Handbook of Chemistry and Physics*, 66th Edn. R.C. Weast (Ed.). CRC Press Inc., Boca Raton, FL, p. F145.
2. Lindsay, W.L. (1979). *Chemical Equilibria in Soils*. John Wiley & Sons, New York.
3. Yan Chu, H. (1994). Arsenic distribution in soils. In: *Arsenic in the Environment, Part I: Cycling and Characterization*. J.O. Nriagu (Ed.). John Wiley & Sons, New York, pp. 17–50.
4. National Research Council (NRC). (1999). *Arsenic in Drinking Water*. National Academy Press, Washington, DC.
5. Johnson, J.A. and Schreiber, M. (2004). *Arsenic: Perspectives Regarding a New Environmental Concern, The Professional Geologist*. American Institute of Professional Geologists, Westminster, CO, pp. 41–44.
6. Smedley, P.L. and Kinniburgh, D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**(5): 517–568.
7. Welch, A.H., Westjohn, D.B., Helsel, D.R., and Wanty, R.B. (2000). Arsenic in ground water of the United States: Occurrence and geochemistry. *Ground Water* **38**(4): 589–604.
8. Gualtieri, J.L. (1973). United States Mineral Resources. In: *Geological Survey Professional Paper #820*. U.S. Geological Survey, Reston, VA, pp. 51–61.
9. Pauling, L. (1970). *General Chemistry*. Dover Publications, Mineola, NY.
10. Robins, R.G. (1985). The aqueous chemistry of arsenic in relation to hydrometallurgical processes, impurtity control and disposal. *Proceedings of CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting*. pp. 1–1–1-26.
11. Welch, A.A., Lico, M.S., and Hughes, J.L. (1988). Arsenic in groundwater of the Western United States. *Groundwater* **26**(3): 333–347.
12. Hem, J.D. (1961). Stability field diagrams as aids in iron chemistry studies. *J. Am. Water Works Assoc.* **53**(2): 211–232.
13. Brewster, M.D. (1992). Removing arsenic from contaminated wastewater. *Water Treatment Technol.* **November**: 54–57.
14. Logsdon, G.S., Sorg, T.J., and Symons, J.M. (1974). Removal of Heavy Metals by Conventional Treatment. *Proceedings of the 16th Water Quality Conference*. University of Illinois, Urbana, IL, pp. 11–133.
15. Shen, Y.S. (1973). Study of arsenic removal from drinking water. *J. Am. Water Works Assoc.* **651**: 543–548.

16. Sorg, T.J. and Logsdon, G.S. (1978). Treatment technology to meet the interim primary drinking water regulations for inorganics, Part 2. *J. Am.Water Works Assoc.* **70**: 379–393.
17. Nishimura, T. and Tozawa, K. (1985). Removal of arsenic from wastewater by addition of calcium hydroxide and stabilization of arsenic-bearing precipitates by calcination. *Proceedings of CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting*. pp. 3–1–3-18.
18. Frank, P. and Clifford, D. (1986). *Arsenic (III) Oxidation and Removal from Drinking Water*. U.S. EPA, EPA-600-52-86/021.
19. Clifford, D. and Lin, C-C. (1991). *Arsenic(III) and Arsenic(V) Removal from Drinking Water in San Ysidro, New Mexico*. U.S. EPA Proj. Sum., EPA/600/S2-91/011.
20. Calmon, C. (1973). Comment. *J. Am. Water Works Assoc.* **651**: 568–569.
21. Rosehart, R. and Lee, J. (1972). Effective methods of arsenic removal from gold mine wastes. *Can. Min. J.* **June**: 53–57.
22. Clifford, D., Ceber, L., and Chow, S. (1983). Arsenic(III)/Arsenic(V) separation by chloride- form ion-exchange resins. XI. *Am. Water Works Assoc. Water Qual. Tech. Conf.*, Norfolk, VA.
23. Kolhatkar, R. (2002). Stable isotope analyses to demonstrate MTBE biodegradation in ground water. *Groundwater Resources Association of California MTBE Symposium*, San Jose, CA, Oct. 17, Abstracts/presentation.
24. Phillips, S.E. and Taylor, M.L. (1976). Oxidation of arsenite to arsenate by *Alcaligenes* faecalis. *App. Env. Microbiol.* **32**(3): 392–399.
25. Sarkar, A.R. and Rahman, O.T. (2001). In-situ removal of arsenci—experiences of DPHE-Danida Pilot Project. In: *Technologic for Arsenci Removal from Drinking Water*. M. Amhed, A. Feroze, M. Ashraf, and Z. Adeel (Eds.). pp. 201–206.
26. Pierce, M.L. and Moore, C.B. (1982). Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**: 1247–1253.
27. Krause, E. and Ettel, V.A. (1985). Ferric arsenate compounds: Are they environmentally safe? Solubilities of basic ferric arsenates. *Proceedings of CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting*. pp. 5–1–5-20.

TREATMENT OF ARSENIC, CHROMIUM, AND BIOFOULING IN WATER SUPPLY WELLS

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INTRODUCTION

Arsenic

Arsenic has been used as a component of pesticides and thus may enter streams or groundwater through waste disposal or agricultural drainage. Arsenic is also present in volcanic gases and is a common constituent of geothermal or spring water.

As small amounts of arsenic can be toxic to humans, it is considered a highly undesirable impurity in water supplies; an upper concentration limit of 50 μg/L, established in 1976 by the U.S. EPA, has now been lowered to 10 μg/L.

Arsenic may form metal arsenides in which its oxidation state is negative (1). Arsenic may also form sulfides and can be present as an accessory element in sulfide ore deposits. In solution in water, the stable forms are arsenate (As^{5+}) or arsenite (As^{3+}) oxyanions. A pH–E_h diagram showing fields of dominance of aqueous arsenates (1) indicates that the monovalent arsenate anion $H_2AsO_4^-$ is expected to predominate between pH 3 and 7 and the divalent species $HAsO_4^{2-}$ takes over from pH 7 to 11. Mildly reducing conditions favor the uncharged arsenite ion $HAsO_2$ (aq).

Chromium

Chromium is an inorganic element that is used in electroplating, leather tanning, wood treatment, pigment manufacture, and cooling tower treatment for corrosion control. Chromium can contaminate drinking water sources through discharges from industries, leaching from hazardous waste sites, or it may occur naturally from the erosion of natural deposits. Two forms of chromium can occur in water sources: chromium (III) and chromium (VI). Chromium (III) is an essential nutrient at trace concentrations. Chromium (VI) is toxic and is the basis for setting the chromium drinking water standard. The ratio of the two forms can vary quite a bit in natural waters. Evidence also exists to suggest that chromium (VI) may be converted to chromium (III) in the human body, particularly in the acidic digestive system.

The U.S. Environmental Protection Agency (EPA) classified chromium (VI) as a human carcinogen by inhalation. In 1991, it reviewed the existing standard for total chromium and the most recent scientific research available. As a result, the EPA actually raised the maximum contaminant level from 50 to 100 parts per billion as total chromium, based on its conclusion that chromium (VI) is not carcinogenic by ingestion.

In California, the drinking water standard is 50 parts per billion for total chromium [the sum of chromium (III) and chromium (VI)]. A public health goal is a "risk assessment" of the concentration of a contaminant in drinking water that poses no significant health risk to the consumer. The recommended public health goal determined by the Cal/EPA Office of Environmental Health Hazard Assessment (state health experts) for total chromium is 2.5 parts per billion.

Well Biofouling

Iron and manganese biofouling (usually associated with "iron bacteria") are common in water supply wells and attached appurtenances. Although biofouling sometimes has no overt symptoms, it may cause clogging, corrosion, and water quality degradation. These problems pose a considerable challenge to water utilities and well owners in North America and around the world. Precise estimates of increased operational and mitigation costs resulting from damage and loss of efficiency from well biofouling are

not available. Nevertheless, it is believed to be widespread, costly, underreported, and not adequately remedied in actual practice, resulting in frequent operating problems. Although preventive maintenance would be more cost-effective, the most common approach to iron biofouling problems in wells is crisis management. Preventive maintenance is seldom employed, however, because suitable maintenance monitoring methods and practical protocols for detecting iron and manganese biofouling problems before they severely affect well production and water quality have not been available (2).

Understanding the cause of water well deterioration and developing ways to sustain water well environments is important in maintaining and improving the quality of life in rural areas. The deterioration of well yield and water quality is a concern to individuals, small communities, and industries that rely on water wells as their principal source of water. Currently, when the quality or quantity of water produced declines dramatically, wells are often abandoned, or treatments are applied with little understanding of the cause of these problems. The cost of replacing these wells can have a significant economic impact on well owners. Correctly identifying the cause of water well problems offers the possibility of effective treatment and maintenance instead of well abandonment. Losses in water well production and water quality have traditionally been attributed to the chemical and physical properties of the water well environment. Many of these problems can be solved by well-established diagnostic and rehabilitative techniques. However, less recognized is that groundwater contains microorganisms such as bacteria, and the activities of these microorganisms also cause significant water well problems. Water well deterioration caused by microbiological activity is termed biofouling. Installing and pumping a well increases the level of oxygen and nutrients in the well and in the surrounding aquifer, encouraging bacterial cells, which are naturally present in groundwater, to anchor themselves to surfaces in the well and around the well intake. Once attached, these bacteria quickly multiply and colonize these surfaces. The bacterial colonies form a gel-like slime or biofilm that captures chemicals, minerals, and other deposits, such as clays and silts, moves to the well during pumping, and forms biomasses.

Some of the byproducts of bacterial growth, such as oxidized iron and manganese, also accumulate in these secretions, which leads to the production of the red or black slimes often found in toilet tanks or observed on pumps and discharge lines when they are pulled from a well. Biofouling of a water well occurs when biofilms accumulate a sufficient amount of debris to interfere with water flow and affect water quality. If uncontrolled, well biofouling can affect well performance in various ways. Biofilms and the debris they collect can quickly coat, harden, and plug the well screen, the sand pack, the surrounding aquifer material, and may even plug water lines and affect the performance of household treatment systems. In addition, the bacteria living within the biofilm can increase the rate of iron oxidation and iron buildup in the well and distribution pipes, which leads to occasional discoloration of well water. Biofouling can also result in the production of odors such as rotten egg or fishy smells, changes in taste, and corrosion of steel and iron casings and pipes. Once developed, a biomass can protect the bacterial cells from environmental changes such as changes in pH, temperature, and fluid velocities, making treatment chemicals less effective and removal of plugging material more difficult, which emphasizes the importance of regular well maintenance. A number of field and laboratory tests exist that can be used to monitor water quality and biological activity in groundwater. If performed regularly 1 month after the well is installed and then once every 6 months, these tests indicate when water quality is changing or when biological activity is increasing. Changes in water quality and increased levels of biological activity indicate that well maintenance is required. Ideally, appropriate well maintenance chemicals should be applied before well performance is significantly affected. Establishing a monitoring schedule, where pumping water levels and well pumping rates are recorded, is also an effective way to identify when preventive maintenance measures are no longer effective and well rehabilitation is required.

Extracellular slimes are composed largely of polysaccharides and, in general, are the major component of the biofouling mass. Biomass associated with viable active cells is a relatively minor component. Figure 1 illustrates how the maximum level of biological activity commonly occurs under redox conditions that are at the periphery of oxidation in the E_h range of -50 to $+150$ mV. Biofouling can be complex and caused by a variety of bacteria. However, the appearance and odor of bacterial slimes are diagnostic.

ARSENIC TREATMENT

Of the 14 treatment technologies that the EPA reviewed, five are relevant technologies for small systems—ion exchange, activated alumina, and membrane technologies (reverse osmosis, nanofiltration, and electrodialysis reversal). Seven alternative technologies are categorized as still emerging (iron oxide-coated sand, granular ferric hydroxide, iron filings, sulfur-modified iron, greensand filtration, iron addition with microfiltration, and conventional iron/manganese removal). The last two technologies—coagulation/filtration and lime softening—are used primarily in larger systems and are not expected to be installed solely for arsenic removal.

Ion Exchange

Ion exchange, in particular, will probably be a very common technology used to comply with the arsenic regulation. It is recommended for systems with low sulfate (<120 mg/L) and total dissolved solids (TDS). The effect of competing ions drives the regeneration frequency and, in turn, the cost. Ions that compete with arsenic are sulfate (the most significant competitor), fluoride, selenium, and nitrate. Systems that have high levels of these contaminants may need a pretreatment phase as well. The EPA has data on co-occurrence but would like to hear how much competition is occurring in the field and how

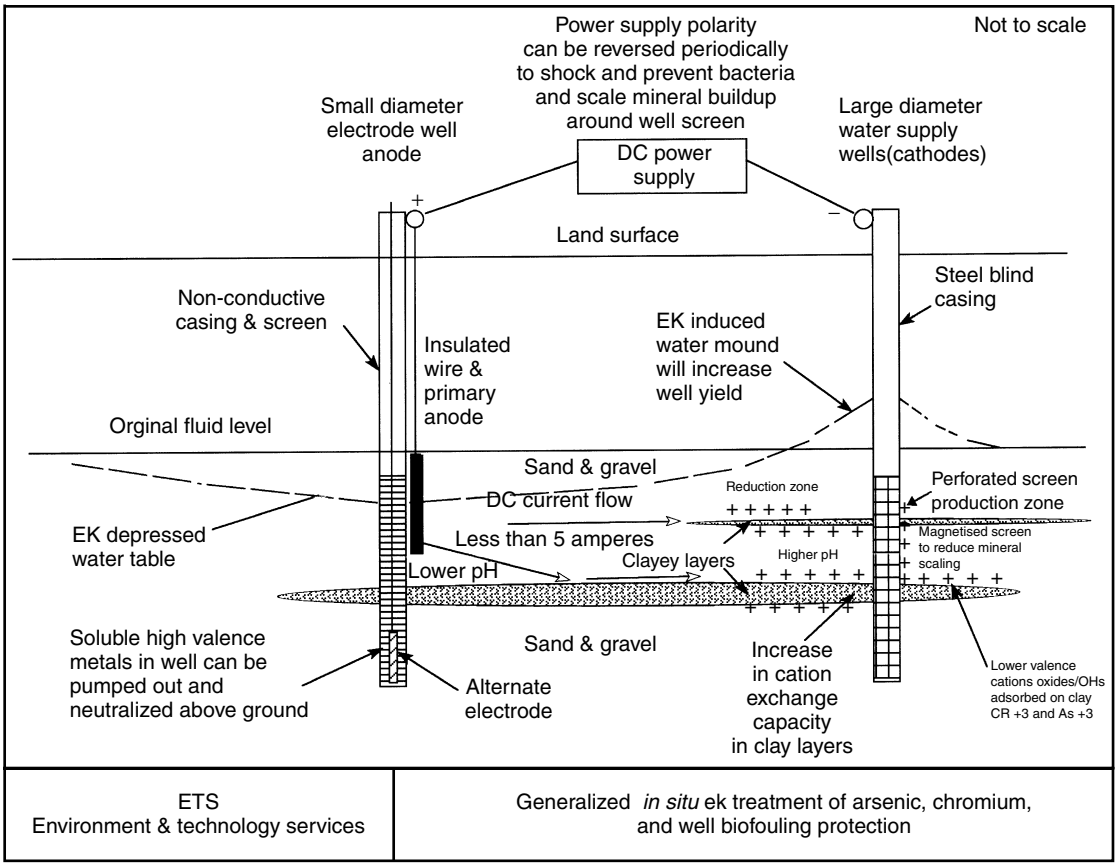


Figure 1. Generalized *in situ* EK treatment of arsenic, chromium, and well biofouling protection.

viable people think this technology would be. The waste stream, or brine, can be reused, which reduces the volume of waste and increases its concentration. The following are frequently asked questions about ion exchange:

1. How often is regeneration feasible? Will it vary by size category?
2. Can the EPA cap sulfate at 120 mg/L? Where is the TDS cap?
3. How often will an ion exchange system need regeneration? How long does it take to regenerate? Can you afford to have two systems to switch back and forth during regeneration? How much back-up water supply is necessary to provide water during regeneration? Do you have that much storage capacity available? How much regeneration is feasible for small systems? Daily, once a week, once a month? Can we expect variation by size?
4. Should we calculate costs for different removal percentages assuming full stream treatment or blending for ion exchange? Can all sources be treated at one location? Do different wells/streams serve different parts of the system?

Coagulation/filtration and lime softening are intended for larger systems. If small systems install these technologies, the EPA expects it would be in package plant form to reduce costs. A package plant is one bought "off-the-shelf" versus one custom designed for a site. A well-trained operator is needed to run these technologies; an off-site operator could utilize remote telemetry. The EPA does not expect these technologies to be installed only for arsenic removal, but if there is another contaminant in the water, it may be practical. Sludge disposal needs to be considered and may be an issue for small systems. Again, the EPA would like information from those experienced with these types of technologies.

All the technologies looked at and discussed so far work best when the arsenic is in the form of arsenic (V). **Pretreatment** converts arsenic (III) to arsenic (V). Surface water tends to favor arsenic (V), but groundwater tends to contain arsenic (III). Data shows that chlorine and potassium permanganate are effective in oxidizing arsenic (III) to arsenic (V). Possible problems include the existence of chlorine, which increases the potential to create disinfection byproducts, and membrane fouling of subsequent treatments such as RO. The EPA's Office of Research and Development is researching other preoxidants (including ozone and hydrogen peroxide, which are expected to be effective) to provide more data in the next few months.

Point of use (POU)/Point of entry (POE) devices may be appropriate for small systems serving 10,000 or fewer and are new elements of the SDWA. POE is whole-house treatment, whereas POU treats water at the tap. The EPA is looking at these devices as possible compliance

technologies to meet the new MCL for small systems. Some of the nontransient, noncommunity systems with large flows of water might use POE and POU devices to treat the minor part of the flow provided for potable use. The POE/POU technologies that are available for arsenic removal are smaller versions of reverse osmosis, activated alumina, and ion exchange. Note that POU/POE technologies must be maintained by the public water system. Therefore, the need exists for substantial record-keeping. It also increases the responsibility on the part of customers, as it requires them to facilitate entry into their homes by the utility for maintenance. The water utility is ultimately responsible for ensuring that these devices are maintained properly. The EPA is trying to determine the system size cutoff where centralized treatment would be more affordable than POU and POE devices.

Waste Disposal will be an important issue for both large and small plants. If a plant is located inland and uses membrane technologies, operators may have to pretreat prior to discharge. If the plant is discharging to a sanitary sewer because of the membranes, there may be very high salinity in the discharge as well as high levels of arsenic that might be above local sewer regulations. Ion exchange, reverse osmosis, and activated alumina treatment brines will be even more concentrated (on the order of 30,000 TDS) and more than likely will require pretreatment prior to discharge to either a receiving body of water or the sanitary sewer.

CHROMIUM TREATMENT

Reverse osmosis (RO) systems can often improve the quality of water. Reverse osmosis water treatment has been used extensively to convert brackish water or seawater to drinking water, to clean up wastewater, and to recover dissolved salts from industrial processes. It is becoming more popular in the home market as homeowners become increasingly concerned about contaminants that affect their health, as well as about nonhazardous chemicals that affect the taste, odor, or color of their drinking water. People considering the installation of a water treatment system to reduce toxic chemicals should first have their water tested to determine how much, if any, hazardous compounds are in the water. Public water supplies are routinely monitored and treated as required under the federal Safe Drinking Water Act and state regulations. Private water systems should be tested at the owner's initiative based on knowledge of land use and contamination incidents in the area (3).

Reducing Contaminants Through RO

Reverse osmosis reduces the concentration of dissolved solids, including a variety of ions and metals and very fine suspended particles such as asbestos, that may be found in water. An RO device may be installed following a water softener to reduce the concentration of sodium ions exchanged for hardness ions. RO also removes arsenic (As), chromium (Cr), nitrate (NO_3^-), certain organic contaminants, some detergents, and specific pesticides.

The Reverse Osmosis Process

In reverse osmosis, a cellophane-like membrane separates purified water from contaminated water. An understanding of osmosis is needed before further describing RO. Osmosis occurs when two solutions containing different quantities of dissolved chemicals are separated by a semipermeable membrane that allows only some compounds to pass through. The osmotic pressure of the dissolved chemical causes pure water to pass through the membrane from the dilute to the more concentrated solution. In reverse osmosis, water pressure applied to the concentrated side forces the process of osmosis into reverse. Under enough pressure, pure water is "squeezed" through the membrane from the concentrated to the dilute side. Salts dissolved in water as charged ions are repelled by the RO membrane. Treated water is collected in a storage container. The rejected impurities on the concentrated side of the membrane are washed away in a stream of wastewater, not accumulated as on a traditional filter. The RO membrane also functions as an ultrafiltration device, screening out particles, including microorganisms, that are physically too large to pass through the membrane's pores. RO membranes can remove compounds in the 0.0001 to 0.1 micron size range (thousands of times smaller than a human hair).

Design of an RO System

Although reverse osmosis is simple, a complete water treatment system is often complex, depending on the quality of the incoming water before treatment and the consumer's needs. Most home RO systems are point-of-use (POU) units placed beneath the kitchen sink to treat water for cooking and drinking. Point-of-entry (POE) systems that treat all water entering the household are more expensive to purchase and operate than POU systems.

A typical home reverse osmosis system consists of pretreatment and posttreatment filters as well as an RO membrane, flow regulator, storage container for the treated water, and dispensing faucet. The pressure for RO is usually supplied by the feed line pressure of the water system in the home, but a booster pump may be needed to produce an adequate volume of treated water. A sediment prefilter is essential for removing relatively large sand grains and silt that may tear or clog the RO membrane or clog a pump or flow regulator. Water softeners are used in advance of the RO system when household water is excessively hard. If the water is chlorinated or contains other oxidizing chemicals such as bromine, an activated carbon prefilter is needed to protect membranes sensitive to these chemicals.

To remove certain pesticides and organic solvents, activated carbon (AC) posttreatment must be included in the system. A standard AC filter positioned after the storage tank removes compounds that cause unpleasant taste and odors, including those from the tank or plastic tubing, just before water is dispensed. To remove high levels of organic chemicals such as trihalomethanes, volatile organic chemicals, and chloramines, an additional prolonged contact carbon filter (PCCF) is placed between the RO membrane and the storage tank. Combining

an activated carbon filter with RO expands the range of chemicals the system can remove. Furthermore, AC treatment is improved because RO removes compounds that adversely affect AC adsorption.

The storage tank, tubing, and dispensing faucet should be made of plastic, stainless steel, or other nontoxic materials. The low pH and mineral content of RO-treated water may corrode copper pipes and allow lead to leach into the drinking water from brass components.

RO Membrane Materials

The most common RO membrane materials are polyamide thin film composites (TFC) or cellulosic types [cellulose acetate (CA), cellulose triacetate (CTA), or blends]. Very thin membranes are made from these synthetic fibers. Membrane material can be spiral-wound around a tube, or hollow fibers can be bundled together, providing a tremendous surface area for water treatment inside a compact cylindrical element. Hollow fiber membranes have greater surface area (and therefore greater capacity) but are more easily clogged than the spiral-wound membranes commonly used in home RO systems.

The flux, or capacity, of the RO membrane indicates how much treated water it can produce per day. Typically, RO membranes for home systems are rated in the range of 10 to 35 gallons per day. Thus, under standard operating conditions, it could take from 2 to 6 hours to fill a two and-a-half-gallon storage tank. CA/CTA membranes have adequate capacity for most households, but TFC membranes should be used if large volumes of treated water are needed.

RO membranes are rated for their ability to reject compounds from contaminated water. A rejection rate (% rejection) is calculated for each specific ion or contaminant as well as for reduction of total dissolved solids (TDS). It is important that consumers know their specific requirements for water quality when buying a system. For example, high rejection rates are essential when high nitrates or lead concentrations in the water must be brought below the EPA maximum contaminant or action levels.

Efficiency of RO Systems

The performance of an RO system depends on membrane type, flow control, feed water quality (e.g., turbidity, TDS, and pH), temperature, and pressure. The standard at which manufacturers rate RO system performance is 77 °F, 60 pounds per square inch (psi), and TDS at 500 parts per million (ppm). Only part of the water that flows into an RO system comes out as treated water. Part of the water fed into the system is used to wash away the rejected compounds and goes down the drain as waste. The recovery rate, or efficiency, of the system is calculated by dividing the volume of treated water produced by the volume of water fed into the system. If not properly designed, RO systems can use large quantities of water to produce relatively little treated water. Most home RO systems are designed for 20% to 30% recovery (i.e., 2–3 gallons of treated water are produced for every 10 gallons put into the system). Home RO systems can operate at higher recovery rates but doing so may shorten membrane life. The flow regulator on the reject stream must be properly adjusted. If the flow is slow, the recovery rate is high, but RO membranes are easily fouled if concentrated impurities are not washed away quickly enough. If the flow is too fast, the recovery rate is low and too much water goes down the drain. Overall water quality affects the efficiency of an RO system and its ability to remove specific contaminants. The higher the TDS, the lower the recovery rate of treated water. The amount of treated water produced decreases by 1% to 2% for every degree below the standard temperature of 77 °F. An RO system supplied with well water at a temperature of 60 °F produces only three-quarters of the volume it would produce at 77 °F. For an RO system to function properly, there must be enough water pressure. Although most home RO systems are rated at 60 pounds per square inch, the incoming feed line pressure of many private water systems is less than 40 psi. The RO system must work against back pressure created in the storage tank as it fills with water and compresses the air in the tank. The RO device must also overcome osmotic pressure, bonding between water molecules, and dissolved impurities; the higher the TDS level, the greater the osmotic pressure. The net water pressure at the RO membrane can be calculated by subtracting back pressure and osmotic pressure from feed line pressure. If the net water pressure at the membrane is lower than 15 psi, treated water production is less efficient and contaminant rejection rates are lower. Auxiliary pumps can be added to the treatment system to boost pressure and improve the quality and quantity of water produced. High-quality RO systems have valves that shut off the flow whenever storage tank pressure reaches two-thirds of the feed pressure; at that point, low net water pressure can result in low rejection rates. In some systems, once the storage tank is filled, surplus treated water is discarded; water loss from such units is frequently excessive. A system that automatically shuts off when the pressure on the tank reaches a given level saves water.

Maintenance of an RO System

An RO system must be well maintained to ensure reliable performance. Clogged RO membranes, filters, or flow controls decrease water flow and systems performance. If fouling is detected in early stages, the membrane can often be cleaned and regenerated. The cleaning procedure varies depending on the type of membrane and fouling. Completely clogged or torn RO membranes must be replaced. In addition, pre- or postfilters must be replaced once a year or more often, depending on the volume of water fed through the system and the quality of the feed water. Damage to RO membranes cannot be easily seen. The treated water must be analyzed periodically to determine whether the membrane is intact and doing its job. Many systems now have a built-in continuous monitor that indicates a high TDS level, a sign that the system is not operating properly. It may also be necessary to test regularly for specific health-related contaminants such as nitrates or lead. Microorganisms, dead or alive,

can clog RO membranes. To prevent biofouling, RO units must be disinfected periodically with chlorine or other biocides provided by the manufacturer. Continuous chlorination can be used with cellulosic membranes to protect the system from biofouling and eliminate the particle-trapping slime that worsens other forms of fouling such as scaling. Chlorine and other oxidizing disinfectants are harmful to thin film composite membranes. If the feed water is chlorinated, an activated carbon unit must be used to remove the oxidizing chemicals before they reach the TFC membrane. Activated carbon (AC) prefilters should not be used on nonchlorinated water supplies because they provide a place for microorganisms to multiply and lead to increased biofouling of the RO membrane surface. It is important to replace AC filters periodically following the manufacturer's instructions, especially after an extended shutdown period during which microorganisms can flourish.

Choosing an RO System

Homeowners who are thinking about buying reverse osmosis systems should determine their initial water quality and their goals in adding water treatment systems. RO removes many inorganic impurities from drinking water, especially nitrate. Its effectiveness depends not only on the type of membrane but on feed water quality, temperature, pressure, and flow control, as well as the type and concentration of specific contaminants to be removed. A typical RO system consists of a sediment filter, pump, reverse osmosis membrane, flow regulator, storage tank, final activated carbon filter (for taste and odors), and dispensing faucet. An AC prefilter is sometimes needed for dechlorination. RO is commonly used to treat only the water used for drinking and cooking at the point of use rather than at the point of entry for all household use. RO membrane types vary in their ability to reject contaminants and differ in capacity (the volume of treated water produced per day). Water pressure is an important factor in determining the RO system's rejection rate, capacity, and recovery rate (amount of treated water produced per amount of feed water used). Maintenance of an RO system is essential for reliable performance. High levels of TDS and microorganisms in the system are commonly the cause of fouled membranes. Treated water should be monitored for TDS and the level of any specific contaminants that may affect health.

A list of home water treatment devices certified by various Department of Health Services can be found on their websites.

BIOFOULING TREATMENT

Historically, there have been three approaches to the declining operation of a water well of any common type. One is to simply abandon the well and install a new well of similar or greater capacity to replace the abandoned well. A second involves attempting to change the operating techniques (e.g., pump times, volumes, sequences of up- and downtimes, and control flow by drawdown limitations) or change some components in the well (e.g., pump, screen) in the hope that the well will recover from the observed problem. The third is to attempt an analytical approach to the problem by determining

—first, the cause;
—second, confirm that the effects witnessed can be related to the cause identified;
—and third, determine and apply a treatment strategy that counteracts the cause and allows the well to function as designed.

Increasing economic and environmental costs and concerns are now restricting the ability of a well user simply to replace a failing well. Economic concerns relate to the increasing costs involved in well replacement and the growing sensitivity for maximizing the use of each well installation by extending its useful life (i.e., environmental sustainability). Environmental concerns are being brought to the fore because groundwaters are no longer seen as an infinite resource. In some areas, aquifers are now being heavily depleted by the demand, and there is little flexibility to provide additional capacity. Another major environmental concern is the impact of various forms of pollution on well fields. In the past decades, general attitudes may be summarized by an "out of sight, out of mind" approach in which groundwater was given a lower status than surface waters. Various chemical leakages from industry, agriculture, and various service industries were not considered as important as those in surface waters. When a pollutant impacted surface water, the effects could often be relatively quickly appreciated through radical eutrophication, deteriorating water quality, and water unacceptable to users. One major difference between surface and groundwaters is the fact that the former flows as large unconfined masses whereas the latter moves as a confined mass within porous media. This difference is very critical to the current understanding of groundwater flow and quality.

It is not easy to appreciate the complex interactions that occur between flowing groundwater and the media through which it is passing as it moves to a well, a spring, or interfaces with another aquifer. For the last century, it has been popularly believed that groundwater is essentially sterile (devoid of biological activity) and that all activities within an aquifer may be explained almost exclusively by a combination of physical and chemical processes. Today, the hydrology of groundwater systems still leans heavily on this assumption. Through the science of subsurface microbiology (the study of microorganisms in the crust of the planet), it is now becoming increasingly evident that groundwater movement and quality are affected by microbiological interactions. In the past decades, these have been ignored, and one of the major consequences has been that the effects of these microorganisms as biological filters (interface) have been ignored. Pollutants within a groundwater system may become entrapped (and possibly degraded) within these biological filters and so not appear in the groundwater resurfacing through a well. Environmental monitoring of the product (postdiluvial, after the "event") water from a well may not necessarily give an "accurate" picture of the chemical loading in

the transient (causal) water itself. There has been a tendency for groundwater users to rely on product ("biofiltered") water for environmental assessment, and yet this water may not accurately allow a risk assessment for that well (due to bioentrapment of some chemicals of concern).

In the next two decades, the realization of the nature of the biological interfaces within and around water wells may cause much tighter environmental constraints to be placed on new well installations, which would mean that greater attention would be paid to extending the service life of existing wells through preventive maintenance and effective rehabilitative programs. The mindset that a water well is a physical object set within a chemical and physical world has to change. This mindset has generated a "traditional" attitude that a dysfunctional well is simply a result of chemically driven corrosion, encrustation, clogging processes, or the physical collapse of the system (through such events as "silting up" and "collapsed" aquifer and well structures).

Acidization has commonly been applied as a remediation technique to dissolve and disperse the clogs and encrustations, and various disinfectants (such as different formulations of chlorine) were used to control any coliform and other bacteria that may be growing down the borehole (and presents a potential health risk). Slime formations were considered by many to be simply physical-chemical accumulates that may result in clogging, encrustation, and corrosion. Even today, camera logging a water well is considered sufficient to view all biological and much of the chemical deposits (e.g., silts and salts) that can be causing problems around a well. Please see the section on the "Preliminary Diagnosis of Biological Fouling of Water Wells Using TV Camera Logging Methods."

Combinations of disinfectants, selected acids and even, in more recent times, dispersants (a.k.a. wetting agents) have become part of the arsenal of weapons used to rehabilitate problems in a well. One of the findings from these actions has been that "no one size fits all" and that each well should be treated as unique and requires customization of the treatment parameters to optimize maintenance practices. This approach stems from observations that each well can be characterized as different from other wells in the same field. Many instances exist where two wells of the same construction and characterization placed within feet (meters) of each other in supposedly the same aquifer formation bear very different characteristics. An unfortunate result of this is that a treatment may be successfully applied to one well in a field but that same treatment may fail on a neighboring well of exactly the same characteristics in construction, operation, and mode of failure (4).

INNOVATIVE *IN SITU* TREATMENT

In situ electrokinetic treatment of chromium, arsenic, and biofouling may provide a cost-effective solution (5). The electrokinetic treatment process involves applying direct current (dc) in a medium (soil and water). The flow of electrons from anode to cathode creates a migration of cations in the medium toward the cathode. The electrolysis of water creates a higher pH and oxidizes the metal or reduces its valence, which renders the metal into a nontoxic form near the cathode. Clayey material may show a dramatic increase in cation exchange capacity under a high pH near the cathode.(6–8) The proposed electrokinetic process can be applied both *in situ* and *ex situ*. Figure 1 presents a more realistic distribution of the various valence states of metals under the proposed *in situ* electrokinetic influence.

Besides the treatment of metals, the beneficial side effects of the *in situ* EK treatment are as follows:

The well itself is set up as a cathode, so iron bacteria will not live on the surface of the well casing and perforation because of the high pH.

The electrokinetically induced water migration toward the cathode (well) may induce an increase in hydraulic head, thus increasing well yield.

No such treatment has been tried on chromium, arsenic, and manganese in a saturated medium to date. There are many successes of the proposed EK process in the laboratory and in soil. However, we have successfully demonstrated the electrokinetic control of selenium and boron in clayey saturated media at two sites in the Panoche Irrigation District, Central Valley, California. We believe that the same EK control can be applied to chromium, arsenic, and biofouling because of the similarity of the multiple valence forms to those of selenium and boron. Due to the simplicity of the cathode and anode setup, we believe that the proposed EK processes will prove cost-effective. The proposed *in situ* EK treatment (once set up) is permanent. It has a one-time capital cost and minimum long-term maintenance costs. The continuous operating electricity demand will not exceed 50 amperes at 30 to 100 Vdc or 1500 to 5,000 watts per site.

BIBLIOGRAPHY

1. Hem, J.D. (1979). Reaction of metal ions at surfaces of hydrous iron oxide. *Geochim. Cosmochim. Acta* **41**: 527–538.
2. Smith, S.A. (1992). *Methods for Monitoring Iron and Manganese Biofouling in Water Wells*. AWWA Research Foundation Publication Number 90617.
3. Kneen, B., Lemley, A., and Wagenet, L. (1995). *Reverse Osmosis Treatment of Drinking Water, Fact Sheet 4*. Cornell Cooperative Extension, New York State College of Human Ecology.
4. Cullimore. (1997).
5. Lehr, J.H. (Ed.). (2001). *Standard Handbook of Environmental Health, Science and Technology*. Chapters 14.4 & 14.6 on Bioremediation & Electrokinetic Treatment of Hazardous Wastes by Walter W. Loo, McGraw-Hill, New York.
6. Driscoll, F.G., (1986). *Groundwater and Wells—Well Failure & Iron Bacteria*. Johnson Filtration Systems, Inc., St. Paul, MN, pp. 646–655.
7. Hem, J.D. (1989). *Study and Interpretation of the Chemical Characteristics of Natural Water*. U.S. Geological Survey Water-Supply Paper 2254.
8. Walter, D.A. (1997), *Geochemistry and Microbiology of Iron-Related Well-Screen Encrustation and Aquifer Biofouling in Suffolk County, Long Island, New York*. U.S. Geological Survey Water-Resources Investigations Report 97-4032.

ARTESIAN WATER

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Artesian water is groundwater that flows freely at the surface from an artesian bore or well. The name artesian comes from the flowing wells constructed in the twelfth century at the Carthusian monastery near Lilliers in the northeastern French province of Artois.

The term "artesian" has also been extended to refer to artesian aquifers, in which the groundwater is under a sufficient pressure head to flow at the surface, and to artesian basins, sedimentary basins that may contain artesian aquifers. The term subartesian refers to the situation where the water level rises above the top of the aquifer but is below ground surface.

The artesian condition is, however, an accident of topography, not necessarily a property of the water, the bore, or the aquifer. For this reason, it is preferable now to use the term "confined" to refer to the aquifer. "Confined" implies the presence of a low permeability confining bed above the confined aquifer, which allows a positive (above ground) hydraulic head to be maintained. Rarely, flowing water can be obtained from an unconfined aquifer without a confining bed, provided there is a sufficient upward head gradient.

Artesian water is common in sedimentary basins, where there are extensive aquifers overlain by confining beds. The classic artesian basin is shaped like a saucer; the aquifer crops out around the elevated margins of the basin, where it can be recharged by rainfall or stream flow (see Fig. 1). The cities of London and Paris lie at the centers of their basins and were among the first cities to exploit artesian water on a large scale. The Great Artesian Basin in eastern Australia is one of the largest examples; it is 1500 km across. However, artesian conditions can occur in other geological formations.

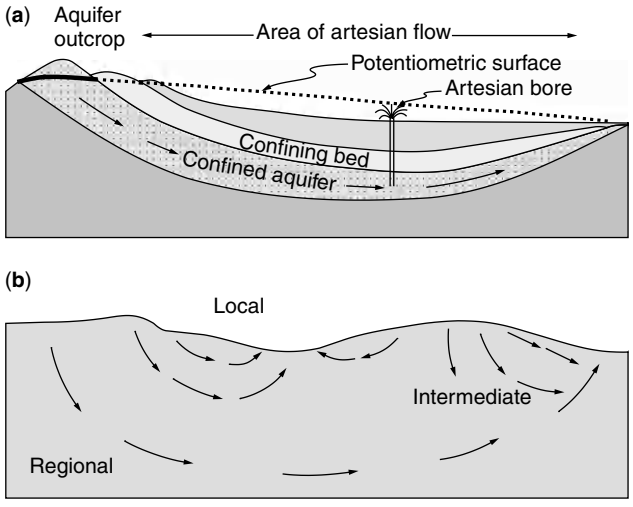


Figure 1. Groundwater flow in a classical artesian basin (**a**) contrasting with cross-formational flow in local, intermediate, and regional flow systems in a nonclassical basin (**b**).

The phenomenon of free-flowing groundwater was first documented sometime in the first millennium B.C. at Dakhla Oasis in the western desert of Egypt, during the course of progressively deepening hand-dug wells. The first to explain the correct nature of artesian wells were Mahammad Karaji (died 1016) and al Biruni (973–1048), but in Europe, the explanation had to await an understanding of the hydrologic cycle. In 1691, Bernadino Ramazzini (1633–1714) described the artesian wells that were commonplace in the Italian city of Modena. He drew a geologic section, although it appears he envisaged underground rivers rather than porous strata as the water source. In 1715, Antonio Vallisnieri (1661–1730), President of the University of Padua, reasoned that rainfall on the mountains was the source of the artesian water at Modena and illustrated his work with geologic sketches of the Alps made by Johann Scheuchzer.

The existence of artesian water began to be widely appreciated in Europe in the early 1800s, after French engineers introduced Chinese drilling technology. The success of the Grenelle artesian bore near Paris, in which water rose to a height of 33 meters and flowed at the rate of 4000 cubic meters per day stimulated the development of artesian water. In the absence of suitable pumps, the availability of free-flowing water was an important economic factor in opening up new lands for agriculture and pastoral use in the Americas and Australia. The existence of the Great Artesian Basin in Eastern Australia was postulated in 1881. Proved by drilling in 1887, it rapidly led to pastoral development. The recognition of waterborne diseases and the contamination of shallow water supplies in cities was also an incentive to developing artesian supplies of clean drinking water in the Eastern United States, Europe, and Australia by the turn of the century.

Such was the impact of free-flowing water on the public that drilling for artesian water was often carried out in geologically unfavorable places (and despite professional advice); the perception was widely held that artesian water would be encountered, providing the boring was deep enough.

Geologic textbooks of the mid- to late 1800s illustrated the structure of classical artesian basins such as the Paris and London Basins, although it was recognized by the end of the century that flowing wells could also occur under different conditions. A series of papers by U.S. Geological Survey authors provided detailed explanations of artesian water. Thomas Chamberlin's classic paper (1), which is recognized as the beginning of the science of hydrogeology in North America, systematically laid down the conditions under which artesian flows would be obtained: the presence of a pervious stratum, impermeable beds above and below, an inclination of the beds so that the edge is higher than the surface at the well, and adequate rainfall.

Chamberlin's observations can now be qualified somewhat. Few, if any, confining beds are now considered completely impermeable, and in many places, the confining beds yield significant amounts of water by leakage to adjacent artesian aquifers. Tóth (2) has drawn together

ideas on regional hydraulic continuity, recognizing cross-formational flow in which it is not necessary to have inclined beds to produce artesian conditions. In many artesian basins, the water is of great antiquity, a million and a half years in the case of the discharge from the Australian Great Artesian Basin, although current rainfall is necessary to maintain the hydraulic head in recharge areas.

In 1928, Oscar Meinzer's paper on the elasticity of artesian aquifers drew together much of the work from the intervening period, demonstrating the concept of elastic storage, whereby flowing water is released by the reduction in hydraulic head and compressibility of the aquifer matrix (3).

However, there were many who denied the conventional theory (held in the main by Geological Surveys) that the origin of the water was meteoric and that the pressure was related to the elevation of the water table in outcrop areas of artesian aquifers. In Australia, distinguished academic geologists such as J. W. Gregory (1906) and Alexander du Toit (1917) invoked juvenile and connate water, rock pressure, and gas bubbling to explain the origin of water and pressure. These ideas were supported by American geologists whose oil-field experience led to the concept of closed and hydraulically isolated systems.

There is still debate surrounding the explanation for the origin of artesian pressure, stimulated by studies of nonclassical basins such as the Hungarian Basin, and this has led to a better understanding of basin hydrodynamics.

Studies of the Great Artesian Basin clearly show the hydraulic continuity of aquifers over large distances and the observed potentiometric heads that decline gently away from the recharge areas. Furthermore, isotopic age dating using chlorine-36 indicates a transit time across the basin of 1.5 million years that correlates with hydrodynamic modeling.

Artesian water is released from elastic storage, and as the pressure is reduced, the aquifer matrix bears more of the hydrostatic pressure. Thus, subsidence occurs in most situations where the compressibility of the aquifer is much greater than that of water itself. Artesian flows may also lead to irreversible consolidation of aquifers, particularly in geologically recent environments that are not fully consolidated. In large artesian systems such as the Great Artesian Basin, free-flowing water is effectively mined from elastic storage, as there is little potential to induce more recharge on the timescale of abstraction. Maintenance of artesian head is the priority for management, given the economic consequences once bores cease to flow. In the Great Artesian Basin, a program is underway to cap and control the flow of artesian bores to maintain the aboveground pressure and to prevent the waste of water, which had been allowed to flow many kilometers in open "bore drains" to water livestock.

Owing to the great depths from which it may come, artesian water is often much warmer than the shallow groundwater and may have to be cooled before use. A feature of artesian bores is that the head of water varies according to the temperature. A bore may cease to flow after the water is shut in and the water column cools. Artesian flows may also cease after degassing in a shut-in bore. Artesian flows are also affected by barometric pressure changes.

Artesian water may also be relatively highly mineralized, owing to the long travel time, and contain gases and dissolved iron, which may precipitate at the surface. The words may, therefore, have a bad connotation in terms of drinking water.

BIBLIOGRAPHY

1. Chamberlin, T.C. (1885). *Requisite and Qualifying Conditions of Artesian Wells*. U.S.G.S. Annual Report No. 5, pp. 131–141.
2. Tóth, J. (1963). A theoretical analysis of groundwater flow in small drainage basins. *J. Geophys. Res.* **68**(16): 4795–4812.
3. Meinzer, O.E. (1928). Compressibility and elasticity of artesian aquifers. *Econ. Geol.* **23**: 263–291.

MODELING CONTAMINANT TRANSPORT AND BIODEGRADATION IN GROUNDWATER

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INTRODUCTION

What Is a Groundwater Contaminant?

When dealing with contaminant transport modeling, we have to be clear from the beginning that almost any substance could be a contaminant. It all depends on the nature of the object which may be at risk and in which concentrations the substance is present. This object often is the human being, and sometimes a special one, like a baby, but sometimes also other living organisms, or even a habitat or ecosystem that may be endangered. The concentration, or more precisely the intake, can determine whether a substance is harmless or even an essential nutrient, or harmful, for example, in case of chloride or zinc. That is the toxicological perspective. From a chemical perspective, there are organic and inorganic contaminants; from a physical perspective, there are dissolved and particulate or free-phase contaminants, and biologically, there are a variety of animals, microorganisms and viruses, or nonliving substances, that could be harmful and thus could be contaminants. In the following, we focus only on the more familiar type of contaminant in groundwater, that is an organic, dissolved, non living substance, and refer the reader otherwise to more comprehensive descriptions of groundwater contaminants.

Why Model Contaminant Transport?

Contaminants released into the subsurface may be spread by transport in groundwater to locations further away. That is why assessing the transport of a contaminant may be useful. A typical objective may be to protect the groundwater resource itself from contamination or

to protect somebody who could be affected by the contaminated groundwater. The latter case is the basis for the source—pathway—receptor approach to risk assessment, which judges the impact of a contaminant by its pathway from a source to a particular receptor that will be potentially harmed by the contaminant. Modeling is only one way to assess contaminant transport, but can describe a complex situation in detail and thus may allow predictions.

Why Model Biodegradation?

Biodegradation is an important factor in the fate of organic contaminants and may reduce the concentration and also the total mass of a contaminant. Although several processes can contribute to the natural attenuation of contaminants, biodegradation is often the main process by which mass may be destroyed; other processes such as sorption merely retain the contaminant mass for later release. Therefore, modeling monitored as well as enhanced natural attenuation, usually has to include biodegradation modeling.

Processes

The key processes to be modeled are advection, dispersion, sorption, and degradation by microbes. However, further processes could also be relevant, for example, ion exchange, precipitation and dissolution of minerals, speciation, and surface-complexation.

Modeling Basis and Related Modeling (Flow, Transport, Hydrogeochemical)

The basis for transport modeling is flow modeling; transport modeling itself is the basis for modeling contaminant transport and biodegradation (see Fig. 1). Often in more general terms this is called reactive transport modeling, which includes transport plus biodegradation and/or hydrogeochemical modeling. To model a field scale problem of reactive transport appropriately, one should plan this as a set of modeling tasks building up to this challenging undertaking.

Scale and Type of Transport

The scale of the problem is an important factor when building a model because it influences the modeling concept and the modeling tools to be chosen. Scales may range from pore scale, for pore blocking by bacterial conglomerates, to regional scale, for agricultural contaminants. Here, we focus on an intermediate to subregional scale, such as a contaminant plume originating from a point source or a remediation operation on a site scale. The processes included in a contaminant transport model may be special transport processes such as fracture networks, multiple porosity behavior, or preferential flow paths, but we will limit the discussion to the standard, equivalent porous medium approach.

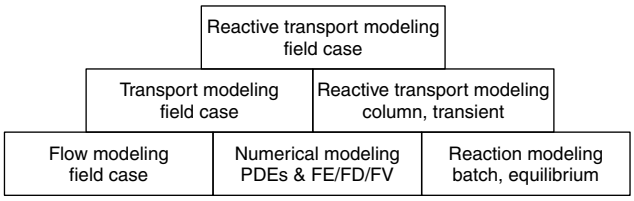


Figure 1. Key pyramid for achieving reactive transport modeling on a field scale.

THE BASIC CONCEPTS

A modeling project starts with the definition of its aims and purpose, and subsequently the modeling concept is built up. Conceptualization of the problem will probably require consideration of several aspects, especially in reactive transport modeling.

Chemistry

The chemical nature of the contaminant, the groundwater, and the aquifer may determine the fate of a contaminant to a high degree. The presence of electron acceptors that are usually needed for the degradation of organic contaminants, electron donors, enables certain reactions to occur in principle. The groundwater pH and redox condition determine which reactions actually can occur at a certain location. All of these may vary spatially and temporally. Also, the occurrence of other contaminants may affect the fate of a particular contaminant substantially. Furthermore, the presence of organic matter, charged surfaces, and minerals in the aquifer constitute pools for sorption of solute species. Altogether, this should be taken into account when defining the set of chemical species and the possible reactions.

It should also be mentioned that chemical reactions are treated as either equilibrium or kinetic reaction, depending on how their rates compare to advection and diffusion timescales and rates; equilibrium is faster than transport, and kinetic is slower. These two reaction types imply different resulting behavior, and also different types of equations, parameters, and numerical solution techniques; more details may be found in the literature on hydro(geo)chemical modeling.

Microbiology

Biodegradation implies that there is a biological activity by which degradation occurs, as opposed to chemical degradation. Populations of bacteria in aquifers constitute biota able to perform degradation in groundwater. Usually, there is a microbial community in an aquifer that has some diversity but is not really flourishing compared to soil or the biosphere. Both features are likely to be affected by biodegradation. The bacteria will try to biodegrade the contaminant when they can gain energy or carbon by this. The way they achieve the biodegradation is via enzymes, which they release or at least make available inside the cell. The kinetics of these enzymes can be described by the Michaelis–Menten formula, which is the starting point for equations used to describe biodegradation in groundwater.

In a constant microbial population feeding on a contaminant that is present in abundance as well as all other substances needed for the reaction, the rate of biodegradation is set by the enzymes available and is a constant in this quasi-steady-state scenario. This

means the enzymes are saturated by the contaminant as a substrate, and this biodegradation kinetics is called *zero-order degradation*. Here, the degradation rate, that is, the change of the contaminant concentration C with time due to biodegradation, is a constant:

$$\frac{\partial C}{\partial t} = const. \tag{1}$$

However, often the contaminant, as the substrate for the bacteria, is not present in abundance, but its availability for the reaction is limited, similar to the concentration of the enzymes. Due to the mass action law, the reaction rate is proportional to the contaminant concentration. This results in a *first-order degradation* with first-order rate constant λ, where

$$\frac{\partial C}{\partial t} = \lambda C \tag{2}$$

Note that a radionuclide decays according to the same type of equation. In both cases, a half-life can be defined based on λ: $T_{1/2} = \ln 2/\lambda$.

The concentration of substrate may decrease during biodegradation, or perhaps the contaminant is not present in large quantities. Hence, a more realistic approach is to account for both former cases. A way of doing so is an empirical form of the Michaelis–Menten kinetics, called Monod degradation kinetics

$$\frac{\partial C}{\partial t} = \mu_{\max} \frac{C}{k + C} \tag{3}$$

where k is the half saturation constant and $\mu_{\max} = \lambda \cdot k$ is the maximum possible degradation rate constant. For small C, $C << k$, the degradation rate is proportional to C, whereas for large C, $C >> k$, it levels off to the constant rate $\mu_{\max}$, as in zero-order degradation.

An even more realistic concept takes into account that bacterial enzymes do not perform the degradation by themselves but merely facilitate a reaction between contaminant and another substance, usually an electron acceptor with concentration EA. The latter has to be present at the same place and time as the contaminant to allow the reaction to proceed. Then the degradation is described by the double Monod formulation:

$$\frac{\partial C}{\partial t} = \mu_{\max} \frac{C}{k_C + C} \cdot \frac{EA}{k_{EA} + EA} \tag{4}$$

And finally, to add some microbiology to it, bacterial populations can grow and die. Furthermore, they can be attached to grain surfaces and even create biofilms, or be transported with the water flow, or a mixture of both. This may affect the biodegradation very much, because the degradation rate is basically proportional to the amount of active bacteria in a unit volume, called X. This is taken into account when using the following equation, which constitutes *higher order degradation* behavior:

$$\frac{\partial C}{\partial t} = \mu_{\max} X \frac{C}{k_C + C} \cdot \frac{EA}{k_{EA} + EA}$$

and

$$\frac{\partial X}{\partial t} = const \cdot \frac{\partial C}{\partial t} \tag{5}$$

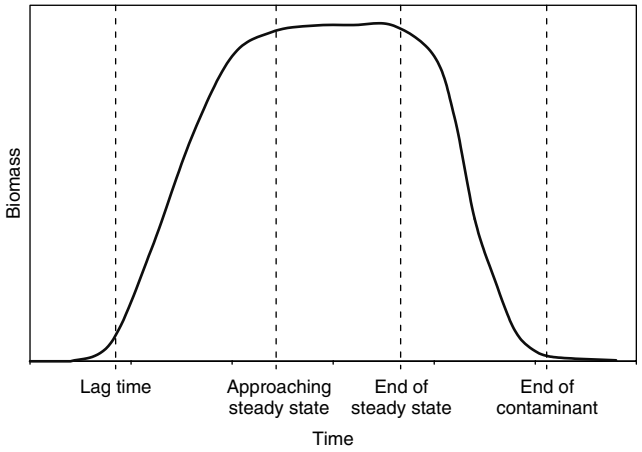


Figure 2. Example of the development of a bacterial population that is degrading a contaminant.

A typical case is that a certain type of bacteria is present in small quantities (see Fig. 2). This population starts to grow, when environmental conditions are favorable for them: there is a contaminant they can feed on and an electron acceptor they can use for the degradation reaction. It takes a particular time, until the size of the population reaches a level that makes a real difference in the contaminant concentration. Then its growth slows down, for example, when one of the substances for the degradation reactions becomes limiting. This could lead to a steady population of microbes, especially because bacteria grow but also die. Finally, when the environmental conditions change again, for example, by final consumption of the contaminant, the decay of bacteria is larger then their growth, and the population declines.

Sometimes the degradation product of a contaminant is a contaminant itself, and so on. Then a whole chain of degradation has to be taken into account, for example, in the biodegradation of PCE (1). Such a chain may be modeled on the basis of first-order degradation of each member of the chain. In this case, it is mathematically a process similar to chains of radioactive decay. However, it could also be modeled as a set of components, which are linked by the degradation-production term, and each could follow any of the mentioned degradation kinetics.

A further possible process is inhibition of a particular biodegradation process by the presence of relevant amounts of a certain substance, for example, oxygen, or of the contaminant itself, which would be called self-inhibition. To account for inhibition, an additional term can be added to the biodegradation equation, which reduces the degradation rate for this case.

A range of processes could also be included in modeling biodegradation, if they are relevant for the specific problem: (1) transport of dissolved species into a biofilm of bacteria; (2) bacterial attachment and detachment to the solid matrix; (3) sorbed contaminants may not be degraded, as long as they are bound to surfaces or organic matter; and (4) bacteria may even feed on a contaminant in a solid phase, on the other hand.

Geochemical and microbial processes are closely linked in groundwater. Microbial activity is based on the

availability of substrates, electron acceptors, redox and pH conditions, yet influences all these conditions, and thus may initiate additional geochemical processes, such as precipitation of minerals. Therefore, a realistic and detailed model of biodegradation reactions in groundwater must also include a set of geochemical reactions.

Dispersion

Hydrodynamic dispersion may seem a minor issue relative to those discussed before. Nevertheless, dispersion at the plume fringe can be a key factor in biodegradation, even more than for a nonreactive contaminant. The velocity-based mechanical dispersion creates mixing between species necessary for reaction on a scale depending on longitudinal and transverse dispersivities. Molecular diffusion does the same on smaller scales down to the pore scale and may even dominate hydrodynamic transverse dispersion, especially in the vertical direction. By its nature, biodegradation at plume fringes tends to create, or at least maintain, high concentration gradients of the consumed species, as opposed to dispersion that smooths them.

Here, the relevance of dispersion is stressed, but for modeling approaches, we refer to transport modeling literature. However, it should be clear that only part of biodegradation happens at the plume fringes and part in the plume core where electron acceptors still may be stored as minerals.

MATHEMATICAL MODELING APPROACHES

Analytical Modeling

The solution of contaminant transport and biodegradation equations by analytical methods is possible for only a limited number of problems that are also simple in terms of boundary conditions, geometry, and biodegradation concepts. Nevertheless, they are very useful in answering basic questions, and they are quick, accurate, and straightforward to implement; Domenico and Schwartz (2) give a good collection of such solutions. Hence, it should always be checked first, if an analytical approach can address the particular modeling objective. The U.S. Environmental Protection Agency (EPA) provides the spreadsheet model *Bioscreen* based on analytical solutions, which, for example, allows obtaining quickly an impression of the effects of parameter values, different reaction models, and source zone extent (3). Finally, these types of approaches are used widely for risk assessment, but rather due to their simplicity and swiftness, than for their general applicability.

Numerical Modeling

Numerical modeling is based on techniques such as finite difference, finite element, or relatives of them. Only a few aspects are presented here that are specific to modeling reactive transport and other coupled equations.

— Reactive processes can be fast or slow compared with timescales of transport processes in aquifers or columns. Fast reactions are treated as an equilibrium process and may be described mathematically by thermodynamic mass action laws; kinetic reactions might be formulated as biodegradation kinetics, as before. Incorporating both imposes additional numerical challenges.

— The slow part of the reaction system is described via partial differential equations, and the fast part via nondifferential equations. There are different ways of combining them (4).

— Transport and reactions can be treated as sequential numerical steps or in one single step. The former is the less accurate method, even if the sequential steps are iterated, and may also require small time steps, whereas the latter is slower and needs more memory (5).

— Biodegradation can be handled as a single step, but alternatively also as a first step providing intermediate products followed by one or several processes of electron acceptor consumption. In the latter case, the first step is usually treated as slow, and the second step as fast. For a current literature survey of one- versus two-step, approaches, see Brun and Engesgaard (6).

NUMERICAL MODELING TOOLS

Purpose

A broad range of codes, packages, and modules deals with transport and biodegradation modeling. They are applied usually to modeling problems that are studied in greater detail, and more complex processes have to be included in the modeling concept. The selection of a modeling tool for a particular study should be governed by the aim of the study, but in practice also depends on the availability of programs and the familiarity of the modeler with particular codes.

Types

One-dimensional geochemical codes can calculate transport and speciation together with a comprehensive list of geochemical reactions, including biodegradation. One of these codes, PHREEQC (7), is probably the most frequently used program with these specifications. It is a thoroughly tested, well maintained and growing program, offers a lot of features including graphical user interface and inverse modeling, and is taught frequently in courses around the world.

For two-dimensional applications, existing numerical programs typically come from an engineering background and include flow and transport modeling with added capabilities for reactive transport. The most famous and most widely used program package in this category is the MODFLOW family (8). Here, several packages for reactive transport simulations have been added to the flow simulation packages: MT3D (9), RT3D (10), and PHT3D (11) and may be applied via one of the commercial MODFLOW packages with a graphical user-interface. Alternatively, BIOPLUME III is a noncommercial code

to simulate natural attenuation of hydrocarbons in two dimensions (12).

Furthermore, there are other programs, which are designed especially to deal with complex, three-dimensional reactive transport simulations incorporating a lot of real complexity. These are often research codes rather than commercially spread programs, and thus they may be less well documented, less user-friendly, less easily available, and restrictions may apply for their use. But they represent the state of the art with respect to a comprehensive biochemical interpretation of field scale biodegradation modeling, and their use is often free of charge. Some examples of codes falling in this category are presented in Table 1.

An important note: The programs named so far represent a snapshot of today. However, these programs are a type of software that may be further developed in the future, but their development may also be discontinued or follow a different route. Therefore they should be seen as examples rather than unchanging recommendations. However, there are organizations that offer up-to-date programs in contaminant transport and biodegradation modeling, and even offer some of them free on-line. Two of them are the U.S. Geological Survey (USGS) (http://water.usgs.gov/software/ground_water.html) and the U.S. Environmental Protection Agency (EPA) (http://www.epa.gov/ada/csmos.html).

Handling

One should be aware that the hard work only starts after selecting the software fitting the purpose and the budget and learning how to run it. At that time, one has to specify actual parameter values, and this issue is even more important for reactive transport modeling than for other types of modeling in groundwater. There are more parameters involved, and often their values are difficult to obtain. This is one of the big and crucial problems in reactive transport modeling, especially for field cases: How to get the parameter values for biodegradation and the large number of components involved? Field tests are expensive and potentially give ambiguous results due to the dynamics and heterogeneity of biodegradation and plumes, but lab tests represent the field site only to a degree. For example, degradation rates found in the lab are typically higher, even by one or two orders of magnitude, than those fitted to field degradation. Nevertheless, laboratory tests can yield valuable information: (1) The biodegradation concept and relative importance of processes seem to be a valid starting point for field case modeling. (2) There are parameters that are more transferable to the field than rate constants, which are, for, example half saturation constants and inhibition coefficients. (3) Modeling of a lab experiments forces the modeler to get a complete and consistent picture of processes involved and parameters to be quantified.

Table 1. Examples of Numerical Programs as Tools for Sophisticated, Three-Dimensional Reactive Transport Simulation in Groundwater. This is not a Complete List of Such Codes

Name	Place or Organization of Development	Reference
BIO3D & BIONAPL3D	University of Waterloo, Canada	(13,14)
CRUNCH	Lawrence Livermore National Laboratory/Pacific Northwest National Laboratory, USA	(15)
Hydrobiogeochem 123D	OAK Ridge National Laboratory/Penn State University, USA	(16)
MIN3P	University of Waterloo and UBC Vancouver, Canada	(4)
TBC	University of Heidelberg, Germany	(17)
UG	IWR, University of Heidelberg, Germany	(18)

There will almost always be some parameters in reactive transport modeling that have to be fitted, preferably by inverse modeling, but maybe also by adjusting them by hand. Both ways work better when more data are available on all aspects of the problem. In any case, the sensitivity of the model to the choice of the parameter values has to be assessed thoroughly, and the fitted values have to be checked afterward for their plausibility, at least if no boundary limits have been used for parameter fitting. The sensitivity of parameters and the range of sensible parameter values determine the inherent uncertainty of the model. However, stochastic approaches are required for these complex, coupled, and nonlinear systems to get a real handle on the range of possible outcomes of certain model properties. Unfortunately, this adds heavily on top of the numerical load required anyway, and thus often a stochastic assessment has to be based on simplified conceptual models.

This leads us to the fact that the hardware for reactive transport modeling is still a limitation in dealing with complex problems, besides the problem of appropriate parameter values. On a standard PC of the current generation, even one-dimensional simulations may take hours to days to complete. This illustrates the need to enhance calculation power by using parallel processing capabilities for these simulations, especially for two-dimensional and three-dimensional problems. However, besides access to such hardware, this also requires software that can run on multiple processors at the same time.

Finally, modeling also means that the user has to deal with modeling results and has to interpret them. One aspect is that numerical modeling results should be frequently checked for consistency and accuracy, which is true even more for reactive transport modeling than for pure transport modeling. Another aspect is that often a large amount of data is produced, which leads to the necessity to visualize intelligently and efficiently the usually time-dependent data to obtain the best

interpretation, especially for two- and three-dimensional data sets.

CLOSING REMARKS

This article is only an introduction to the field and touches on several subjects. For an excellent and clear book to get into this topic, we recommend Zheng and Bennett (19). Furthermore, the IAHS red book series provides a cross section of contemporary scientific contributions, for example, Thornton and Oswald (20) for natural and enhanced attenuation of contaminants or Stauffer et al. (21) and Kovar and Hrkal (22) for a broad range of issues on groundwater flow and contaminant transport modeling.

Acknowledgments
Dr. Ian Watson of the Department of Civil and Structural Engineering, University of Sheffield, UK, helped in reviewing and improving this entry.

BIBLIOGRAPHY

1. Wiedemeier, T.H., Rifai, H.S., Newell, Ch.J., and Wilson, J.T. (1999). *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, New York.
2. Domenico, P.A. and Schwartz, F. (1997). *Physical and Chemical Hydrogeology*. John Wiley & Sons, New York.
3. Newell, C.J., McLeod, R.K., and Gonzales, J.R. (1996). *BIOSCREEN—Natural Attenuation Decision Support System*. User's Manual, Version 1.3, EPA/600/R-96/087.
4. Mayer, K.U., Frind, E., and Blowes, D.W. (2002). Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. *Water Resour. Res.* **38**(9): doi:10.1029/2001WR000862.
5. Saaltink, M.W., Carrera, J., and Ayora, C. (2000). A comparison of two approaches for reactive transport modelling. *J. Geochem. Exploration* **69**: 97–101.
6. Brun, A. and Engesgaard, P. (2002). Modelling of transport and biogeochemical processes in pollution plumes: Literature review and model development. *J. Hydrol.* **256**(3–4): 211–227.
7. Parkhurst, D.L. and Appelo, C.A.J. (1999). *User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Geological Survey, Denver, CO, Water-Resources Investigations Report 99-4259, p. 310. Available: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.
8. USGS. (1997). *Modeling Ground-Water Flow with Modeling Ground-Water Flow with MODFLOW and Related Programs*, USGS Fact Sheet FS-121-97. Available: http://water.usgs.gov/nrp/gwsoftware/modflow.html
9. Zheng, C. and Wang, P.P. (1999). *MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems*, Documentation and User's Guide, Contract Report SERDP-99-1. U.S. Army Engineer Research and Development Center, Vicksburg, MS.
10. Clement, T.P. (1997). *A modular computer model for simulating reactive multi-species transport in three-dimensional groundwater systems*, Rep. PNNL-SA-28967. Pacific Northwest Natl. Lab., Richland, WA.
11. Prommer, H., Barry, D.A., and Zheng, C. (2003). MODFLOW/MT3DMS-Based Reactive Multicomponent Transport Modeling. *Ground Water* **41**(2): 247–257.
12. Rafai, H.S., Newell, C.J., Gonzales, J.R., Dendrou, S., Kennedy, L., and Wilson, J.T. (1998). *BIOPLUME III—Natural Attenuation Decision Support System*. User's Manual, Version 1.0, EPA/600/R-98/010.
13. Schirmer, M., Molson, J.W., Frind, E.O., and Barker, J.F. (2000). Biodegradation modelling of a dissolved gasoline plume applying independent laboratory and field parameters. *J. Contam. Hydrol.* **46**: 339–374.
14. Molson, J.W., Barker, J.F., Frind, E.O., and Schirmer, M. (2002). Modeling the impact of ethanol on the persistence of benzene in gasoline-contaminated groundwater. *Water Resour. Res.* **38**(1): doi:10.1029/2001WR000589.
15. Steefel, C.I. (2001). *GIMRT, version 1.2: Software for Modeling Multicomponent, Multidimensional Reactive Transport*. Users Guide, Technical Report UCRL-MA-143182. Lawrence Livermore National Laboratory, Livermore, CA.
16. Yeh, G-T., Salvage, K.M., Gwo, J.P., Zachara, J.M., and Szecsody, J.E. (1998). *HydroBioGeoChem: A Coupled Model of Hydrologic Transport and Mixed Biogeochemical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media*. Report ORNL/TM-13668. Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN.
17. Schäfer, D., Schäfer, W., and Kinzelbach, W. (1998). Simulation of reactive processes related to biodegradation in aquifers—1. Structure of the three-dimensional reactive transport model. *J. Contam. Hydrol.* **31**(1–2): 167–186.
18. Bastian, P., Birken, K., Lang, S., Johannsen K., Neuß, N., Rentz-Reichert, H., and Wieners, C. (1997). UG: A flexible software toolbox for solving partial differential equations. *Computing and Visualization in Science* **1**: 27–40.
19. Zheng, C. and Bennett, G. (2002). *Applied Contaminant Transport Modeling*. John Wiley & Sons, New York.
20. Thornton, S.F. and Oswald, S.E. (Eds.). (2002). *Natural and Enhanced Restoration of Groundwater Pollution*. Red book, IAHS Publication no. 275. IAHS Press, Wallingford, UK.
21. Stauffer, F., Kinzelbach, W., Kovar, K., and Hoehn, E. (Eds.). (2000). *Calibration and Reliability in Groundwater Modelling: Coping with Uncertainty*. Red book, IAHS Publication no.265. IAHS Press, Wallingford, UK.
22. Kovar, K. and Hrkal, Z. (Eds.). (2003). *Calibration and Reliability in Groundwater Modelling: A Few Steps Closer to Reality*. Red book, IAHS Publication no. 277. IAHS Press, Wallingford, UK.

BIOFOULING IN WATER WELLS

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BIOFOULING EFFECTS ON PRODUCTION EFFICIENCY AND WATER QUALITY

Biofouling as a term has its origins in pre-World War II studies of marine fouling and generally refers to coating, encrustation, and corrosion associated with the

attachment of organisms to surfaces, including human-engineered structures. The phenomenon arises from the tendency of life across all known kingdoms to cling to and use surfaces. Biofouling takes many forms, ranging from bacterial-viral films plaguing urinary tracts to fouling of water intakes and other maritime structures (and even baleen whales) by films that also include macroorganisms such as barnacles and zebra mussels.

Biofouling of water wells and associated downstream systems tends to result from the formation of biofilms by bacteria. It is now widely recognized that biofouling is the first or second most costly deteriorating factor for groundwater systems in North America (1–3), and the problem has been recognized as important worldwide (4–6) for many years (7), although not universally accepted.

The composition of biofilms in any particular water well most likely echoes the populations of microflora in the associated aquifer and earth materials through which recharge passes. Those that thrive or persist are adapted to the environmental conditions in the well and contributing aquifer and vary by aquifer conditions (3,8). Where conditions permit, biofilm communities may closely resemble those in surficial soils, or they may be distinct.

In transmissive media systems such as aquifers and associated water wells, an important function of biofilms is to manipulate oxidation-reduction gradients and to accumulate and recycle resources (nutrients, metals, and organic carbon). One result of this activity is the deposition of reactive metal oxides and sulfides and rapid transformation of other redox-sensitive species, particularly in the nitrogen and sulfur series. The oxides are bulky solids and, along with slimes, contribute to blocking pore spaces and various engineered apertures.

The best known form of well water biofouling, iron and manganese biofouling, develops from both direct microbial function and indirect or passive interactions among biofilm, aqueous solutions, and surfaces. Ferrous iron compounds [Fe(II)] or ions (Fe^{2+}) can also be oxidized to the ferric [Fe(III)] state by nonbiological (abiotic) oxidants such as chlorine or oxygen, so the precipitation of iron by bacterial action is often hard to distinguish from abiotic processes, and both mechanisms are considered to operate in wells (8). Autooxidation of Mn in ambient ground waters is not favored due to the high E_h of the Mn(II)–Mn(IV) transformation (approx. +600 mV at pH 7.0), thus the transformation is presumptively mediated by the presence of biofilms. The formation of metal oxides is synergistic: as reactive iron oxihydroxides such as ferrihydrite are formed, more metal oxides deposit abiotically. Bacterial extracellular polymer (ECP) slimes that sequester metal ions and metal oxide colloids are involved in these interactions in a process analogous to iron sequestration treatments used to control iron precipitation.

The formation of iron sulfides and sulfur-oxidizing biofilms are two other significant water well biofouling phenomena where sulfide is present in groundwater. Sulfide is formed by microbial sulfate-reducing respiration and secondarily in some systems by putrefaction. Iron sulfides (which form dense black deposits) form spontaneously when aqueous sulfide ions come in contact with Fe^{2+} in solution. Sulfide oxidizers commonly form biofilms in the water columns of wells accessing sulfide groundwater. These biofilms can be highly viscous and have high integrity, easily blocking apertures. Chlorine and chlorine-based disinfectants can react with such components of the biofilm to produce halogenated organics.

Sulfides and other particles, such as calcite redeposited from solution (often also mediated by microbial activity), enhance the clogging potential of these biofilms. In some systems, mineral FeS_x clogs occur at the lower redox potentials that favor them (typically in the aquifer), and sulfur-oxidizer slimes form at higher E_h and pH (typically in the well water column).

Other less commonly described forms of metal oxidizing biofouling have been described, including aluminum biofouling (9). Aluminum hydroxide is coprecipitated with sulfate in high-organic-carbon white deposits. The composition varies according to variations in aeration. A variation is aluminum complexed in biofilms, often with iron deposited. Similar deposits have been described for samples from North Carolina in the United States.

Biofouling becomes a matter of public health concern when biofilms harbor or permit the proliferation of pathogens or indicator bacteria. If biofilms harbor and enhance survival of pathogens, they may result in illness. If the biofilms resist disinfection treatments, pathogens may avoid destruction. A recognized practical problem is positive results in total coliform tests that can be attributed to adaptive biofilm microflora that grow in commonly used growth media that is intended to be selective for the total coliform group of bacteria.

BIOFOULING EFFECTS ON WELL WATER SYSTEMS AND WATER QUALITY

Biofouling affects well water quality and well and water system metallic components in a variety of ways. Often the earliest manifestation of biofouling is the water quality degradation that accompanies mass bacterial growth and associated iron, manganese, and sulfur transformations. Typical symptoms are

- "red" or "black" water, increased turbidity (often far above typical groundwater), transiently high chlorine demand, and taste and odor problems that can result in a lack of confidence in the quality of the water supply.
- alteration of water quality in pumped samples. Biofouling can have a significant impact on the representativeness of groundwater samples from wells. Fluctuating Fe and Mn levels occur as Mn and Fe complexed with ECP may occur in suspension and can be detected in high levels in analytical results from unfiltered samples. Iron biofilms efficiently remove Fe and Mn, as well as other metals, from solution through chelation and deposition on reactive Fe(III) and Mn(IV) oxide mineral surfaces (6,8).

Chemical digestion of Fe- and Mn-biofilm samples indicate the presence of metals (e.g., Pb, As, Se) not detected in associated water samples (8). Thus, sample water pumped from biofouled wells can have metal levels lower than ambient ground water outside of the influence of the well (2,10–12).

- Work summarized in Smith (3) and subsequent work in alluvial aquifers and engineered systems (13) shows that (1) low total Fe (at or below the 300-μg/L standard) and (2) total Fe:Mn ratios of samples near 1:1 or upset (i.e., Mn:Fe >1:1) are typical of pumped water samples from biofouled water wells in microbially active alluvial aquifers.
- Elevated iron and manganese concentrations in pumped groundwater are also typically the result of bacterial activities in the aquifer, including respiratory Fe(III) and Mn(IV) reduction in the presence of abundant organic carbon and also corrosion of metal equipment. If unfiltered samples containing biofilm colloids are digested, very high Fe and Mn levels may be recorded (13).
- Biofilm influences have significant impacts on oxidation-reduction potential (3,8,13) and explain discrepancies between E_h values calculated from different couples and between calculations and measured values (8).
- Corrosion is enhanced by biofilm action and may occur where corrosion-incrustation index calculations predict that it would not occur. Such microbially influenced corrosion (MIC; 14) can also affect materials not expected to be subject to corrosion, accelerates well aging, and contributes corrosion-product constituents to water samples (15).
- Intermittent total coliform positive test results, mostly caused by bacteria not necessarily part of the total coliform group, but possessing the galactosidase enzyme.

It is important to note that corroding, encrusting, and nonencrusting biofouling effects, as well as test results that pose health concerns, often occur simultaneously.

BIOFOULING EFFECTS ON SYSTEM HYDRAULIC PERFORMANCE

In a well, biofouling phenomena may encrust or loosely plug well borehole intake areas and screens, pumps, and other downstream equipment. The initial process is the formation of a biofilm on surfaces in the well (casing, screen, pump) and in the aquifer in the vicinity of the well. The time course of this process to result in water quality or pumping problems may vary considerably, depending on site-specific conditions:

- Clogging (both formation/well and pump/discharge systems). Well clogging is usually expressed as reduced specific capacity (yield in volume/time unit versus drawdown during pumping).
- Corrosion: Cathodic depolarization of steel surfaces, erosion by organic acids, and intergranular cracking corrosion of stainless steels.
- Biofilms on interior pipe walls become increasingly hard or thicker over time. This tuberculation (the entire complex of corrosion/encrustation) can reduce the hydraulic capacity of a system. Tubercles increase hydraulic resistance by reducing diameter and by increasing the roughness of the interior surface of the pipe, dramatically increasing the energy cost to pump.
- Moreover, encrustations pack around lineshafts and bearings inside column pipe and reduce shaft life due to increased friction and reduced cooling. These developments may be aggravated by well operating choices (8).
- Biofouling shares top troublemaking honors with abrasion and clogging by silt and sand in groundwater systems for water supply, long-term dewatering, and on-site treatment to remove contamination (1,16,17). In fact, the two problems are frequently interactive (1,18–20), and biofilms may immobilize solid-phase silica (8), contributing to clogging.

With regard to well hydraulic performance,

- Reductions in specific capacity due to biofouling vary locally, but annual reductions are on the order of 1 to 3.4 on Long Island, NY, ranging up to 47% annually (21), for example.
- Considerable biofouling buildup can occur before well specific capacity is impacted.
- Wells accessing aquifers with low hydraulic conductivity (K) show faster and more enhanced performance decline compared to wells in formations with higher K.
- Higher Fe and Mn levels, particularly when oxidizing conditions prevail, can accelerate performance decline, although rapid biofouling clogging can occur at low levels. Higher total P, sulfate and organic carbon are also associated with enhanced biofouling development and clogging (6,8,22).

See related items, EVALUATION OF MICROBIAL COMPONENTS OF BIOFOULING, and WELL MAINTENANCE, for diagnostic methods and their applications where biofouling occurs in wells.

BIBLIOGRAPHY

1. Borch, M.A., Smith, S.A., and Noble, L.N. (1993). *Evaluation and Restoration of Water Supply Wells*. AWWA Research Foundation, Denver, CO.
2. Chapelle, F.H. (1993). *Ground-Water Microbiology and Geochemistry*. John Wiley & Sons, New York.
3. Smith, S.A. (1992). *Methods for Monitoring Iron and Manganese Biofouling in Water Supply Wells*. AWWA Research Foundation, Denver, CO.
4. Alcalde, R.E. and Gariboglio, M.A. (1990). Biofouling in Sierra Colorado water supply: A case study. *Microbiol. Civ.*

Eng., FEMS Symposium No. 59. P. Howsam (Ed.). E.&F.N. Spon, London, pp. 183–191.

5. Barbic, F., Krajcic, O., and Savic, I. (1990). Complexity of causes of well decrease. *Microbiol. Civ. Eng., FEMS Symposium No. 59*. P. Howsam (Ed.). E.&F.N. Spon, London, pp. 198–208.
6. Houben, G.J. (2003). Iron oxide incrustations in wells. Part 1: Genesis, mineralogy, and geochemistry. *Appl. Geochem.* **18**: 927–939.
7. Harder, E.C. (1919). *Iron-Depositing Bacteria and Their Geologic Relations*. U.S. Geological Survey Water Supply Paper 113, U.S. Geological Survey, Washington, DC.
8. Walter, D.A. (1997). *Geochemistry and Microbiology of Iron-Related Well-Screen Encrustation and Aquifer Biofouling in Suffolk County*, *Long Island, New York*. Water Resources Investigation Report 97-4032. U.S Geological Survey, Coram, NY.
9. McLaughlan, R.G., Knight, M.J., and Steutz, R.M. (1993). *Fouling and Corrosion of Groundwater Wells: A Research Study*. National Centre for Groundwater Management, University of Technology, Sydney, Australia.
10. Vuorinen, A. and Carlson, L. (1985). Special of heavy metals in Finnish lake ores; selective extraction analysis. *Int. J. Environ. Anal. Chem.* **20**: 179–186.
11. Mouchet, P. (1982). From conventional to biological iron removal in France. *JAWWA* **84**: 158–167.
12. Van Riemsdijk, W.H. and Hiemstra, T. (1993). Adsorption to heterogeneous surfaces. *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown (Eds.). CRC Lewis, Boca Raton, FL, pp. 1–36.
13. Smith, S. and Hosler, D.M. (2001). *Report of Investigations with Recommendations, Biological Fouling of the Pressure Relief Drainage System*, *Pablo Canyon Dam, Montana*. Bureau of Reclamations, Denver, CO.
14. Videla, H.A. (1996). *Manual of Biocorrosion*. CRC Press Lewis, Boca Raton, FL.
15. Oakley, D. and Korte, N.E. (1996). Nickel and chromium in ground water samples as influenced by well construction and sampling methods. *Ground Water Monitoring and Remediation* **16** (1): 93–99.
16. Howsam, P. and Tyrrel, S., (1989). Diagnosis and monitoring of biofouling in enclosed flow systems—experience in groundwater systems. *Biofouling* **1**: 343–351.
17. Smith, S.A. (1990). Well maintenance and rehabilitation in North America: An overview. In: *Water Wells Monitoring, Maintenance, and Rehabilitation*. P. Howsam (Ed.). E.&F.N. Spon, London, pp. 8–16.
18. Howsam, P., Misstears, B., and Jones, C. (1995). *Monitoring, Maintenance and Rehabilitation of Water Supply Boreholes*. Report 137, Construction Industry Research and Information Association, London, UK.
19. Smith, S.A. (1995). *Monitoring and Remediation Wells: Problems Prevention and Cures*. CRC Lewis, Boca Raton, FL.
20. Alford, G. and Cullimore, D.R. (1999). *The Application of Heat and Chemicals in the Control of Biofouling Events in Wells*. CRC Press Lewis, Boca Raton, FL.
21. Walter, D.A. (1997). *Effects and Distribution of Iron-Related Well-Screen Encrustation and Aquifer Biofouling in Suffolk County*, *Long Island, New York*. Water Resources Investigation Report 96-4217. U.S Geological Survey, Coram, NY.
22. Cullimore, D.R. (1993). *Practical Manual of Microbiology*. CRC Press Lewis, Boca Raton, FL.

IN SITU BIOREMEDIATION OF CONTAMINATED GROUNDWATER

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INTRODUCTION

Globally, the use of groundwater for various purposes is enormous. It is used as potable, industrial (especially cooling), and irrigation water on a huge scale. At least twelve megacities (population over 10 million) could not function without groundwater, and typically at least 25% of the water for these cities comes from aquifers (1). China alone has over 500 cities, and two-thirds of the water for them comes from aquifers.

Despite this importance, the number of instances of groundwater contamination due to accidental spills or unsatisfactory disposal is beyond counting. Up to a certain point, contamination can be attenuated by natural processes, especially biodegradation. In this regard, the biologically active zone is the vadose (unsaturated) zone where attenuation rates are highest. Contaminant removal continues in the saturated zone but usually at much lower rates, and migration of contaminants to the saturated zone can disperse the contaminants. Although it brings about dilution, this latter process often cannot be relied upon for complete decontamination.

Beyond a threshold, this natural attenuation cannot continue, and a decision has to be made whether or not to intervene with cleanup technology. This decision is now based on risk assessment. Risk assessment usually uses source–pathway–receptor analysis, and its outcome also determines, which treatment technology is to be used if treatment is necessary.

RISK ASSESSMENT

The objective of source–pathway–receptor analysis is the identification of the linkage(s) between them. Risk-based remedial design has as an objective the selection of the strategy to break the linkages and thus remove the risk. If, for example, there is a source of pollution and potential receptors (usually human) but no pathway to link them, or the pathway(s) can be blocked, then the risk is removed. If the receptor is human, then it is more likely that the risk will be removed by treating the source.

WHERE IS THE BOUNDARY BETWEEN GROUNDWATER AND SOIL TREATMENT?

Necessarily, if groundwater is to be treated by in-situ technologies, then the boundary between soil and water treatment becomes blurred, especially for vadose zone treatment.

SOME STATISTICS

The U.S. EPA has a recorded history of the treatment technologies applied to contaminated soil and groundwater at Superfund and other priority sites, which is updated through annual status reports (ASRs). As this history spans several decades, it is instructive to examine the record to identify the main technologies and trends in usage. Figure 1 shows that ex situ pump and treat methods have dominated groundwater treatment. This involves pumping the groundwater to the surface and selecting a treatment. Monitored natural attenuation (MNA) is not regarded as an engineered technology (2), but it is briefly described.

Specifically at Superfund sites (Fig. 2), *in situ* groundwater treatment remedies have been chosen 169 times at 135 sites (3). Air sparging has been chosen most frequently, followed by bioremediation. However, a comparison of those projects at the predesign, design, or installation stages (preoperational or future) and the operational and complete (current and historical) shows that the popularity of bioremediation has increased and that of air sparging has dropped dramatically.

Groundwater remedy type	Number of sites
Pump and treat	713
In situ treatment	135
Monitored natural attenuation	201
Other	822

Figure 1. Total number of sites with a groundwater remedy (3). Sites may be included in more than one category.

IN SITU BIOREMEDIATION TECHNOLOGIES

The treatment of groundwater in-situ has several advantages and disadvantages compared to pump and treat. The advantages include reduced site disturbance, which is crucial when a site is still being used; remediation around or under buildings without disturbance; and reduced worker exposure to volatile compounds. The quoted disadvantages include that site assessment must fully describe the hydrogeology and contaminant distribution, leading to increased cost; difficulty in control of reaction conditions; difficulty in accurately predicting end points; and therefore, the need for careful monitoring of the process. As it is difficult to take samples during *in situ* treatment, then it is difficult to assess if contamination hot spots have been remediated.

Additionally, in bioremediation, several other factors must be considered. Regularly quoted advantages of bioremediation are

- It is often less expensive than other techniques.
- Because the contaminants are mineralized, they are permanently eliminated.
- Long-term liability is thus eliminated.
- It has "green" credentials, representing a sustainable option.

Likewise, there are quoted disadvantages:

- Bioremediation cannot treat all contaminant types; most notably heavy metals cannot be biodegraded.
- Low permeability soil makes in-situ bioremediation of groundwater untenable.
- It may be too slow in certain circumstances.

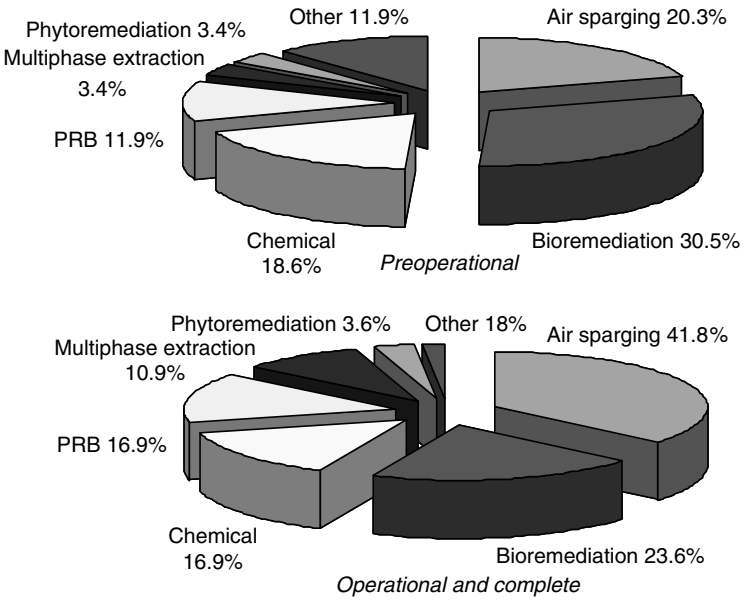


Figure 2. *In situ* groundwater treatment projects by technology, fiscal years 1982–2002 (adapted from Reference 3).

- It is often regarded as "incomplete" in that the contaminants may not be removed completely.
- Physicochemical conditions that are not ideal for microbial growth can slow the process down considerably.
- There is a worry that metabolites may be toxic.

As a result, the suitability of bioremediation has to be assessed case by case, and small-scale treatability studies are required (4), which adds to the time and expense of a project.

Aerobic or Anaerobic?

More than any other factor, it is likely that oxygen limitation occurs in groundwaters, and the most rapid biodegradation processes normally involve oxygenase enzymes (5). The supply of oxygen for *in situ* bioremediation adds considerably to the expense and the technical difficulty. This supply involves the use of either blowers or vacuum pumps to draw air through the system. A measure of the pivotal role of oxygen is in the use of hydrogen peroxide to enhance aeration. That its use has been considered at all is remarkable: concentrations of H_2O_2 above 100 to 200 mg/L are toxic to microorganisms; it can be consumed very quickly, limiting treatment to the regions near the injection well; a groundwater circulation system must be created; and good soil permeability is essential.

Recent advances in the knowledge of anaerobic biodegradation microbiology have opened up the prospect of greater acceptance of anaerobic bioremediation where maintaining aerobic conditions is not feasible. The existence of microorganisms capable of coupling the anaerobic reduction of Fe^{3+} to the oxidation of organic compounds shows promise (6). Virtually our entire knowledge of anaerobic metabolism of hydrocarbons has been gained since around 1990 (for reviews, see References 7 and 8). Several alkylbenzenes, alkanes or alkenes, are anaerobically biodegraded by denitrifying, ferric iron-reducing or sulfate-reducing bacteria. Another group of anaerobic hydrocarbon-degrading bacteria are "proton reducers" that rely on syntrophic associations with methanogens (8). As some of the most significant groundwater pollutants are chlorinated solvents, then a role for microbial reductive dehalogenation is feasible. Although slow, even the reductive dechlorination of dioxins is possible (9). A recent discovery has shown that even benzene can be oxidized completely under anaerobic conditions by pure cultures, using nitrate as the electron acceptor (10). Benzene is a particular problem in groundwater because it is relatively soluble and mobile.

Monitored Natural Attenuation

This technique involves monitoring the natural physical, chemical, and biological processes in soil and groundwater that are used to destroy a pollutant or limit its spread or migration (11). In nearly all situations, however, microbial reactions are the dominant processes driving natural attenuation (12), so it can be considered a long-term *in situ* bioremediation process.

Monitored natural attenuation may be useful where natural processes within the polluted area are effective in stabilizing or reducing the size of a contaminated groundwater plume, but there cannot be unacceptable impacts or risks to receptors. Monitoring and modeling are used to enable predicting the rate of attenuation and the rate of migration of the pollutant with some degree of confidence. The overall cost-effectiveness of MNA must take into consideration the long-term expenses involved in monitoring compared to the cost of a more intrusive approach, which is likely to be more costly during operational remediation, but requires no long-term monitoring.

Bioventing

This method uses indigenous microbes to biodegrade organic contaminants in the unsaturated zone above the water table. Technically, then, it is an *in situ* source treatment for contaminated soil (13), but it can be considered here as it inevitably results in soil water remediation. Bioventing is, after all, designed to remove contamination from the vadose zone to prevent future contamination of groundwater.

It combines supplying extra oxygen with vapor extraction to induce forced airflow through the contaminated area and enhance natural biodegradation (Fig. 3). Air is blown into the center of the area of contaminated soil above the water table and sucked out through peripheral boreholes to off-gas treatment prior to emission to the atmosphere. In its engineering manifestations, it closely resembles soil vapor extraction (SVE), but the two technologies have fundamentally different goals. SVE endeavors to maximize volatilization of low molecular weight contaminants, with some incidental bioremediation. Bioventing, however, endeavors to maximize biodegradation of the contaminant(s) regardless of molecular weight, with some incidental volatilization (14).

To enhance the biological process, nutrients can be supplied to the contaminated area. The injection of oxygen stimulates the microbes in the contaminated soil to

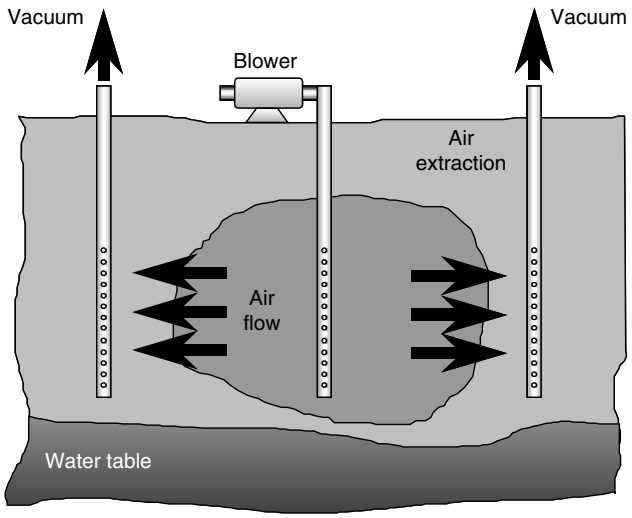


Figure 3. Bioventing.

degrade the organic contaminants to CO_2 and water. The process also mobilizes volatile compounds (either present in the soil or produced during biodegradation) to move toward boreholes, making extraction simpler.

Bioventing has now been used successfully at over 1000 sites and seems best suited to the bioremediation of middle distillate fuels such as diesel and jet fuel (15), but also nonchlorinated solvents, some pesticides, wood preservatives, and other organic chemicals have been removed. It is not successful in limited permeability soils, and application to the saturated zone relies on the water level being reduced (16). However, it can be successfully combined with biosparging.

Biosparging

Biosparging is similar to bioventing, in that air is injected, but in this case it is introduced below the water table (in the saturated zone) (Fig. 4) to increase the dissolved oxygen concentration in the groundwater and thus stimulate the activity of the indigenous microorganisms, thereby stimulating aerobic bioremediation. It can also have a similar stimulatory effect in the unsaturated zone. Like bioventing, nutrients may be added to enhance the biological process.

The success of the technique depends on adequate diffusion of the injected air away from the boreholes into the surrounding groundwater and soil. The location and number of boreholes depend primarily on the subsurface soil structure and permeability, and like bioventing, biosparging is best suited to permeable soils (16). Like bioventing, biosparging uses equipment that is readily available and easy to install.

Pump and Treat

The contaminated aqueous phase from the saturated zone is pumped, via a recovery well, to a treatment tank on the surface. In the treatment tank, nutrients, oxygen, and other electron acceptors (e.g., sulfate and nitrate) are added before the groundwater is pumped back into the ground via an injection well and recirculated through the contaminated zone (Fig. 5). The oxygen and nutrients in the injected groundwater stimulate the microbes in the contaminated zone to biodegrade contaminants dissolved in the groundwater and present in the soil. Groundwater extraction and injection continue until monitoring data

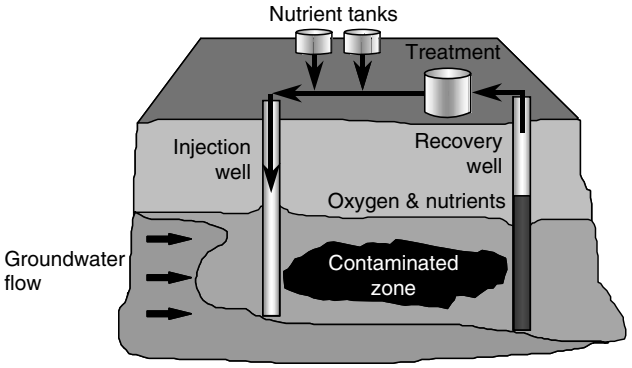


Figure 5. Pump and treat.

show that the remedial objectives have been achieved. Technically, then, when pump and treat is operated as a bioremediation technology, it combines features of ex situ (water is pumped to the surface) and *in situ* (biological treatment continues underground).

Pump and treat is a technology of great flexibility because the surface treatment need not be biological. In fact, a treatment train employing a variety of different technologies is possible at the surface. A much higher degree of process control is possible at the surface, for example, temperature, pH. For these reasons, pump and treat has historically been a very popular treatment for contaminated groundwater. However, there have been frequent questions over the efficacy of pump and treat, probably because, as the technology has become accepted, expectations have become too high (17).

Permeable Reactive Barriers

A PRBs consists of a reactive material that is placed in the path of flowing groundwater (Fig. 6), and due to the permeability of the chosen reactive material, it removes contaminants from the flow as the groundwater passes through. These barriers allow the passage of water while prohibiting the movement of contaminants. Agents within the barrier are materials such as zero-valence metals, for example, Fe^0, chelators, sorbents, and microbes (18). The contaminants are either degraded or retained in concentrated form by the barrier material, which may need to be replaced periodically.

PRBs have considerable flexibility in that combined chemical and biological treatments are possible within

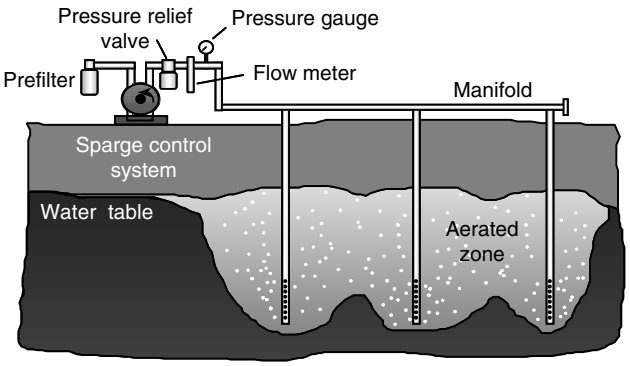


Figure 4. Biosparging.

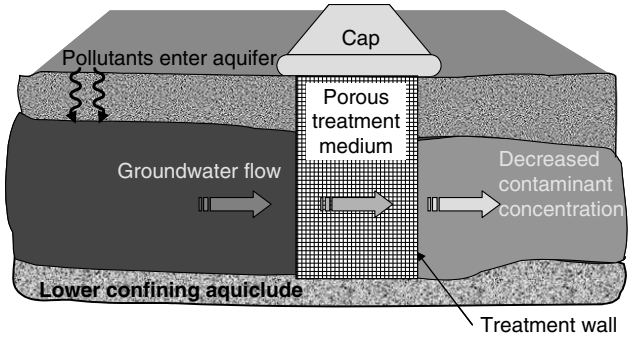


Figure 6. Permeable reactive barrier.

the same barrier, or barriers can be sequenced. For example, a contaminated aquifer beneath a petrochemical site may typically contain both chlorinated solvents and petroleum hydrocarbons. The chlorinated compounds may be removed by zero-valence iron in the permeable reactive barrier. With time, the permeable barrier will become colonized by bacteria, and bioremediation of petroleum hydrocarbons will occur, given the correct conditions. Alternatively, hydrocarbon-oxidizing bacteria may be deliberately added (the practice of bioaugmentation). Another aspect of the flexibility of the PRB is that in many cases it can be installed at working sites with minimal disruption to normal operations.

COSTS

The costs of all remediation technologies are constantly shifting and vary greatly from country to country. So quoted figures per tonne or per cubic meter of contaminated groundwater or soil would soon be out of date. Rather, it should be possible to identify economies of scale if confidence is gained in a technology and it is used increasingly at full scale. This confidence in bioremediation has been lacking in the past, and in many parts of the world, it is still not accepted at full scale.

If a technology is following a typical economies of scale pattern, then the more it is used, the more costs will decrease. The US EPA (19) examined the correlation between unit costs and quantity treated for six different soil and groundwater remediation technologies: bioremediation, thermal desorption, soil vapor extraction, on-site incineration, pump and treat, and permeable reactive barriers. Some important findings were reported:

1. Four of the six technologies (bioventing, thermal desorption, soil vapor extraction and pump and treat) evidenced a correlation between unit cost and quantity treated, thus exhibiting an economies of scale pattern.
2. Bioventing had the best correlation of these four technologies.
3. No other bioremediation technology exhibited any such correlation.
4. Pump and treat groundwater remediation systems showed a correlation for both unit capital costs and unit average operating costs.

The lack of correlation for the other bioremediation technologies may simply result from lack of data from a sufficiently large number of full-scale projects, but the signs are encouraging that bioventing has proven to be a market success.

BIBLIOGRAPHY

1. Morris, B.L., Lawrence, A.R.L., Chilton, P.J.C., Adams, B., Calow, R.C., and Klinck, B.A. (2003). *Groundwater and Its Susceptibility to Degradation: A Global Assessment of the Problem and Options for Management*. Early Warning and Assessment Report Series RS.03-3. United Nations Environment Programme, Nairobi, Kenya.
2. U.S. EPA. (1999). *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites*. OSWER Directive 9200.4-17P.
3. U.S. EPA. (2004). *Treatment Technologies for Site Cleanup: Annual Status Report*. 11th Edn. EPA-542-R-03-009.
4. Boopathy, R. (2000). Factors limiting bioremediation technologies. *Bioresource Technol.* **74**: 63–67.
5. Dagley, S. (1975). A biochemical approach to some problems of environmental pollution. *Essays Biochem.* **11**: 81–138.
6. Crawford, R.L. (1991). Bioremediation of groundwater pollution. *Curr. Opin. Biotechnol.* **2**: 436–439.
7. Holliger, C. and Zehnder, A.J.B. (1996). Anaerobic biodegradation of hydrocarbons. *Curr. Opin. Biotechnol.* **7**: 326–330.
8. Heider, J., Spormann, A.M., Beller, H.R., and Widdel, F. (1999). Anaerobic bacterial metabolism of hydrocarbons. *FEMS Microbiol. Rev.* **22**: 459–473.
9. Adriaens, P., Fu, Q., and Grbic-Galic, D. (1995). Bioavailability and transformation of highly chlorinated dibenzo-*p*-dioxins and dibenzofurans in anaerobic soils and sediments. *Environ. Sci. Technol.* **29**: 2252–2260.
10. Coates, J.D., Chackraborty, R., Lack, J.G., O'Connor, S.M., Cole, K.A., Bender, K.S., and Achenbach, L.A. (2001). Anaerobic benzene oxidation coupled to nitrate reduction in pure culture of two strains of *Dechloromonas*. *Nature* **411**: 1039–1043.
11. BioWise. (2000). *Contaminated Land Remediation: A Review of Biological Technology*. DTI/BW/18/5000/12/2000/NP.
12. Smets, B.F. and Pritchard, P.H. (2003). Elucidating the microbial component of natural attenuation. *Curr. Opin. Biotechnol.* **14**: 283–288.
13. U.S. EPA. (2001). *Use of Bioremediation at Superfund Sites*. EPA 542-R-01-019.
14. U.S. EPA. (1995). *Bioventing Principles and Practice*. Volume 1: Bioventing principles. EPA/540/R-95/534a.
15. U.S. EPA. (1995). *Soil Vapor Extraction (SVE) Enhancement Technology Resource Guide*. EPA/542-B-95-003.
16. Martin, I. and Bardos, P. (1995). *A Review of Full Scale Treatment Technologies for the Remediation of Contaminated Soil*. EPP, Richmond, VA.
17. U.S. EPA. (1996). *Pump-and-Treat Ground-Water Remediation. A Guide for Decision Makers and Practitioners*. EPA/625/R-95/005.
18. U.S. EPA. (2001). *Treatment Technologies for Site Cleanup: Annual Status Report (Tenth Edition)*. EPA-542-R01-004.
19. U.S. EPA. (2001). *Remediation Technology Cost Compendium—Year 2000*. EPA-542-R-01-009.

PROCESS LIMITATIONS OF *IN SITU* BIOREMEDIATION OF GROUNDWATER

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Based on the origin and susceptibility to microbial interaction, hydrocarbons may be divided into two broad

classes: petroleum hydrocarbons and complex chlorinated hydrocarbons.

Petroleum hydrocarbons are largely associated with the production, storage, or use of fuels, lubricants, and chemical feedstocks. Petroleum hydrocarbons have been demonstrated to be biodegradable by numerous species of bacteria. Over a period of 3.5 billion years, bacteria have been able to evolve genetic resources that allow some of them to potentially use petroleum hydrocarbons as a source of food.

Complex industrial hydrocarbons include chlorinated aliphatic and aromatic hydrocarbons, MTBE, pesticides and herbicides, and polymers. These new synthetic compounds have been manufactured for about 100 years. Bacteria have not had time to evolve the genetic information required to utilize them as a source of food. Due to recalcitrance to microbial attack, these complex industrial chemicals are termed xenobiotic.

Successful *in situ* bioremediation of groundwater has been demonstrated at sites impacted with petroleum hydrocarbons. The most successful method of application has been through stimulation of indigenous microbial species. Microbial stimulation is the process of ensuring that environmental conditions, nutrient availability, and requirements for an electron acceptor are adequate in the contaminated portions of the aquifer.

The most common cause for failure of saturated zone *in situ* bioremediation is the lack of adequate mass transport of the electron acceptor (usually oxygen). In this regard, the physical setting of the site is critical. Overall permeability and the scale and degree of heterogeneity are the factors governing the advective and diffusional transport rates of contaminants and remediation reagents in the subsurface. If mass transport rates are too low, saturated zone *in situ* bioremediation is not a viable option.

Given adequate mass transport properties, site-specific microbiological conditions can also impact the process. Unfortunately, the presence of indigenous microbes and efficient mass transport may still prove insufficient for effective bioremediation. Specific reasons for the poor performance of *in situ* bioremediation systems relate to unoptimized subsurface conditions.

There is uncertainty with regard to the effect of hydrocarbon availability on the effectiveness of biodegradation. Can bacteria degrade hydrocarbons adsorbed to surfaces or degrade hydrocarbons with low levels of solubility? Or must the hydrocarbon be solubilized before it can be biodegraded? Contradictory laboratory evidence and field evidence have been published for both scenarios. With the predominance of evidence indicating that solubilization must take place, degradation reactions with extracellular bacterial exudates are much less likely.

The answer is likely consortia specific and dependent on the ability of the bacteria to synthesize appropriate biosurfactants. This ability may be absent in some instances.

Although petroleum hydrocarbons are amenable to primarily aerobic biodegradation, for it to occur the indigenous bacteria must have the appropriate genetic information. This genetic information is specific and precise. The presence of a specific hydrocarbon will stimulate the synthesis of an oxygenase enzyme that is expressly configured to react with that stimulating hydrocarbon.

For remediation, indigenous microbes generally possess the genetic information required for appropriate enzyme production and the contaminant will stimulate the production of those enzymes. General microbial stimulation has the potential to produce a large amount of biomass that may not take part in the biodegradation process and actually cause harm through biofouling and plugging of injection wells, galleries, or surrounding formations. There is potential to lose critical subsurface mass transport capabilities.

BACTERIAL TRANSPORT

There are practical limits to the degree of cleanup obtainable using bioremediation. Hydrocarbons at the low parts per million (ppm) level may not be capable of supporting significant levels of microbial activity even under stimulation. Sites with relatively high levels of hydrocarbon impact may actually be better candidates for bioremediation than those lightly impacted at levels slightly above regulatory action levels. Toxicity related to the presence of heavy metals, such as chromium, arsenic, or lead, or low temperature of the groundwater have been observed to inhibit bacterial growth in a variety of settings. Stimulating electron acceptors must also be available at sufficient concentrations; native sulfate concentrations less than about 20 mg/L do not stimulate sulfate reducing bacteria even in the presence of usable carbon substrates.

Xenobiotic industrial compounds are often recalcitrant to direct aerobic microbial attack. However, over the last 20 years a biodegradation process termed co-oxidation (or cometabolism) has been successfully demonstrated by researchers. For example, the aerobic degradation of trichloroethylene (TCE) has been accomplished using monooxygenase and dioxygenase enzymes produced through the use of petroleum hydrocarbons as a metabolizable substrate (food source) and stimulus for enzyme production. This general process is termed co-oxidation and the hydrocarbon substrate used as a food source is the cometabolite. Many different hydrocarbon substrates have been observed to stimulate the generation of cooxidation enzymes. The currently known cometabolic substrates fall into two broad classes:

1. Analog substrates, which are hydrocarbons that have a geometry similar to the targeted xenobiotic compound.
2. Methanotrophic (which is different than methanogenic) microbial systems have proved particularly effective at generating xenobiotic active enzymes.

Enzymes with co-oxidizing potential have a strong natural affinity for the hydrocarbon that originally stimulated its generation. The enzyme is genetically tailored to the compound used as a food source. Over 300 mol of methane are required to biodegrade 1 mol of TCE via co-oxidation. The efficiency of the co-oxidation process is extremely poor. Under field conditions where

mass transport is a critical success factor, a 300-fold decrease in the effectiveness of the reactants in the contaminated zone often can be impractical.

Accurate assessment of potential limiting factors such aerobic terminal electron acceptor (dissolved oxygen), geochemical conditions (pH, temperature, conductivity), and macronutrients (orthophosphate and ammonia as nitrogen) should be documented as part of the bioremediation evaluation process. Bioremediation is a dynamic process requiring monitoring of the hydrological, geochemical, and biological conditions over the life of a project.

NATURAL ATTENUATION: GROUNDWATER REMEDIATION BY NO ACTION

In a time of reappraisal for the allocation of financial resources to environmental action, a question of ever increasing importance is the consequence of no action concerning the release of petroleum or chlorinated hydrocarbons into groundwater. An important portion of that answer comes from the application of site-specific health based risk assessments. However, in instances where human consumption or exposure is not an issue, no action may be a reasonable alternative, even at elevated dissolved contaminant concentrations. The issue then becomes the determination of the consequence of no action under conditions where the sole process for remediation is natural attenuation.

The physical, chemical, geological, and biological processes that take place in a contaminated aquifer are complex. In most instances, a "native" aquifer is in a long-standing state of chemical equilibrium between the groundwater and the geologic matrix through which it flows. The release of anthropogenic hydrocarbons into an aquifer upsets that equilibrium. The dissolved concentration of the contaminant as it migrates through the aquifer is controlled by adsorption, dispersion, volatilization, and degradation. Adsorption affects the overall residence time of the release and dispersion affects the downgradient shape and dissolved concentration in the plume. Only volatilization and degradation contribute to the removal of contaminant from the aquifer, and at low concentrations degradation is the dominant mechanism for attenuation.

The mechanisms for attenuation through degradation can be broadly divided into two categories, biological and abiotic chemical action. This discussion is predicated on relatively "normal" groundwater conditions under which biological action proceeds at a rate orders of magnitude greater than abiotic processes. Extremes of pH, redox conditions, ionic strength, or temperature may make an exception to that generalization. Transformation can be chemically complex, dependent on the environmental conditions described above and affected by aquifer heterogeneity related to granular or fracture variability.

The factor controlling the rate of aerobic degradation is the availability of oxygen and the rate at which it can be introduced into the groundwater (through the groundwater–table interface) or the rate at which oxygen-rich groundwater can pass through the zones of adsorbed contamination. Each pound of petroleum hydrocarbons requires about 3.08 pounds of oxygen for complete degradation (1).

Typical *in situ* aerobic decay rates for groundwater are in the range of 35 μg/L·d (equivalent to about 0.5 oz/d per cubic yard of aquifer matrix).

Natural attenuation occurs both in the source zone and in the dissolved phase plume. In the source zone, oxygen will be rapidly consumed and portions of the aquifer will then host anaerobic degradation. Anaerobic degradation is limited by the availability of appropriate anaerobic electron acceptors such as nitrate, sulfate, or iron. When their availability is limited, degradation will stop after the production of aliphatic and aromatic organic acids; similarly, at low levels of dissolved oxygen (DO), aerobic degradation may also stop with the production of organic acids. The intrinsic biodegradation process and the alternative terminal electron acceptors are shown in Fig. 1 (2).

Optimum aerobic biodegradation occurs with the dissolved oxygen above 2 mg/L. Below that, the aerobic degradation rate of aromatic hydrocarbons will decrease dramatically. Conversely, under complete anaerobic conditions, nitrate reducing, iron reducing, and suflate reducing bacteria can effectively degrade hydrocarbons. However, at DO concentrations as low as 0.1–0.4 mg/L, anaerobic degradation rates will be reduced to just a few percent of optimum.

Because of all the mechanisms described above, hydrocarbon plumes tend to achieve a stable shape and size even when there is a continuous source of free phase hydrocarbon release. Steady state is achieved when the area of the plume edge is great enough to provide for a natural degradation rate equivalent to the rate of hydrocarbon infiltration. The edges of the dissolved plume do not have enough DO to support optimum rates of aerobic degradation but have too much DO to allow for optimum anaerobic degradation. The interior of a plume will support anaerobic natural attenuation, which is typically limited by the availability of iron in the mineral matrix and sulfate in the native groundwater and to a lesser extent the mineral matrix as well. However, once the source of hydrocarbon has been removed, a dissolved plume will narrow and dissipate from the edges inward, due to the availability of DO from groundwater along those edges.

The selection of a no action natural attenuation option should be based on an appropriate analysis of data gathered during the assessment of the site. First-order decay rates are appropriate for the evaluation of degradation kinetics at low concentrations, less than 1 ppm (an appropriate level to assume at the periphery of a plume). Given first-order decay rates, the analysis has a focus that is twofold—the effect of attenuation over time and the effect over distance.

Attenuation over time is measured at the edges of a plume using concentration measurements gathered repeatedly from specific monitor wells. The minimum recommended time is one year, with quarterly sampling from the selected monitor wells. The data for each well is then semilog plotted as log concentration against time. The slope of the line is the first-order decay constant in percent per day.

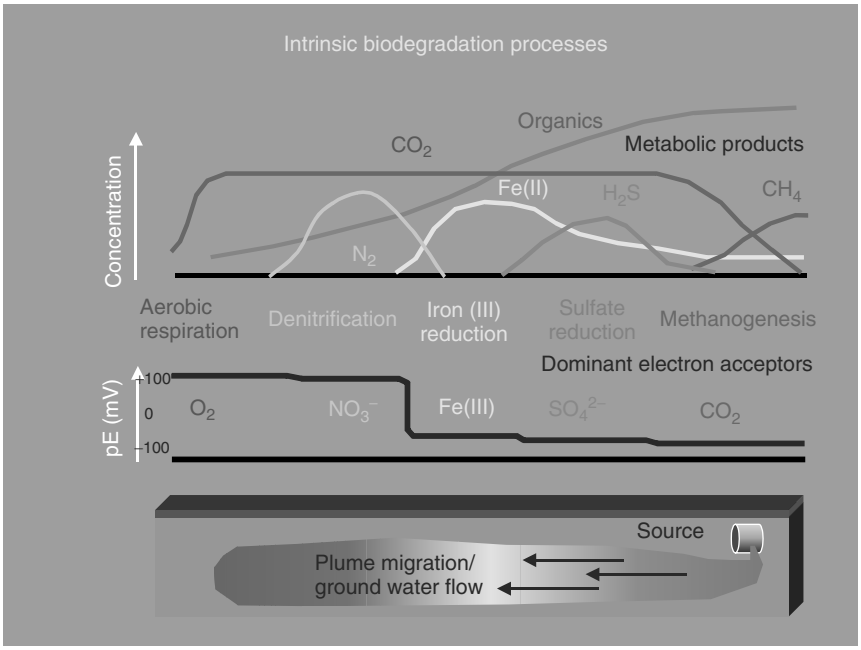


Figure 1. Intrinsic biodegration process (2). Petroleum hydrocarbons are referred to as organics in the diagram.

Attenuation with distance more accurately incorporates the effects of aquifer heterogeneity. Data for this analysis is obtained from a minimum of three monitoring wells, preferably along the long axis of the plume. This data is semilog plotted as log concentration versus distance. The slope of this line is equal to the decay constant divided by the groundwater velocity.

With this data, decisions can be made based on the site-specific contaminant dynamics under no action natural attenuation. This, in conjunction with a health based risk assessment, can allow for sound decision-making by the business and regulatory community.

In summary, the adoption of a no action alternative is most applicable to the dissolved phase plume only. Except for volumetrically small releases, it will still be necessary to remove or remediate the source zone of an impacted aquifer, after which natural attenuation may be a reasonable approach to the residual dissolved phases. Also implicit in this approach is that no action does not preclude the performance of requisite assessment activity, which can represent a significant long-term liability in some cases. Nonetheless, after proper source abatement, assessment, and analysis, the reliance on natural attenuation mechanisms for the final stages of cleanup is a cost effective and, if properly managed, environmentally sound resolution to aerially extensive dissolved phase hydrocarbon contamination.

NATURAL ATTENUATION: THE EFFECT OF PUMP AND TREAT REMEDIATION

In situ groundwater remediation has matured over the past 25 years, particularly with regard to understanding the dynamics of the interactions between contaminants, the impacted saturated soil matrix, and microbiological activity. Recent interest in the phenomenon of natural attenuation has served to illustrate the variety of microbial ecosystems that are present in a contaminant plume, each system determined by redox conditions and availability of electron acceptors. While natural attenuation is an attractive alternative to those responsible for groundwater contamination, the regulating communities are more skeptical. The need for proactive groundwater pumping remediation and the efficacy of natural attenuation pose a potentially complex balance that is governed by the subsurface conditions of each individual site. There is no universal applicable rule for the resolution of that balance. It is the responsibility of remediation designers to make those site-specific determinations and to provide the regulating community with information sufficient to support the proactive and the natural attenuation portions of each individual cleanup. Our purpose here is to point out some of the most significant factors impacting that balance.

The first and most dominant control is the nature of the saturated soil matrix. Several factors must be evaluated for remedial design:

1. The degree and scale of sediment heterogeneity, which determines how much and what portion of a contaminated aquifer can be affected with advective groundwater flow. Low permeability regions must rely on diffusional transport, which will dominate the overall remediation rate in the treatment zone.
2. The time of exposure to the contaminant is a direct function of the impact of heterogeneity described above. The contaminant will diffuse into the nonadvective portions of the aquifer soil matrix. At a minimum, remediation will take as long as the initial exposure. Due to the adsorptive retardation reactions, remediation is likely to take longer than the exposure time.

3. The geochemical composition of the soil matrix is also a factor in remedial design. Carbonaceous material and clays have a much higher propensity for the adsorption of organic contaminants. Iron oxides, in turn, have high adsorptive capacity for metal contaminants. Iron and sulfur minerals may be sources of electron acceptors as redox conditions are modified through the interaction of indigenous microbial populations and the contaminant.
4. The background geochemical makeup of the groundwater as well as that in the contaminant plume is an important remedial design factor. Dissolved oxygen, sulfate, nitrate, and iron can all potentially serve as alternate terminal electron acceptors to aid in the degradation of organic contaminants. Ferrous iron, hydrogen sulfide, and carbon dioxide are indicative end products of those reactions.
5. The distribution of the organic contaminant is another factor affecting remedial design. Free phase hydrocarbons should be recovered proactively with an extractive technology (pump and treat) or in the case of CVOCs possibly an *in situ* chemical oxidation injection technology. In cases where impact is shallow, excavation and disposal is still an extremely viable option.

The treatment of dissolved and adsorbed hydrocarbons is the point at which the balance between proactive remediation and natural attenuation must be determined.

One of the most important contributions that a pump and treat system makes to the *in situ* remediation of contaminated groundwater is plume capture and hydraulic control in the source zone and the core of the dissolved and adsorbed plumes. Background groundwater that is drawn through the plume perpendicular to the natural groundwater flow direction must also be evaluated.

In the past, the focus of pump and treat remediation has been on how it acts to flush and remove the contaminant. The contributions made by recent developments on the mechanisms of natural attenuation reside in the role of electron acceptors present at background concentrations within the aquifer. From the exterior to the interior of a plume, the specific electron acceptor zones are aerobic, denitrification, sulfate/iron reducing, and methanogenic.

The boundary between each specific redox zone and the active electron acceptor is controlled by the kinetics of the degradation process in each zone and the advective transport rates of groundwater through that zone. In most instances, the dominant effect is the groundwater transport rate.

The natural concentrations of these electron acceptors cover a wide range. Natural oxygen levels commonly range from 2 to 8 mg/L. Groundwater sulfate concentrations in soils derived from sedimentary rocks are typically in the 25-mg/L range, with higher values of several hundred mg/L not uncommon. Ferric oxides are commonly present in soils in the range of 0.5–5%; the ability of indigenous iron reducing bacteria to access that iron will vary from location to location. Given adequate permeability and the presence of appropriate electron acceptors, natural enhancement of pump and treat systems is possible and worth the relatively inexpensive analyses (some of which can be done with field kits) required to evaluate.

NATURAL ATTENUATION: TRANSVERSE DISPERSION AS THE NATURAL DRIVING FORCE

Dispersion is the process by which the interface of contaminated groundwater with native groundwater does not remain abrupt. The leading edge of a contaminant plume will arrive at a given point more rapidly than it would if advection alone were the acting driving force. The mean transport velocity of the contaminant mass remains the same, but concentration gradients are setup. This occurs simultaneously with the phenomenon of the contaminant occupying, with time, an increasing volume of groundwater. There are two fundamental types of dispersion—longitudinal and transverse. Both are accentuated by the inhomogeneous and anisotropic physical configuration of the permeable matrix within a groundwater system. There is also a contribution to both from diffusional transport as well.

Longtitudinal dispersion is caused by differences in groundwater velocity through pore spaces that vary in width or tortuosity. The result is dispersion that occurs along the direction of groundwater flow. Transverse dispersion is driven by groundwater flowing around individual particles in the aquifer matrix; the effect occurs perpendicular to the groundwater flow direction. Transverse dispersion is effective in mixing contaminated groundwater with native groundwater at the edges of an elongated plume and occurs only when there is a point source of contamination. In the context of natural attenuation, longitudinal dispersion is purely a dilution phenomena; transverse dispersion provides an influx of electron acceptors.

Both types of dispersion are dependent on horizontal and vertical variations in permeability. Increasing anisotropy and heterogeneity increase the magnitude of dispersion. Groundwater velocity also plays a role: At low velocities the effects of diffusion may equal those of dispersion.

The ratio of longitudinal to transverse dispersivity ranges from 1 to 24; most commonly, horizontal transverse dispersivity is 20% to 10% of the longitudinal dispersivity, and vertical transverse dispersivity is 2% to 1% of the longitudinal dispersivity. Instead of "football" shaped plumes, this difference in vertical and horizontal dispersivity tends to generate plumes that in three dimensions are "surfboard" shaped. The determination of the specifics of the effect of dispersivity on a contaminant concentration at a given time and location in an aquifer is an extremely complex process that requires detailed knowledge of the physical configuration of the aquifer matrix and solution to partial differential equations for final values. In many instances, a purely empirical approach is the only practical means of assessment rather than modeling.

The physical scale that is examined also has an impact: values of dispersivity change as one examines an aquifer on the scale of inches, feet, or thousands of feet.

Transverse dispersion is what serves to physically mix groundwater containing contaminants with adjacent groundwater that is unimpacted and contains natural electron acceptors. The phenomenon is probably best understood in terms of angle of divergence, that is, the angle between the two edges of the plume as it migrates from a point source. In granular materials that angle can be as low as 2° and in groundwater flowing through fracture systems as high as 20°. The most accurate determination of the angle of divergence is from information gathered as close as possible to the point representing the source of contamination.

The picture we normally have of a contaminant plume as it migrates away from a point source is one that is (in the two horizontal dimensions) tear drop shaped. The plume initially spreads downgradient and cross gradient until some point is reached at which the distal edges of the plume first travel parallel to the advective groundwater flow direction, and then begin to turn inward to the plume axis and close.

The distal portion of the plume is the dominant area where longitudinal dispersion (as well as transverse dispersion) is in effect. Adsorption and other attenuation reactions also take place, but for the purposes of this discussion those effects are ignored. Under pure hydrodynamic effects, a plume should dilute itself taking the shape of a cone at a constant angle of dispersion. This assumes that the nature of the geologic matrix and groundwater velocity stay constant, which is unlikely, especially in the vertical component. The most common result is that the downgradient shape of the plume is a consequence of attenuation caused by the migration of electron acceptors into the margins of the plume through the force of transverse dispersion—not through purely hydrodynamic flow effects.

NATURAL ATTENUATION: METHANOGENIC SYSTEMS

The ultimate no action alternative may be the use of methanogenic microbial systems. In this case, the electron acceptor is the contaminating hydrocarbon that may contribute to the degradation of petroleum and xenobiotic hydrocarbons There is a difference between methanotrophic bacteria and methanogenic bacteria. Methanotrophs use oxygen to oxidize methane into carbon dioxide (CO_2). Methanotrophic bacterial systems have received a great deal of attention over the last 15 years since it has been found that methane monooxygenase (the enzyme generated by methanotrophs to react with methane) can degrade a wide variety of chlorinated hydrocarbons. The process is known as cometabolism and is definitely an aerobic process.

Methanogenesis is the process of degrading hydrocarbons with the end product being methane (CH_4) gas and carbon dioxide. The general reaction is as follows:

$$2C\ (\text{organic contaminant}) + 2H_2O \rightarrow CO_2 + CH_4$$

This is a strictly anaerobic process; methanogenic bacteria are poisoned by the presence of oxygen at levels as low as 0.18 mg/L of soluble oxygen (as O_2).

The redox conditions under which these two different microbial systems operate are literally at opposite ends of the spectrum: methanotrophic reactions occur at the Eh range of +250 mV while methanogenic reactions occur at the Eh range of −200 mV.

As an aside, methanogenic bacteria are one of the three classes of bacteria termed Archaebacteria, which are representative of organisms that first appeared on Earth some 3.5 billion years ago. Although their activity is inhibited by oxygen, these bacteria are robust enough to appear in a wide variety of natural locations such as the intestinal tracts of ruminant mammals like cows, sewage digesters, groundwater, and soil.

The concentrations of methane and carbon dioxide are expressed as mole percent. This data is somewhat remarkable since this should be a difficult reaction to initiate. Oxygen, nitrate, and sulfate are all toxic or inhibitory to methanogenic activity. That means that at any site at which evidence of methanogenesis is present (methane gas), there has been a series of biodegradation reactions that have consumed the alternative electron acceptors. Migrating from the exterior to the interior of a plume, the type of redox conditions (Eh) will change from + 250 mV to − 200 mV, with oxygen, nitrate, ferric iron, and sulfate progressively being consumed.

The degradation of chlorinated xenobiotic compounds under methanogenic conditions is particularly enhanced via reductive dehalogenation reactions that involve substitution of hydrogen in the CVOC carbon chain. This can take place from the direct actions of bacteria and from the presence of molecular hydrogen that is produced from water during the methanogenic process.

Conceptually, methanogenesis might be considered "the ultimate of no action alternatives." The physical/chemical requirement for the removal of all other potential terminal electron acceptors infers that the hydrodynamics of such a system are relatively quiescent. The transport of alternate electron acceptors into the core of the contamination plume must be at a rate slow enough to allow for the consumption of all alternate electron acceptors before the methanogenic core zone is reached.

If this situation occurs, it can be a positive argument for absolutely no action involving pump and treat systems. That would increase groundwater velocities, introducing inhibitory electron acceptors into the active methanogenic zone. Groundwater systems in fine grained soils, where transport properties are poor, would be ideal for the exploitation of methanogenic degradation.

Of course, one problem with methanogenic degradation is the kinetics of the process. Methanogenic degradation occurs at rates that are orders of magnitude slower than the rates seen with other electron acceptors. However, at some sites with poor transport conditions or inaccessibility (i.e., a deep groundwater table), this may still be a reasonable alternative.

The number and types of hydrocarbons degraded under methanogenic conditions are very limited. Some laboratory studies have demonstrated the methanogenic degradation of toluene and *o*-xylene with no degradation of *m*-xylene, *p*-xylene, ethylbenzene, or benzene. Others have found

evidence of degradation of benzene with recalcitrance toward other compounds.

The methanogenic process appears to be extremely selective and not capable of the complete degradation of all contaminants present in a typical hydrocarbon plume on the order of years. In addition, there is likely a great deal of microbial heterogeneity with specific degradation capacity varying from location to location. In instances where a specific compound has been released (such as toluene used as a solvent), methanogenesis may be a viable natural attenuation process. It also has value in the natural dehalogenation of chlorinated compounds.

In instances where an aquifer has good transport qualities and a supply of natural electron acceptors, natural attenuation alone can be a viable process and acceptable to the regulatory community. However, responsible parties must be prepared for the long-term monitoring that will often be required in support of a natural attenuation program—more accurately termed monitored natural attenuation by the regulating community. In other cases, supplementation of electron acceptors or improvement of groundwater dynamics through pump and treat may provide an adequate minimal approach. But, in most instances, methanogenesis as the "ultimate of no action alternatives" is not going to be practically applicable.

BIBLIOGRAPHY

1. Kun, J. (2004). *Practical Design Calculations for Groundwater and Soil Remediation*. CRC Press, Boca Raton, FL, p. 219.

2. Sloan, R. (2004). Slide: intrinsic biodegradation processes. In: *Aerobic and Anaerobic Bioremediation and Monitored Natural Attenuation of VOCs Short Course*. National Ground Water Association (NGWA) Conference on MTBE and Perchlorate, Costa Mesa, CA, June 3–4, p. 102.

BLACK MESA MONITORING PROGRAM

Bureau of Indian Affairs and Arizona Department of Water Resources—U.S. Geological Survey

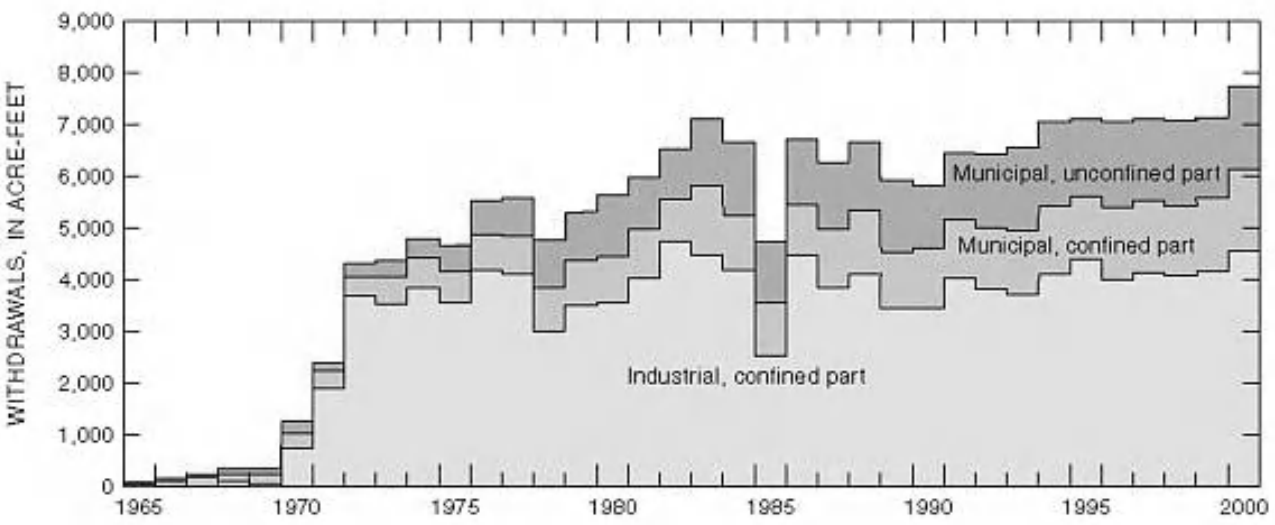
PROBLEM

The N aquifer is the major source of water for industrial and municipal users in the 5,400 square-mile Black Mesa area of northeastern Arizona. The aquifer consists of three rock formations-the Navajo Sandstone, Kayenta Formation, and Wingate Sandstone, which are hydraulically connected and function as a single aquifer.

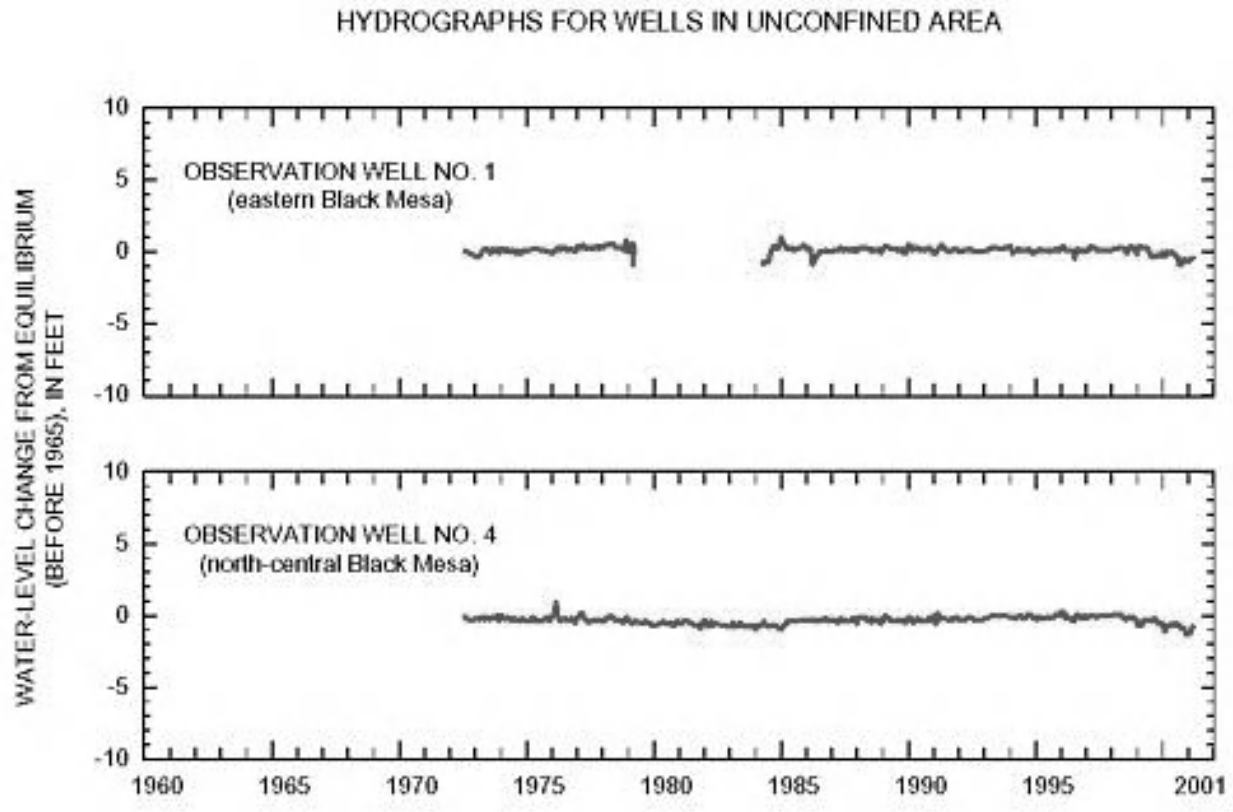
Annual withdrawals from the N aquifer for industrial and municipal use have increased from about 70 acre-ft in 1965, to 4,300 acre-ft in 1972, to 7,700 acre-ft in 2000. The Navajo Nation and Hopi Tribe live in the Black Mesa area, and they depend on ground water from the N aquifer to

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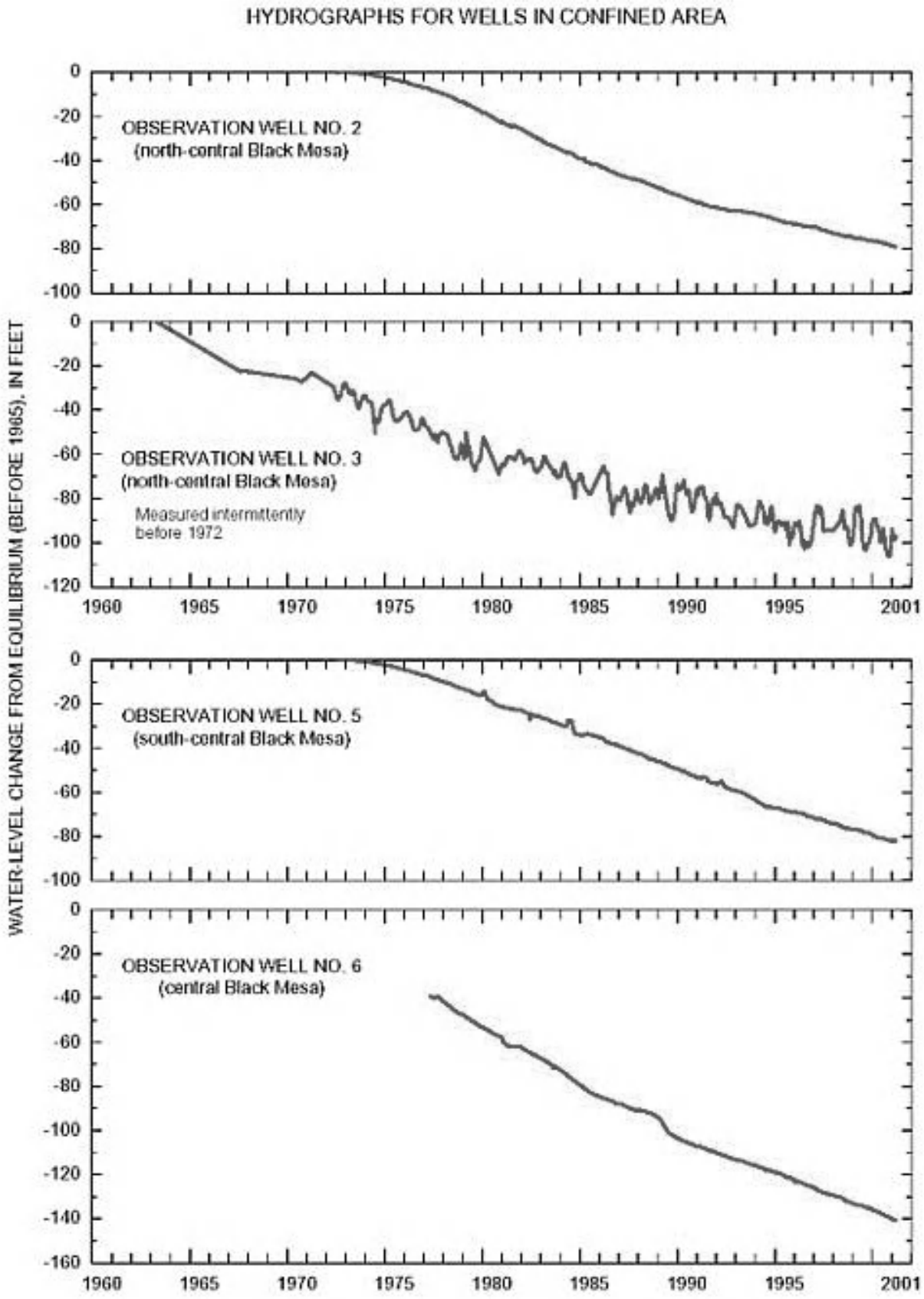


Withdrawals from the N aquifer, Black Mesa area, Arizona, 1965–2000.



meet municipal, domestic, livestock, and irrigation needs. In addition, the springs and streams fed by groundwater discharge are an important part of their culture. Peabody Western Coal Company began operating a strip mine in the northern part of Black Mesa in 1968. The company withdraws water from the N aquifer for a slurry pipeline to transport coal to a powerplant in Laughlin, Nevada. Withdrawals by the company accounted for about 70–80 percent of the total withdrawals in the early and mid 1970's and have been about 60 percent of the total withdrawals from 1978 to 2000.

The Navajo Nation and Hopi Tribe have been concerned about the effect of this increasing pumpage on long-term water supply, discharge in streams and springs,


HYDROGRAPHS FOR WELLS IN CONFINED AREA
WATER-LEVEL CHANGE FROM EQUILIBRIUM (BEFORE 1965), IN FEET
OBSERVATION WELL NO. 2
(north-central Black Mesa)
OBSERVATION WELL NO. 3
(north-central Black Mesa)
Measured intermittently
before 1972
OBSERVATION WELL NO. 5
(south-central Black Mesa)
OBSERVATION WELL NO. 6
(central Black Mesa)
0
-20
-40
-60
-80
-100
-120
-140
-160
1960
1965
1970
1975
1980
1985
1990
1995
2001

and quality of ground water. This concern led to the establishment of a long-term program in 1971 to monitor ground-water levels, ground-water discharge, ground-water quality, and surface-water discharge. From the 1960's to 2001, water levels in the N aquifer declined by over 50 feet in 9 of 19 long-term monitoring wells in confined areas. No large changes have been detected in ground-water levels in unconfined areas, ground-water discharge, ground-water quality, or surface-water discharge.

OBJECTIVE

To collect hydrologic data in a monitoring network that is designed to determine the long-term effects of industrial and municipal ground-water withdrawals on the N aquifer.

APPROACH

A long-term monitoring program has been established to collect hydrologic data in the Black Mesa area. Data are collected that describe the ground-water system, surface-water flow, and ground-water quality. Continuous measurements of ground-water levels have been made in six wells since 1972. Continuous data describing streamflow have been collected for 23 years in Moenkopi Wash, and for 3 to 6 years in three other streams. Once a year, ground-water levels are measured in about 26 wells, discharge is measured from 4 springs, and water-quality data are collected from 12 wells and 4 springs. Annual ground-water withdrawal data are collected from about 35 municipal well systems. Peabody Western Coal Company provides annual ground-water withdrawal data for industrial use.

These hydrologic data are entered into a computer data base. A report is prepared each year of the program. The report contains the data collected each year, and it shows comparisons of annual and long-term changes in ground-water levels, ground-water discharge, surface-water flow, and water quality. Long-term water-level changes in the six continuous-observation wells show that water levels in those confined areas have declined 80 to 140 feet and water levels in those unconfined areas have not changed.

RELEVANCE AND BENEFITS

The long-term available supply of water in the Black Mesa area is critical to many parties. The Hopi Tribe and Navajo Nation use water to meet their needs for public supply, irrigation, and livestock. In addition, sustained springflow and streamflow are important to their culture. Peabody Western Coal Company uses water to transport coal in a slurry pipeline to a powerplant. The hydrologic data collected in this monitoring program are needed to understand the available water supply and the effects of industrial and municipal ground-water withdrawals.

The U.S. Geological Survey has a commitment to provide data and information to Indian Tribes and other Interior Department Agencies. The Office of Surface Mining of the Interior Department uses the data from this program to facilitate their oversight and regulation of the coal mining operations of Peabody Western Coal Company.

The long-term ground-water, surface-water, and water-quality data collected for this program provides an important opportunity to investigate and gain a better understanding of a hydrologic system of bedrock geology in an arid climate in which there are many competing water-use interests.

BRINE DEPOSITS

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INTRODUCTION

Brines are warm to hot, saturated to nearly saturated, highly saline, ocean and lake waters, containing Ca, Na, K, and Cl and minor amounts of other elements, typical of pore fluids in restricted basins. From an oceanographic perspective, brine is seawater that, due to high evaporation rates or freezing, contains more than the usual amount of dissolved salts, typically about 35%. A brine lake is essentially a salt lake. Brine lakes, like the Dead Sea, the Great Salt Lake in Utah, the Mono Lake region in northern California, and the Salton Sea region in southern California, develop as a result of high evaporation rates in an arid desert that lacks an outlet to the ocean (Fig. 1). The salt is derived from either minerals washed out of the surrounding watershed or from a geological deposit or area previously connected to the ocean.

A brine cell or pocket is a small inclusion usually the shape of an elongated tube about 0.05 mm in diameter that contains residual liquid more saline than seawater. A brine pit is a salt well or opening at the mouth of a salt



Figure 1. Mono Lake, a terminal brine lake situated in northeastern California. Tufa occurs at saline lakes worldwide, but not in the abundance and variety in shape as at Mono Lake. Mono brine shrimp are unique to this lake.

spring, from which water is taken to be evaporated for making salt.

Brines also occur in the subsurface notably as subsurface oil-field waters and geothermal mineralizing fluids. Subsurface brines in sandstone and other porous rocks are largely regarded as connate or buried seawater. Some brines also form locally by solution of rock salt beds.

SEAWATER BRINES

Seawater is relatively complex, but also relatively concentrated (1). Its principal ions are Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^- and SO_4^{2-}. Minor constituents include the elements Br, Sr, F, Ar, Li, Rb, I, Al, Fe, Zn, and Mo. Variable minor constituents include C, N, O, Si, P, and Ba. Seawater brines become more concentrated by evaporation, and in this process, deviation from ideal chemical behavior is greater (2). Microscopic cavities in such minerals as halite contain trapped brines representative of ancient seawater. Due to the protection of the brine provided by the halite crystal, such water has not undergone any significant chemical changes. The ionic ratios in these trapped brines are similar in composition to evaporating modern seawater.

Three properties of seawater and its brines predominant in evaporate production are concentration, density, and vapor pressure. Total salts are commonly stated in salinity, reflecting the resulting concentration from evaporation. The evaporation rate, however, indicates how much brine has undergone concentration via evaporation. Brine density is most important in its control of the circulation pattern in evaporate basins. The density of brines derived from seawater rises sharply from the 1.03 g/cm^3 of normal seawater to 1.29 g/cm^3 at the beginning of halite deposition. Vapor pressure is also important in its control of the rate of evaporation. Other properties include heat capacity, light transparency, and viscosity. Brines have substantially lower heat capacity, slightly lower thermal conductivity, and are less transparent to light than seawater.

BRINE OCCURRENCES

Geologically, brines are generated in a variety of environments and under varying sedimentary processes (2). Two main types of evaporate deposits are recognized: capillary evaporites and open-water evaporites (3). Capillary evaporites precipitate from interstitial brines that have a preexisting sedimentary layer. They contain remains of the host sediment, so capillary evaporites are always more or less dirty. Open-water evaporites precipitate from exposed water bodies. The detrital fraction, which is often eolian derived, makes up a small portion of these salt layers, so open-water evaporites are generally very clean.

The primary depositional settings are (1) coastal intertidal and supratidal zones called sabkhas, (2) small lagoons on coasts and atolls, (3) large deep-water marine basins, (4) sub-sea-level basins with inflow of marine water, and (5) nonmarine interior basins. Tectonically, these deposits occur along continental margins and shelves, interior shallow and deep cratonic basins, and rifted continental margins.

Brine deposits are typically extremely localized and reflect their unique conditions of formation. Brine deposits including salt are derived from four primary sources: seawater, sedimentary bedded deposits, surface playa deposits, and salt domes. Such areas and conditions include deserts of the southwestern United States, High Andean salares, Middle Eastern sabkhas, the East African Rift Valley, and subsurface Permo-Triassic deposits.

Recent studies have discovered brine pools on the seafloor within the Gulf of Mexico. These deposits are characterized by a distinct surface and shoreline. The pools are derived from the Luann Salt Layer and form in crater-like depressions that contain very concentrated brines and methane. These pools also support dense peripheral mussel beds.

Extensive evidence also exists that brines commonly form deep along midocean ridge hydrothermal systems. Such occurrences result from heating of sea-water-derived hydrothermal fluids at supercritical conditions, although it is not clearly understood how these brines are stored in the crust. One widely accepted model is the development of dense brines formed by formation of a two-layer system, whereas a recirculating brine layer underlies a single-phase seawater cell. If the temperature of the seawater cell remains high enough for substantial supercritical two-phase separation, the brine layer will grow. Should temperatures drop into the single-range region, the brine layer erodes.

Brines have also been recently discovered on other planets within our solar system. A growing body of evidence indicates that an ocean exists but is hidden beneath the icy crust of Jupiter's moon, Europa. Hydrated salts are indicated by spectral evidence and thermal evolution models of Europa's interior and laboratory studies of meteorites. The hydrated mineral deposits may reflect exposure of salty ocean water to the surface. On Mars, evaporate deposits may represent significant sinks of mobile anions and cations among the materials composing the Martian surface and upper crust. The nature of evaporate-precursor brines formed under Martian conditions is poorly understood at this time. Salts depress the freezing point of water significantly, so the presence of salts in the Martian soil could explain why water might be flowing in very high latitudes.

EVAPORITE MINERALOGY AND THE CONCEPT OF FACIES

Brines fall into three main types based on the predominating acid radical: chloride brines, sulfate brines, and alkali or volcanic brines. They include bitterns (natural brines) with other chlorides, bromides, iodides, and sulfates. The metallic ions in greatest abundance are sodium, magnesium, calcium, and potassium. Chloride type brines include many terrestrial brines as well as seawater. Terrestrial brines that contain chloride in excess of sodium are comparatively rare. Chloride type brines contain a higher proportion of sulfate than seawater. Seawater is an impure solution of sodium chloride and contains enough chloride to combine with all the sodium (the most abundant metallic

ion) and part of the magnesium (the second most abundant metallic ion). The transition from chloride to sulfate type brines is gradational, whereby sulfate is the predominate acid radical. Alkali brines contain carbonate, sulfate, and borate; chloride is present in subordinate amounts.

Based on provenance, brines can be divided into marine brines that are concentrated from ocean water, continental brines concentrated from groundwater, and formation waters circulating in deeper bedrock horizons.

Evaporites are sedimentary deposits composed of minerals that have precipitated from brines concentrated during evaporation. These deposits are products of waters of inland desert basins, as well as interstitial waters of sediments located along ocean margins. Evaporites also occur from replacement of rocks that are not evaporites by evaporate minerals (4). Sedimentary processes vary significantly. Source fluids for evaporate precipitation can be classified by the degree of solute concentration of undersaturated brines. The three types distinguished include waters of low salinity or hypohaline waters, intermediate salinity or mesohaline waters, and high salinity or hypersaline brines.

Evaporites have a distinct and characteristic mineralogy. In the study of their geochemistry, origin, and geologic setting, mineralogy is the most important characteristic (2). Critical minerals derived from the evaporation of seawater are summarized in Table 1, along with the general facies sequence for marine evaporites. Facies in geological terms characterizes the critical variations or stages in the mineralogy of evaporite rocks during brine evaporation. Facies in this context essentially represent subdivisions of the evaporate process, recognizable through the appearance of new albeit critical minerals, regardless of proportion. For example, the mere presence of halite would characterize the assemblage as within the halite facies. The appearance of a potash-magnesia, halite, calcium sulfate, or calcium carbonate mineral is part of natural crystallization which occurs as water is removed during evaporation. This process is dependent on a balance between the proportions of various components in seawater and the corresponding mineral solubility in the brine. An extensive listing of the most common evaporate minerals is presented by Braitsch (5) and Sonnenfeld and Perthuisot (3).

Structurally, evaporates occur in two widely different structural forms: beds or lenses, and as salt structures which includes such features as bosses, plugs, ridges, and domes. Lenses and bed type deposits, such as the great Permian Basin, extend throughout parts of Kansas, Colorado, Oklahoma, Texas, and New Mexico. Nonbedded structures are common along or near the Gulf of Mexico. Bedded salt deposits vary in thickness but are typically of the order of 15 to 45 feet. The thickness of salt domes or diapirs remains uncertain.

BRINE RESOURCES

Known resources of evaporate and brine resources in the United States range from 100 years for potassium compound and iodine production, to unlimited, reflecting seawater as a source. The birthplace of subsurface brine production was in the Michigan Basin, an intracratonic basin that hosts thick successions of carbonates and evaporate-bearing strata.

Natural subsurface brines are the feedstock for a wide variety of industrial minerals and chemicals. For example, bromide is produced in Arkansas from the Upper Jurassic Smackover Formation, magnesium chloride and bromide are produced from the Devonian Detroit River Group in Michigan; lithium carbonate is produced in Chile and California from aquifers beneath playas and salares; iodide is produced from the Lower Pennsylvanian Morrow Formation in Oklahoma and coproduced in Japanese natural gas wells; and calcium chloride is produced near Slave Lake, Drumheller, and Brooks, Alberta.

Table 1. Summary of Evaporite Facies[a]

Facies	Subfacies	Mineralogy	Salinity, wt. %	Density, g/cm^3	Fraction Evaporated, wt. % H_2O	Concentration × Seawater, wt H_2O	Concentration × Seawater, Vol. of Brines
	Bittern subfacies	Bischoffite, tachyhydrite			99.2	120	
Potash-magnesia (supersaline)	Potash subfacies	Carnallite, sylvite, kainite, kieserite, halite, anhydrite or polyhalite	380	1.31	98.7	75	78.0
	$MgSO_4$ subfacies	Epsomite, bloedite, halite, polyhalite or anhydrite	375	1.29	98.4	65	68.0
Halite facies		Halite, anhydrite or gypsum	300	1.20	91.0	11.5	12.2
$CaSO_4$ facies		Gypsum or anhydrite, dolomite	150	1.10	72.0	3.5	3.6
Dolomite facies		Dolomite, calcite	35	1.02	0	1.0	1.0
$CaCO_3$ facies							
	(normal marine)	Calcite, aragonite	10	1.01	—		
	(brackish)		1	1.00	—		
	(terrestrial)		0	1.00	—		

[a] Modified after Reference 2.

BRINE PRODUCTION

Brines are extracted via several means, including underground mining, solar evaporation, and solution mining and mechanical evaporation. Underground halite deposits are conventionally mined by drilling and blasting. Vertical shafts are about 20 feet in diameter and extend to depths of 500 to more than 2000 feet below ground into the salt deposit. In the United States, 70% of the salt produced is extracted from natural or synthetic brines or seawater; the remaining is mined as a solid.

Products developed from brines include specialized industrial minerals used in the chemical industry for the manufacture of glass, fertilizers, pharmaceuticals, and batteries (6). Specialized industrial minerals produced include soda ash, potash, borax and boric acid, potassium chloride and sulfate, lithium, and nitrate and iodine. Salt produced from brine, and a small amount of dry salt, is used to produce chemicals such as chlorine gas and caustic soda (sodium hydroxide), among others. Deep unused brine-bearing aquifers are also used for to reduce greenhouse gas emissions via subsurface injection.

BIBLIOGRAPHY

1. Goldberg. (1965).
2. Holzer, W.T. (1979). Mineralogy of evaporites. In: *Mineralogical Society of America Short Course Notes*, *Marine Minerals*. Vol. 6, pp. 211–294.
3. Sonnenfeld, P. and Perthuisot, J.P. (1989). *Brines and Evaporites*. American Geophysical Union, Short Course in Geology, Vol. 3.
4. Friedman, G.M. (1978). Depositional environments of evaporite deposits. In: *Marine Evaporites*. Society of Economic Paleontologists and Mineralogists (SEPM) Short Course No. 4, W.E. Dean and B.C. Schreiber (Eds.). pp. 177–184.
5. Braitsch, O. (1971). *Salt Deposits Their Origin and Composition*. Springer-Verlag, New York.
6. Jensen, M.L. and Bateman, A.M. (1979). *Economic Mineral Deposits*, 3rd Edn. John Wiley & Sons, New York, pp. 553–562.

CONNATE WATER

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CHEMISTRY

Because of its long contact with rock material, connate water can change in chemical composition throughout the history of the rock and become highly mineralized (see Table 1). Connate water can be dense and saline compared with seawater; connate water salinities can range from 20 to more than 300 grams per liter. For comparison, seawater salinity is approximately 35 grams per liter total dissolved solids (1).

AGE

Some of the oldest connate water may stay beneath the land surface for millions of years, which is in contrast to the age of groundwater, which ranges from a few years or less to tens of thousands of years. Because of its long underground residence, connate water may move long distances, even though its velocity may be very low (3).

Table 1. Geochemical Composition of Connate Water Compared to Aquifer Water[a]

Chemical Component	Connate, mg/l	Aquifer, mg/l
Na^+	65,000	2,600
K^+	500	64
Mg^{2+}	28,000	210
Ca^{2+}	165,000	430
Ba^{2+}	0.1	0.1
Sr^{2+}	1,300	6.5
Fe^{2+}	0.1	0.1
Cl^-	138,360	5,100
Br^-	10	10
SO_4^{2-}	260	1,900
HCO_3	100	150
Organics	55	5
pH	5.8	7.65

[a]Ref. 2.

OIL RESERVOIR MONITORING

Crude oil is always produced with connate water, and the water-to-oil ratio is often greater than 10 to 1; therefore, the oil and gas exploration industry extensively monitors connate water (4). Connate water tends to rise toward the surface during oil and gas extraction, so resistivity logs track connate water movement to recognize and mitigate coning problems associated with excessive production yields (5). Distinguishing the difference between connate water and other types of underground water (e.g., meteoric water) through water analyses can aid in both oil and gas exploration. Variations in fluid composition can help to delimit reservoir boundaries and reveal the connectivity of different strata. Saline waters are generally more favorable for locating petroleum reservoirs. If the trapped fluid is saline, then there is less chance that any associated petroleum has been degraded by contact with meteoric water or flushed from the reservoir (1).

BIBLIOGRAPHY

1. Robin, R. (2001). *Oilfield Water Notes.* University of Saskatchewan. Available: http://www.usask.ca/geology/classes/geol463/46304.pdf.
2. Kane, R.D. (2000). InterCorr International, Inc. *Use of Portable Monitoring Units to Assess Microbial Activity, Corrosion and Souring in Water Handling and Injection Systems.* Available: http://www.corrosionsource.com/CS2000/session01/paper0107/paper0107.htm.
3. Bouwer, H. (1978). *Groundwater Hydrology*. McGraw-Hill, New York, p. 7.
4. IPEC. (2001). Integrated Petroleum Environmental Consortium. *Locating Oil-Water Interfaces In Process Vessels.* Available: http://ipec.utulsa.edu/Ipec/lopresti_abs.html.

5. JPT. (2002). Journal of Petroleum Hydrology. *Technology Update*. Available: http://www.spe.org/spe/cda/views/jpt/jptMaster/0,1513,1648_2300_5376_3,00.html.

CONSOLIDATED WATER BEARING ROCKS

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INTRODUCTION

Consolidated rocks (otherwise known as bedrock) consist of rock and mineral particles of different sizes and shapes that have been welded together by heat and pressure or chemical reaction into a rock mass. Aquifers of this type are commonly composed of one or more of the following rocks: sandstone, limestone, granite, or lava. Water flows through these rocks through fractures, gas pores, and other openings in the rock.

CONSOLIDATED ROCKS

Consolidated rocks are usually classified according to their origin. There are three types: sedimentary, igneous, and metamorphic.

SEDIMENTARY ROCKS

Sedimentary rock is formed by the deposition of material suspended in water; the material may have been material weathered from older rocks, plant or animal remains, or precipitated chemicals. Important types of sedimentary rock aquifers include sandstone, carbonate rock, and conglomerate.

Sandstone

Sandstone is a cemented form of sand and gravel; the sand grains are cemented together when dissolved silica and calcium contained in the pore fluid precipitate. Sandstone shows great variation in water yielding capacity which is controlled chiefly by its texture and the nature of the cementing materials. Thus, whereas coarse-grained sandstone with rather imperfect cement may prove excellent aquifers, fine-grained varieties, especially those that are thoroughly cemented, may be the worst types from which no yield of water is possible (1).

Carbonate Rocks

Carbonate formations include limestone ($CaCO_3$) and dolomite (a mixture of $CaCO_3$ and $MgCO_3$). These deposits exhibit mostly secondary porosity due to fracturing and dissolution openings because $CaCO_3$ is soluble in rainwater. Limestones vary widely in density, porosity, and permeability, depending on the degree of consolidation and development of permeable zones after deposition. Openings in limestone may range from microscopic original pores to large solution caverns forming subterranean channels sufficiently large to carry the entire flow of a stream (2). Large springs are frequently found in limestone areas.

The dissolution of calcium carbonate by water causes prevailingly hard groundwater in limestone aquifers; by dissolving the rock, water, also tends to increase the pore space and permeability with time. Solution development of limestone forms a karst terrane, characterized by solution channels, closed depressions, subterranean drainage through sinkholes, and caves. Such regions normally contain large quantities of groundwater (3). Major limestone aquifers occur in the southeastern United States and in the Mediterranean area (4,5).

Conglomerates

Conglomerates like sandstone are cemented forms of sand gravel. As such, their porosity and yield have been reduced by the cement. Conglomerates have limited distribution and are unimportant as aquifers (6).

IGNEOUS ROCKS

Igneous rocks are formed from the cooling and solidification of molten magma originating in the earth's core. Important consolidated rock aquifers include basalts.

The important points in this context are as follows:

1. Basalts rocks are often vesicular. Vesicles, in them are of considerable size and number, and if they are interconnected (by fracture), they can serve as aquifers.
2. Contraction joints (like columnar joints) and other fractures, if present, also contribute to the porosity and permeability of basalts.
3. Basalts originate as lava flows, so sometimes, they may overlie buried valleys that offer good groundwater potential.

The Columbia River Plateau covering eastern Washington and Oregon, and Idaho, averages about 500 m in thickness and is one of the largest basalt deposits in the world. Basalt aquifers are critically important water sources for the Hawaiian Islands. Most of the largest springs in the United States are associated with basalt deposits.

Rhyolites are less permeable than basalt. Granites have very low porosity and permeability; what little exists is primarily due to fracturing. Although not important as aquifers, these materials are candidates for the host rock for high-level radioactive waste.

METAMORPHIC ROCKS

These are sedimentary or igneous rocks that have been altered by heat or pressure. They generally form poor aquifers.

BIBLIOGRAPHY

1. Singh, P. (1978). *Engineering and General Geology*. Katson, Ludhiana.

2. Brucker, R.W. et al. (1972). Role of vertical shafts in the movement of groundwater in carbonate aquifers. *Ground Water* **10**(6): 5–13.
3. LeBrand, H.E. and Stringfield, V.T. (1973). Karst hydrology—a review. *J. Hydrology* **20**: 97–120.
4. Burdon, D.J. and Papakis, N. (1963). *Handbook of Karst Hydrogeology with Special Reference to the Carbonate Aquifers of the Mediterranean Region*. Inst. Geology and Subsfc. Research, United Nations Spec. Fund, Karst Groundwater Inv., Athens.
5. LaMoreaux, P.E. et al. (1970). *Hydrology of Limestone Terranes, Annotated Bibliography of Carbonate Rocks*. Geological Survey of Alabama Bull. 94(A), Alabama.
6. Todd, D.K. (1995). *Ground Water Hydrology*. Wiley, Toronto, Canada, p. 51.

SENSITIVITY OF GROUNDWATER TO CONTAMINATION

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For this discussion, groundwater sensitivity is defined as *the likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the specified position* (1,2). Sensitivity is a widely applied concept that has several uses. Sensitivity analyses often lead to the development of maps showing the relative sensitivity of groundwater across a geographic area. These maps are used as a screening tool for land-use decisions and have increasingly been used in source water protection. Sensitivity analyses are also used in program development, such as identifying areas where groundwater monitoring will occur. The concept of groundwater sensitivity also has educational value because hydrogeologic concepts are easily expressed and the audience can visualize relationships between land use and aquifer protection.

WHAT MAKES AN AQUIFER SENSITIVE TO CONTAMINATION?

Groundwater sensitivity applies to a variety of situations; each requires a different level of analysis. Sensitivity, vulnerability, and susceptibility, which are often defined differently, are used interchangeably in this discussion. The simplest scenario involves transport of a conservative contaminant in water from the land surface to groundwater. This scenario can be modified to consider land use, account for attenuation or retardation of contaminants, consider a point below the top of the saturated zone, or consider risk to human or ecological receptors at some point within an aquifer.

Under the scenario where a conservative contaminant is transported from the land surface to groundwater, factors that affect sensitivity include the permeability of geologic materials, the thickness of the unsaturated zone, and recharge. Highly permeable geologic materials transmit water quickly and thus increase sensitivity (see HYDRAULIC CONDUCTIVITY/TRANSMISSIBILITY). In heterogeneous deposits, the geologic material that has the lowest permeability typically has the greatest effect on the rate of water movement, provided the geologic material is sufficiently thick, laterally continuous, and does not have extensive macroporosity. As the thickness of the unsaturated zone increases, sensitivity decreases because water can be stored and has a farther distance to travel. Sensitivity increases as the quantity of recharge increases because contaminants are transported by recharge water. Recharge is often computed from a water budget by subtracting evaporation from precipitation and assuming no runoff or soil storage.

Even in sensitive hydrogeologic settings, groundwater will not become contaminated unless there is a source of contamination. We can generalize about how groundwater quality will be affected by land use (see LAND USE IMPACTS ON GROUNDWATER QUALITY). Agriculture can contribute significant quantities of nitrates and pesticides to an aquifer, nonsewered residential areas can contribute large quantities of nitrates and chlorides (3), and industrial and older sewered residential areas can contribute large quantities of volatile organic chemicals (VOCs), chlorides, and some metals such as manganese. Within each of these land uses, specific management practices further affect contaminant volumes. Several studies show direct, although not necessarily linear relationships, between the quantity of chemical applied at or near the land surface and concentrations in sensitive aquifers. Thus, for example, groundwater is more sensitive in areas that use greater fertilizer application rates.

Nearly all contaminants attenuate to some extent within the unsaturated zone. The extent and rate of attenuation depend on the properties of the contaminant and on the chemical, physical, and biological properties of the geologic materials (Table 1). These properties are too numerous to discuss individually, but adsorption and degradation are the two primary attenuation processes that affect contaminants. Contaminants that are not readily adsorbed percolate to groundwater and result in increased sensitivity. Except in highly weathered, acidic soils, these are chemicals that have a negative charge, such as chloride, nitrate, and acid herbicides (2,4-D, Dicamba). Contaminants that are quickly degraded biologically or chemically represent a lower risk to groundwater than more persistent contaminants. In addition to the properties of a chemical, degradation is affected by factors such as temperature, the presence of oxygen, and pH. For example, most halogenated contaminants are persistent except under reducing conditions, nitrate is persistent in the presence of oxygen, and benzene is persistent in the absence of oxygen.

We are often interested in the sensitivity at some point below the top of the saturated zone, such as at a well. In addition to having a greater distance to travel, a contaminant may be affected by geochemical changes within the saturated zone. Trojan et al. (4), for example, showed that in the glacial aquifers of Minnesota, nitrate was quickly attenuated in the upper few meters of groundwater, even though these aquifers were mapped

Table 1. Characteristics of Different Classes of Contaminants. This Information is Generalized and Varies within Each Contaminant Class and Between Different Geologic Deposits and Hydrologic Environments

Contaminant Class	Examples	Adsorption	Persistence	Toxicity
Halogenated organics with one or more benzene rings	PCBs, dioxins, many pesticides, chlorobenzenes	High, increases with greater extent of halogenation	High, increases with greater extent of halogenation	High, increases with greater extent of halogenation
Polyhalogenated aliphatics	Industrial solvents (TCE, PCE), some pesticides	Low, increases with greater extent of halogenation	Moderate, increases with greater extent of halogenation	Moderate, increases with greater extent of halogenation
Nonhalogenated polynuclear aromatics	Pyrene, benzo(a)pyrene	Moderate but increases rapidly with increasing molecular weight	Moderate but increases rapidly with increasing molecular weight	Moderate but increases rapidly with increasing molecular weight
Other nonhalogenated aromatics	Benzene, toluene	Low	Low to high, depending on geochemical environment	Low except for some chemicals, such as benzene
Nonhalogenated aliphatics	Oil, alkanes,	Moderate to high	Low to high, depending on geochemical environment	Low
Metals	Lead, copper	Moderate to high	High	Moderate to high
Nonmetals	Arsenic, boron	Moderate but varies widely	High	Moderate to high
Anions	Chloride, nitrate	Low	High	Low
Radionuclides	Cesium-137, radon-222	High	High	High

as sensitive to contamination. In this case, denitrification was the most likely cause for disappearance of the nitrate. In other scenarios, contaminants may be adsorbed within an aquifer.

Few sensitivity methods consider the risk to receptors. Risk analysis does not consider whether a chemical will reach groundwater but whether it will pose a risk to receptors. Risk is a function of dose and toxicity. Thus, consumption of 1,1,2-trichloroethene (TCE) at a concentration of 5 μg/L poses a greater risk than consumption at 1 μg/L; consumption of TCE at 5 μg/L [maximum contaminant level (MCL) = 5 μg/L] poses a greater risk than consumption of xylene at 5000 μg/L (MCL = 10,000 μg/L). Because we have to consider specific exposure points (e.g., a well), the quantity of contaminant being transported, and the contaminant toxicity, estimates of sensitivity based on risk can be very complicated.

Table 2 provides a summary of factors that affect groundwater sensitivity to contamination. Figure 1 provides a schematic showing how different factors affect sensitivity. Figure 2 shows how sensitivity varies when different receptor points or contaminants are considered.

METHODS FOR ASSESSING SENSITIVITY

The Commission on Geosciences, Environment, and Resources (2) provides an excellent discussion of methods for assessing sensitivity. The most commonly employed methods are overlay and index methods. These involve combining various physical properties of the hydrogeologic system. Each property is assigned a score or other sensitivity value based on perceived sensitivity. Overlay and index methods use many of the factors in Table 2. DRASTIC (5) is a widely employed index and overlay method that uses seven factors in the sensitivity assessment. Overlay and index methods can be relatively simple and may require small amounts of information. Sensitivity analyses using these methods often result in plan view maps depicting relative groundwater sensitivity, usually through a color-coded scheme. These maps are useful interpretive and screening tools. The scale of these maps is usually not appropriate for site-specific decisions, although they have been used for this purpose.

Analytic or numeric methods predict the time it takes contaminants to reach groundwater. These methods typically consist of mathematical models. Attenuation of chemicals is often considered. Examples include PRZM (6), GLEAMS (7), and LEACHM (8). An advantage of analytic and numeric methods is that they quantify the processes that affect the movement of water and contaminant. The accuracy of these methods depends on the quality of data used in the model.

Statistical methods use statistical techniques, such as regression analysis, to predict the likelihood of contamination. These methods require data on contaminant concentrations and may require additional information to derive sensitivity estimates. For example, concentrations of nitrate may be correlated with depth to water and sand content in the vadose zone. Because they use actual data, statistical methods can provide accurate estimates of sensitivity, information on variability in a sensitivity analysis, and estimates of certainty. They are, however, data intensive.

LIMITATIONS OF THE SENSITIVITY CONCEPT

In 1993, the Commission on Geosciences, Environment, and Resources prepared a report on ground water vulnerability assessments (2). The Commission, "in struggling with the manifold technical and practical difficulties

Table 2. Summary of Factors that Affect Groundwater Sensitivity

Property	Effect on Sensitivity	Low Sensitivity	High Sensitivity
		Hydrologic Factors	
Aquifer material	Rate at which water moves within an aquifer	Shale, most hard rocks, clay, silt	Limestone, sandstone, sand, gravel
Depth to bedrock	Distance that water must travel to reach groundwater	Large distances (>50 feet)	Short distances (<10 feet)
Depth to water	Distance that water must travel to reach groundwater	Large distances (>50 feet)	Short distances (<10 feet)
Recharge	Amount of water reaching groundwater	Small quantities (<1 inch)	Large quantities (>10 inches)
Soil material	Rate at which water moves to or within groundwater	Clay, silt, organic soils	Sand, gravel
Thickness of confining layers	Rate at which water moves to or within groundwater	Large thickness (>20 feet)	Small thickness (<5 feet)
Topography	Amount of water reaching groundwater	Upland areas where water runs off	Lowland areas where water accumulates
Type of bedrock	Rate at which water moves to or within groundwater	Unfractured shale and hard rocks	Limestone, sandstone, fractured rock
		Other Factors	
Soil/aquifer material	Attenuation of chemical	High organic or clay content	Low organic or clay content
Contaminant	Persistence, mobility, toxicity	Rapidly degraded, low mobility, low toxicity	Persistent, highly mobile, highly toxic
Land use	Amount and type of chemical released	Low chemical inputs (forest, grassland)	Large chemical input (row crop agriculture, nonsewered communities)

affecting the performance of vulnerability assessments today, nearly concluded that their limitations are so great as to be of no use in management decision-making." Though the concept of sensitivity is applicable to land-use decisions, program development, or education, there are two important concerns over their use.

First, the analyses and resulting products, usually maps, are only as good as the data that go into them. Sensitivity analyses generally do not result in collection of new data and rely instead on existing information. Geologic maps, soil maps, and climate data are often available, but values for depth to water and hydraulic conductivity may be difficult to find. Data become more limiting when factors such as specific contaminants, land use, and risk are considered.

Second, maps or other products developed from sensitivity analyses can be misused. Many people who make land-use decisions rely on these maps. They often assume that sensitive areas will become contaminated and less sensitive areas will not, and they are often not aware of the way the maps were developed. Examples of misuse include

- using a 1:100,000 sensitivity map to site a landfill;
- assuming that all areas mapped as sensitive have equal sensitivity;
- assuming that the same data were available throughout a mapped area; and
- using a sensitivity analysis based on a conservative tracer to predict sensitivity to contamination with pesticides.

Researchers have increasingly modified existing methods to provide better tools to local users of sensitivity maps. Rupert (9) improved the effectiveness of a modified DRASTIC ground water vulnerability map by calibrating the point rating schemes to actual groundwater quality data by using nonparametric statistical techniques and a geographic information system. Snyder et al. (10) used a particle tracking model in conjunction with DRASTIC to evaluate groundwater vulnerability. Erwin and Tesoriero (11) related the occurrence of elevated nitrate concentrations in samples from public supply wells to natural factors to assess aquifer susceptibility using logistic regression. Holtschlag and Luukkonen (12) used a vulnerability model that incorporated several contaminant properties to predict atrazine leaching. Although researchers have generally focused on improving the accuracy of sensitivity estimates, the problems discussed before can also be overcome by improving data accessibility, providing information about the reliability

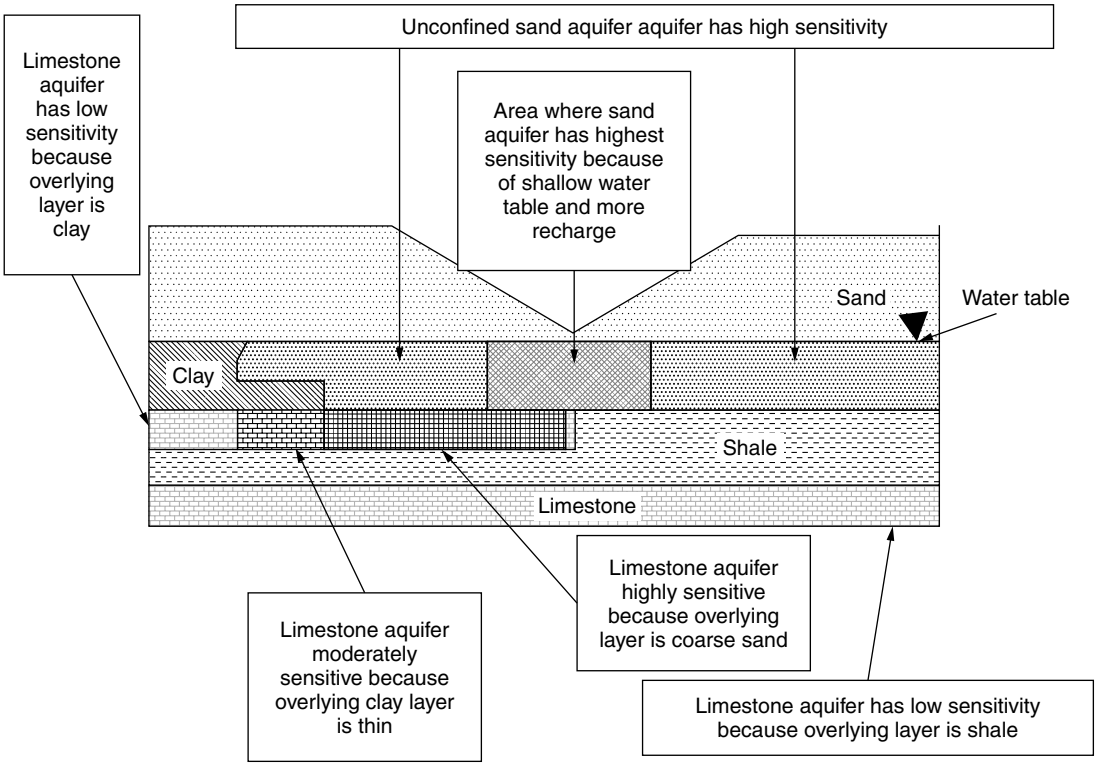


Figure 1. Schematic representation of geologic factors that affect groundwater sensitivity.

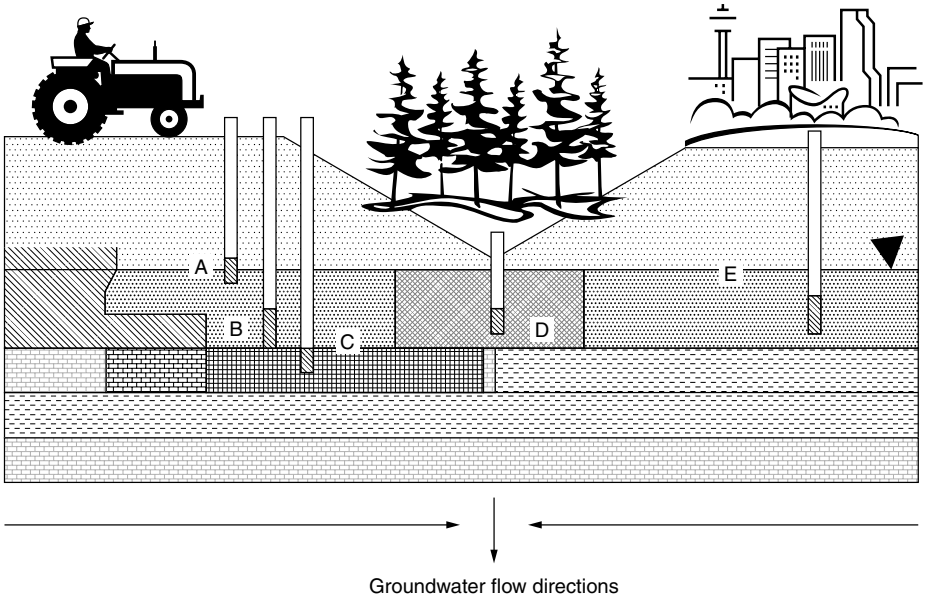


Figure 2. Schematic illustrating how a variety of factors affect groundwater sensitivity. Considering transport of a conservative chemical, the groundwater is considered sensitive at each of five well locations (A, B, C, D, E). At location A, the aquifer is most sensitive because the well is screened at the water table. The chemicals of concern are nitrate and pesticides from agriculture. At location B, the well may be less sensitive than at A because contaminants can be degraded or adsorbed within the aquifer. The chemicals of concern are nitrate and pesticides from agriculture. At location C, the well may be less sensitive than at B if the contaminant is degraded or adsorbed, but if the aquifer is fractured, sensitivity may be greater than at B. The chemicals of concern are nitrate and pesticides from agriculture. At location D, the well may be less sensitive than at all other well locations because the overlying land use does not contribute contaminants. Contaminants introduced at other locations may be degraded or adsorbed before reaching the well. At location E, sensitivity is similar to that at B but the contaminants of concern are VOCs and trace elements from commercial, industrial, and residential land use.

of data, providing estimates of variability or uncertainty, and training users.

SUMMARY

Understanding groundwater sensitivity and identifying areas where groundwater is sensitive to contamination is a potentially useful tool for managers, planners, and educators. Sensitivity analyses often lead to the production of maps showing relative sensitivity across a geographic area. Despite a potential for misuse, researchers have increasingly focused on improving the accuracy of these maps, including calibration, for local applications.

BIBLIOGRAPHY

1. United States Environmental Protection Agency. (1993). *A Review of Methods for Assessing Aquifer Sensitivity and Ground Water Vulnerability to Pesticide Contamination*. US EPA, Washington, DC.
2. Commission on Geosciences, Environment and Resources. (1993). *Ground Water Vulnerability Assessment: Predicting Relative Contamination Potential Under Conditions of Uncertainty*. National Academy Press, Washington, DC.
3. Trojan, M.D., Maloney, J.S., Stockinger, J.M., Eid, E.P., and Lahtinen, M.J. (2003). Effects of land use on ground water quality in the anoka sand plain aquifer of minnesota. *Ground Water*. **41**(4): 482–492.
4. Trojan, M.D., Campion, M.E., Maloney, J.S., Stockinger, J.M., and Eid, E.P. (2002). Estimating aquifer sensitivity to nitrate contamination using geochemical information. *Ground Water Monitoring and Remediation* **22**(4): 100–108.
5. Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., and Hackett, G. (1987). *Drastic: A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings*. EPA-600/2-87-035. US EPA, Ada, OK.
6. Carsel, R.F., Smith, C.N., Mulkey, L.A., Dean, J.D., and Jowise, P. (1984). *User's Manual for the Pesticide Root Zone Model (PRZM): Release 1*. US EPA, Environmental Research Laboratory, Athens, GA.
7. Knisel, W.G., Leonard, R.A., and Davis, F.M. (1989). *GLEAMS User Manual. Southeast Watershed Research Laboratory*. Tifton, GA.
8. Wagenet, R.J. and Hutson, J.L. (1987). *LEACHM: A Finite-Difference Model for Simulating Water, Salt, and Pesticide Movement in the Plant Root Zone, Continuum 2*. New York State Resources Council, Cornell University, Ithaca, NY.
9. Rupert, M.G. (2001). Calibration of the drastic ground water vulnerability mapping method. *Ground Water* **39**(4): 625–630.
10. Snyder, D.T., Wilkinson, J.M., and Orzol, L.L. (1997). Use of A Ground-Water Flow Model With Particle Tracking to Evaluate Ground-Water Vulnerability, Clark County, Washington. USGS Water-Supply Paper 2488.
11. Erwin, M.L. and Tesoriero, A.J. (1997). *Predicting Ground-Water Vulnerability to Nitrate in the Puget Sound Basin*. USGS Fact Sheet FS-061-97.
12. Holtschlag, D.J. and Luukkonen, C.L. (1998). *Assessment of Ground-Water Vulnerability to Atrazine Leaching in Kent County, Michigan: Review, Comparison to Results of Other Studies, and Verification*. USGS Water-Resources Investigations Report 98–4006.

WATER CONTAMINATION BY LOW LEVEL ORGANIC WASTE COMPOUNDS IN THE HYDROLOGIC SYSTEM

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Laboratory methods have improved dramatically during the past decade with much lower detection levels enabling some interesting results of human impact on the condition of the hydrologic system. Low levels of organic contaminants are present in surface and groundwaters throughout the nation. Methyl tert butyl ether (MtBE) and some chlorinated solvents have been measured at low levels in public supply wells near rivers. Low levels of chloroform and other trihalomethanes produced as a result of the water disinfection process (also called disinfection byproducts) appear nearly ubiquitous in the urban environment. The source of disinfection byproducts is from the use and application of treated water in the urban environment for landscape irrigation, transport of household wastewater through leaky sewer systems, and also from leaky water pipe systems emanating form water treatment plants. An additional constituent which has low risk-based level, N-nitrosodimethylamine (NDMA), has also been found associated with water treatment plant disinfection byproducts.

A well-known nation wide study was conducted by the U.S. Geological Survey (USGS) in 1999 to 2000. The USGS collected surface water samples from 139 streams in 30 states across the lower 48 states (Fig. 1). The streams tended to be downstream of intense urban or livestock areas and consequently were suspected of contamination. The surface water samples were analyzed for organic wastewater contaminants (OWCs). The results of the surface water sample evaluation were published in Environmental Science & Technology (1) and in a USGS Open-File Report (2).

The USGS found that 80% of the streams sampled generally contained low concentrations of OWCs in the <1.0 μg/L range, impacted primarily by residential, industrial, and agricultural products. Seven chemical groups (steroids, nonprescription drugs, insect repellent, detergent metabolites, disinfectants, plasticizers, and fire retardants) were found in more than 60% of the stream samples, and three groups (detergent metabolites, steroids, and plasticizers) contributed to almost 80% of the total measured concentration. More than one-third (33 of 95 target OWCs) of the chemicals detected are known or are suspected of exhibiting at least weak hormonal activity and have the potential to disrupt normal endocrine function (Fig. 2).

One source of the chemicals identified is products and materials typically used in farming and industry. Additionally, a significant contribution was from residential

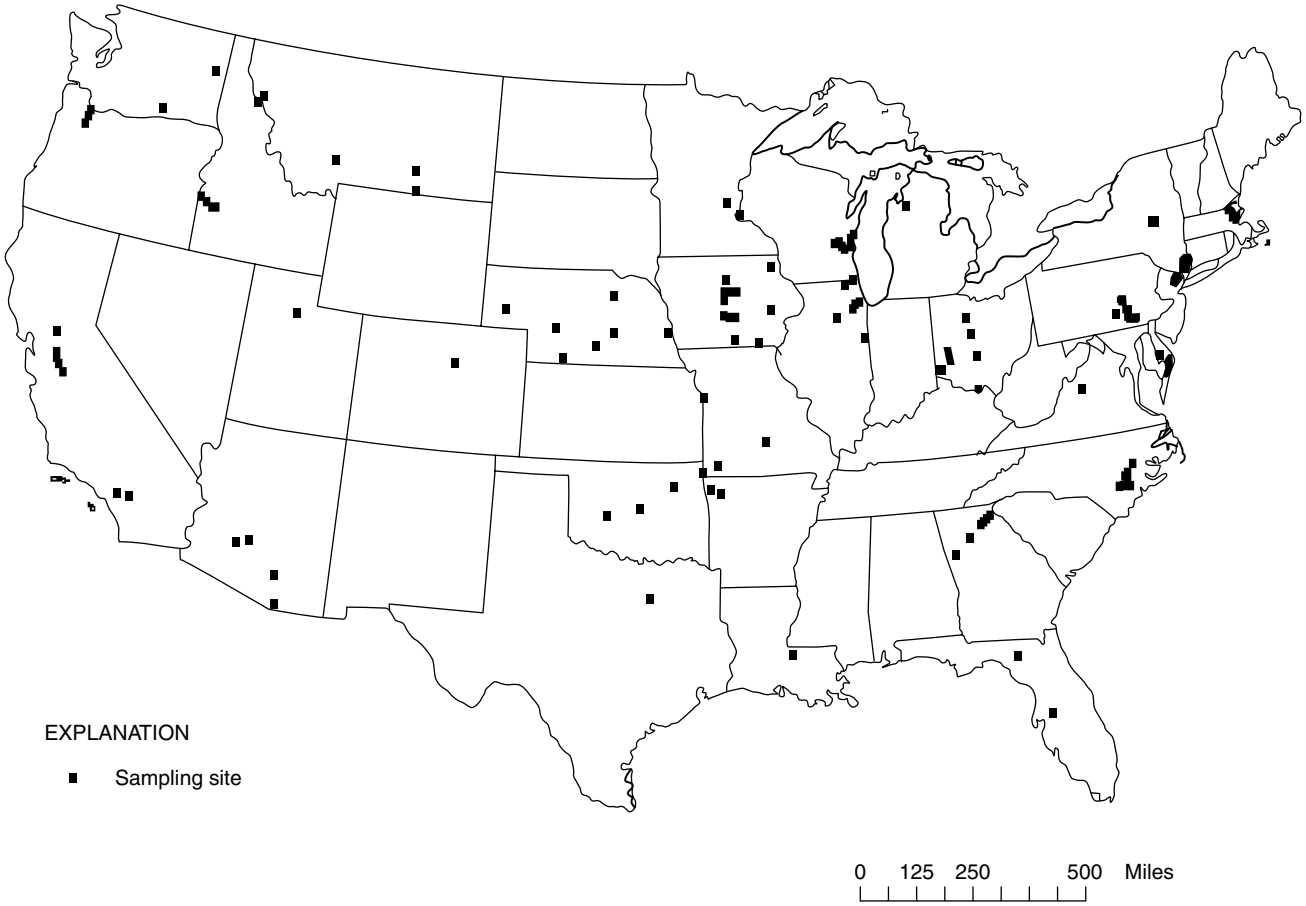


Figure 1. Sampling locations of USGS study (courtesy of USGS, Ref. 1).

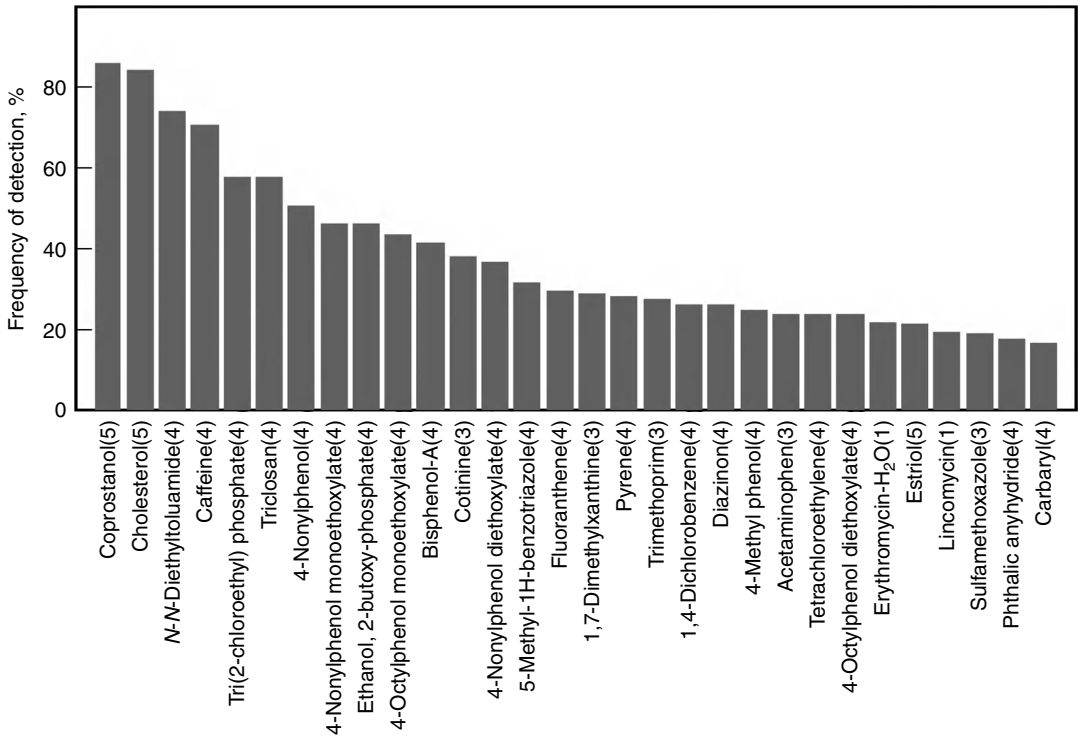


Figure 2. Most frequently detected compounds. The analytical method number is provided (in parentheses) at the end of each compound name (1).

use, drugs typically found in the medicine cabinet, and disposed of as is or as processed human waste in toilets and sinks. Some commonly detected constituents include caffeine in 70.6% of the samples at a maximum concentration of 5.7 μg/L, insect repellent *N*, *N*-diethyltoluamide in 74.1% of the samples at a maximum concentration of 1.1 μg/L, plant/animal steroid cholesterol in 84.3% of the samples at a maximum concentration of 60 μg/L, and fecal steroid coprostanol in 85.7% of the samples at a maximum concentration of 150 μg/L. The USGS study shows that many of the chemicals used in modern life survive human waste processing, current wastewater treatment plant processing, as well as biodegradation in the natural environment, and are detected as contaminants in potential water supplies.

A long list of contaminants have been documented in surface waters throughout the country partly due to the low laboratory detection levels. Considering the interconnection of surface water and groundwater, and the ability of these contaminants to move in the subsurface environment, our shallow groundwater resources are vulnerable to and likely impacted by contamination from these surface water sources. In California, the Ambient Groundwater Monitoring and Assessment Program (GAMA) implemented by the State Water Resources Control Board (SWRCB) is a program to assess the water quality and relative susceptibility of groundwater resources to contamination throughout the state. This assessment of relative contamination vulnerability is made based on the results of two types of analyses that are not routinely carried out at public water supply wells: ultra low-level measurement (part per trillion) of volatile organic compounds (VOCs), and groundwater age dating (using the tritium-helium-3 method). In addition, stable isotopes of oxygen are measured to help determine recharge water source location. Interpreted together with existing water quality and hydrogeologic data, these parameters assist in assessing the flow field of a groundwater basin, and indicate the degree of interconnection between near-surface sources (or potential sources) of contamination, and deeper groundwater pumped at high capacity production wells.

In GAMA studies that were conducted by the USGS and Lawrence Livermore National Laboratory under contract to SWRCB, the two most frequently detected volatile organic compounds were disinfection by products (trihalomethanes) dominantly chloroform, and methyl *tert* butyl ether (MtBE), which were found more frequently and at higher concentration in samples from rivers than in samples from nearby shallow public supply wells, suggesting the rivers may be the source of the groundwater occurrences (4,5). Additionally, chloroform was found associated with wellhead disinfection systems and may be present due to back-flushing of treated water (6). In one study of the Los Angeles Basin area, it was determined that the overall distribution of low level VOCs in groundwater was related to the hydrological and engineered recharge facilities (4). In a study of the Sacramento area, the frequent detection of one VOC (Perchloroethylene PCE) was believed to be due to mobilization of numerous point sources from spills or leaks at dry cleaners or other businesses, or possibly, from leaky sewer lines that hold small amounts of PCE (5).

Although these common chemicals are detected in very low or trace amounts, the possible cumulative or synergistic effects of these chemicals on plants, animals, and humans is currently unknown. Additional data from the USGS is forthcoming. There are no potential adverse health effects of these chemicals at such low documented concentrations.

If treatment or remediation is deemed appropriate, advanced oxidation, enhanced bioremediation, or improved water polishing/filtering could be added to existing wastewater treatment plants to reduce contaminants of these types from entering the environment. More limited pretreatment for septic systems could also help to reduce these chemicals in the environment. For individual water users, small point-of-use treatment systems could be used to remove trace amounts of contaminants (3).

This is a chemical society: Chemicals are widely used on a daily basis at a personal level in the household (personal care products, gasoline, solvents, pesticides, etc), and for a better quality of life in industry and agriculture (wide variety of chemicals). Anthropogenic impacts on the environment, which were largely uncontrolled until the last thirty years, are still unavoidable even with the current best standards of practice. Further, society is still continuing to understand the environmental impacts of past chemical handling and disposal practices as laboratory and investigative analytical tools improve. With population increasing at the current rate, projections are for increased demands on water supply, increased stress of the existing water supply and hydrologic systems, and shortages in dry years, unless steps are taken to increase water supplies and reliability through strategies including water conservation, recycling, desalination, conjunctive use, and artificial recharge. No doubt there will continue to be more "new" chemicals found to be present in our hydrologic system in the future that we did not know about before, but may have been present for some time. This will require planned adaptive management approaches and practices to assess the potential affects on humans and ecosystems, to develop alternative management strategies and remediation if appropriate, and to have on-going educational programs beginning at the elementary school level to edify society as to the information and risks so that society can make informed decisions as to how these challenges should be managed in the future.

BIBLIOGRAPHY

1. Kolpin, D.W. et al. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance, USGS. *Environ. Sci. Technol.* **36**(6): 1202–1211.
2. Barnes, K.K., Kolpin, D.W., Meyer, M.T., Thurman, E.M., Furlong, E.T., Zaugg, S.D., and Barber, L.B. (2002). *Water-Quality Data for Pharmaceuticals, hormones, and Other Organic Waste Water Contaminants in U.S. Streams, 1999–2000*. USGS Open File Report 0-2-94, Iowa City, IA.
3. Jacobs, J.A. and Parker, T. (2002). *Low Concentrations of Organic Contaminants in the Hydrologic System*. *Groundwater*

Resourc. Assoc. 11th Annu. Meet., September 18, 2002, Newport Beach, CA.

4. Moran, J.E., Hudson, G.B., Eaton, G.F., and Leif, R. (2004). *Ambient Groundwater Monitoring and Assessment—A Contamination Vulnerability Assessment for the Sacramento Area Groundwater*. Lawrence Livermore National Laboratory UCLR-TR-203258.
5. Shelton, J.L., Burow, K.R., Belitz, K., Dubrovsky, N.M., Land, M., and Gronberg, J.A. (2000). *Low-Level Volatile Organic Compounds in Active Public Supply Wells as Groundwater—Water Tracers in the Los Angeles Physiographic Basin, California*. U.S. Geological Survey Water—Resources Investigations Report 01-4188.
6. Moran, J.E., Hudson, G.B., Eaton, G.F., and Leif, R. (2002). *A Contamination Vulnerability Assessment of the Livermore—Amador and Niles Cone Groundwater Basins*. Lawrence Livermore National Laboratory UCLR-TR-148831.

DARCY'S LAW

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Darcy's law is a mathematical relationship originally determined by Henry Darcy in 1856 that permits quantification of fluid flow through porous media. Many sophisticated theoretical and practical derivations have been based on Darcy's law (1), and it has become the foundation for quantitative groundwater flow science and soil physics (2). In its most useful form, the formula can be used to calculate the amount of water (or other fluid) flowing through a given cross-sectional area of a porous substance and equates volumetric discharge per unit time (q) to the product of area (A), hydraulic gradient (I = change in head per unit length) and a coefficient (K = saturated hydraulic conductivity). In its simplest terms, the relationship may be expressed as $q = KIA$.

Figure 1 provides a schematic diagram for establishing the relationship in a laboratory soil column test for one-dimensional flow. Note that $\Delta h/L = I$. For a given porous media in a tube of cross-sectional area A, the hydraulic conductivity, K, can be determined as the only unknown in the equation. By changing the hydraulic head, it is also possible to confirm that the relationship between head and discharge is linear for most materials. It should also be possible to determine the head or discharge conditions for which the relationship deviates from the linear form and therefore the threshold beyond which Darcy's law is no longer applicable.

Since it was determined, Darcy's law has been found valid for any Newtonian fluid. It is important to note, however, that the relationship holds only for laminar (nonturbulent) flow of fluids in homogeneous porous media and that it was established under saturated flow conditions for one-dimensional flow. The Darcy equation is strictly applicable only when the cross section being considered is much greater than the dimensions of its microstructure, so that it can reasonably be regarded as uniform. Most groundwater movement takes place in small interstices, so that an aquifer provides considerable resistance to water movement, allowing laminar flow.

The determination of laminar flow depends upon the magnitude of the Reynold's number, a dimensionless ratio of inertial forces to viscous forces. At low Reynold's numbers, viscous forces dominate, and Darcy's law is valid. There follows a transition zone in which inertial forces become more important; Darcy's law cannot be accurately applied to the nonlinear laminar flow in this zone (3). Flow in the turbulent zone is both nonlinear and nonlaminar, and deviations from Darcy's Law can become very large. In many aquifer materials, however, the assumption of laminar water flow may not cause any inaccuracies.

Flow analysis predictions based upon Darcy's law in the presence of massively fissured rocks such as karstic limestones or highly fractured crystalline rocks can lead to large errors. Flow in such cases cannot be described adequately by a linear relationship such as Darcy's law, and a more detailed analysis is required. In very large interstices such as those found in many limestone and volcanic areas, groundwater flow is almost identical to the turbulent flow of surface water (1). Others have claimed that in clays that have very small pores and low hydraulic conductivities the very low flow rates are less than proportional to the hydraulic gradient (4,5). A possible explanation is that much of the water in such material is strongly held by absorptive forces and may be more rigid and less mobile than ordinary water (6). Similar processes may explain the large store of water held in peat soils that have very low hydraulic conductivities (7,8).

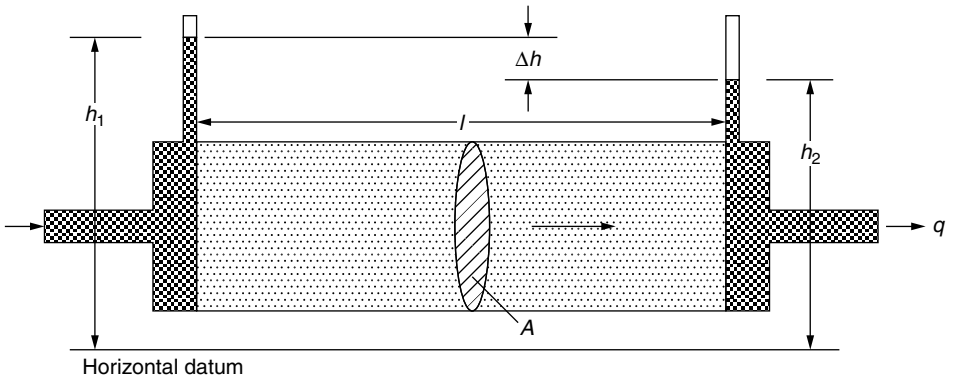


Figure 1. Schematic diagram of a soil column test for establishing components of Darcy's law.

As Hofmann and Hofmann (3) discuss, Darcy himself was careful not attribute too much to the specific magnitudes of individual data readings. Rather, he emphasized two aspects that his data supported, the proportionality of flow rate to total hydraulic head and the inverse proportionality of flow rate to column length (9). The limited experimental accuracy and scope were recognized by Darcy and have remained apparent to hydrologists ever since. By itself, Darcy's law suffices to describe only steady flow conditions, so that for most field applications it must be combined with mass conservation (or the continuity law) to obtain the general flow equation or, for saturated conditions, the Laplace equation. A direct solution of the latter for groundwater flow is generally not possible, and hence there is a need for various approximations or indirect methods of analysis. An important extension of Darcy's law to groundwater flow is its application in three-dimensions; see Childs (10) and Shaw (11) for more detail.

Fundamental to the application of Darcy's law is knowledge of the hydraulic conductivity of the saturated medium. The factors affecting hydraulic conductivity include those associated with the fluid and those associated with the aquifer, including temperature, salinity, pore space geometry, and soil or rock surface roughness (1). Hydraulic conductivity is often measured on a variety of scales ranging from a laboratory soil column, as shown in Fig. 1, to field-scale borehole tests and timed movement of tracers. As the scale of approach increases, often the estimation of hydraulic conductivity increases because of the incorporation of ever larger and more extensive fracture systems. A practical difficulty is that virtually any matrix considered, even on the laboratory scale, will be heterogeneous to some extent. Such heterogeneities do not theoretically prohibit the use of Darcy's law, but they lend uncertainty to generalizations on a large scale. It is for this reason that statistical models employing probabilistic parameter distributions are sometimes used to model the spatial variability of hydraulic conductivity (3).

However, particular problems emerge in assessing spatial variability in hydraulic conductivity and applying Darcy's law to groundwater flow when media are anisotropic, which is the case for highly layered soils such as peats where hydraulic conductivity may differ in the vertical direction by several orders of magnitude across just a few centimeters (8). Furthermore, full saturation of soils may be prevented by gases occupying pore spaces after entrapment upon rapid infiltration or gas production as a result of biogenic decomposition. This can lead to a reduction of hydraulic conductivity (12). Many wetland soils are compressible and so the field worker must be careful not to misapply rigid soil theories to these soils. Instead, compressible soil calculations have been developed but are not yet widely applied (8,13,14).

Despite concern about its strict validity, Darcy's law constitutes an adequate description of groundwater flow and fluid flow through porous media. It can be successfully applied to virtually all normal cases of groundwater flow and is equally applicable to confined and unconfined conditions (1).

BIBLIOGRAPHY

1. Ward, R.C. and Robinson, M. (2000). *Principles of Hydrology*. McGraw-Hill, London.
2. Freeze, R.A. (1994). Henry Darcy and the Fountains of Dijon. *Groundwater* **32**: 23–30.
3. Hofmann, J.R. and Hofmann, P.A. (1992). Darcy's law and structural explanation in hydrology. In: *PSA 1992: Proceedings of the 1992 Biennial Meeting of the Philosophy of Science Association*, Volume 1. D. Hull, M. Forbes, and K. Okruhlik (Eds.). Philosophy of Science Association, East Lansing, MI, pp. 23–35.
4. Millar, R.J. and Low, P.F. (1963). Threshold gradient for water flow in clay systems. *Proc. Soil Sci. Soc. Am*. **27**: 605–609.
5. Swartzendruber, D. (1962). Non Darcy behaviour in liquid saturated porous media. *J. Geophy. Res*. **67**: 5205–5213.
6. Hillel, D. (1982). *Introduction to Soil Physics*. Academic Press, New York.
7. Ingram, H.A.P. (1983). Hydrology. In: *Ecosystems of the World 4A, Mires: Swamp, Bog, Fen and Moor*. A.J.P. Gore (Ed.). Elsevier, Oxford, pp. 67–158.
8. Holden, J. and Burt, T.P. (2003). Hydraulic conductivity in upland blanket peat; measurement and variability. *Hydrological Proc.* **17**: 1227–1237.
9. Darcy, H. (1856). *Les Fontaines Publiques de la Ville de Dijon*. Victor Dalmont, Paris.
10. Childs, E.C. (1969). *Introduction to the Physical Basis of Soil Water Phenomenon*. John Wiley, London.
11. Shaw, E.M. (1994). *Hydrology in Practice*. Stanley Thornes, Cheltenham.
12. Beckwith, C.W. and Baird, A.J. (2001). The effects of biogenic gas bubbles on water flow in poorly decomposed blanket peat. *Water Resources Research* **37**: 551–558.
13. Premchitt, J. and Brand, E.W. (1981). Pore pressure equalisation of piezometers in compressible soils. *Geotechnique* **31**: 105–123.
14. Baird, A.J. and Gaffney, S.W. (1994). Cylindrical piezometer responses in a humified fen peat. *Nordic Hydrology* **25**: 167–182.

GROUNDWATER DATING WITH RADIOCARBON

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INTRODUCTION

Groundwater age, based on measurement of the concentrations of chemical and isotopic substances in water, refers to the time elapsed since the introduction of the chemical or isotopic substance into the water, or to be more precise, the time elapsed since the chemical or isotopic substance was recharged and isolated from the modern reservoir. Although we often refer to dating of groundwater, we are actually dating a chemical substance that is dissolved in the groundwater, not the water itself. Unless we recognize and account for all the physical and chemical processes that affect the concentrations of tracers in an aquifer, the

tracer-based age is not necessarily equal to the transit time of the water carrying the substance. Rather than referring to groundwater dating, it would probably be more correct to say we are interpreting temporal aspects of chemical and isotopic substances in groundwater.

For many applications in hydrology, we are interested in the travel time of water through an aquifer. The accuracy of the age determined depends in part on how perfectly the chemical and isotopic substances we are using as dating tools are transported in the aqueous phase. The concentrations of all tracers are, to some degree, affected by transport processes, and in the case of some tracers, such as chlorofluorocarbons, their concentrations can also be affected by chemical processes such as degradation and sorption during transit.

Various environmental isotopes and tracers are used to determine the age of groundwater. Carbon-14 is used to date ground waters older than 1000 years. Chloroflurocarbons (Freon) and tritium techniques are used to date groundwater that is less than 50 years old (Table 1).

The residence time of water underground has always been a topic of considerable speculation. But with the advent of radioisotopes, determination of the age of groundwater has become possible (1).

Carbon-14 (^{14}C), commonly referred to as radiocarbon, is continuously being produced in the atmosphere. This results from cosmic ray bombardment of nitrogen nuclei. Atmospheric testing of thermonuclear weapons doubled the ^{14}C concentration in the atmosphere. Carbon-14 is expressed in terms of percent of modern carbon (pmC). ^{14}C is useful when dating groundwaters that are between 1000 and 30,000 years old.

This isotope is present in groundwater as dissolved bicarbonate originating from the biologically active layers of the soil where CO_2 is generated by root respiration and the decay of humus (2).

^{14}C

The ^{14}C generated in the atmosphere is carried down to the earth's surface by precipitation and becomes incorporated into the biomass or transported into waterbodies such as lakes, oceans, and groundwater. ^{14}C undergoes radioactive decay (to ^{14}N), so that once isolated from the atmosphere, the amount of ^{14}C decreases with time according to the equation

$$(^{14}C)_t = (^{14}C)_o e^{-kt}$$

where $(^{14}C)_t$ is the amount present at time t, $(^{14}C)_o$ is the amount present at $t = 0$, and k is the decay constant, which is related to the half-life $t_{1/2}$ by the equation

$$t_{1/2} = \ln 2/k$$

To determine the time since water lost contact with the atmosphere, it is necessary to know $(^{14}C)_o$. This is determined by tree rings for the most recent 7000 years; there is no accurate way to determine it prior to 7000 years ago, so it is generally assumed arbitrarily to have been constant. This gives rise to a timescale in "^{14}C years," which may be different from astronomical years (3).

There are some complications in the behavior of ^{14}C during recharge, so that the "absolute" age of a groundwater cannot be determined reliably. However, if the ^{14}C concentration is measured at several points along a flow line within an aquifer, the differences in age between the points and hence the flow velocity can be determined. One complication is that dissolution of carbonate minerals or oxidation of organic matter within the aquifer may add "old" or "dead" (no detectable ^{14}C) carbon to the water and give an erroneously old age. The contribution of carbon from these sources can sometimes be estimated from $^{13}C/^{12}C$ measurements and chemical arguments (4), so that corrections can be made. Another complication is mixing. A low ^{14}C concentration may mean that we are looking at relatively "old" water, or it may mean that we are looking at a mixture of relatively "young" water and "dead" water. ^{14}C measurements can be interpreted as ages only when mixing is insignificant.

Measurements of water samples taken from deep wells in deserts of the United Arab Republic and Saudi Arabia indicate ages of 20,000 to 30,000 years (5). This period is compatible with the Wisconsin Ice Age, when these desert areas last had high rainfall capable of recharging the underlying major aquifers.

Table 1. List of Environmental Tracers and Isotopes Used for Age Determination

Environmental Isotope/Tracer	Age Range, Years
Chloroflurocarbons (CFC-11, CFC-12, and CFC-113)	0 to 50
Tritium	0 to 50
Tritium/Helium-3	0 to 30
Carbon-14	1000 to 30,000

BIBLIOGRAPHY

1. Todd, D.K. (1995). *Ground Water Hydrology*. Wiley, Toronto, Canada, pp. 24–25.
2. Wigley, T.M.L. (1975). Carbon-14 dating of groundwater from closed and open systems. *Water Resour. Res.* **11**: 324–328.
3. Drever, J.I. (1982). *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, NJ.
4. Wigley, T.M.L. (1976). Effect of mineral precipitation on isotopic composition and ^{14}C dating of ground water. *Nature* **263**: 219–221.
5. Thatcher, L. et al. (1961). Dating desert ground water. *Science* **134**(3472): 105–106.

GROUNDWATER DATING WITH H–HE

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PRODUCTION AND DECAY BEHAVIOR OF ATMOSPHERIC TRITIUM

Tritium (^3H) is a relatively short-lived radioactive isotope of hydrogen that is produced naturally in the

atmosphere and enters the hydrologic cycle through meteoric precipitation. Natural atmospheric ^3H results from the interaction of nitrogen-14 (^{14}N) and cosmic-ray neutrons (n) by

$$^{14}N + n \longrightarrow {}^3H + {}^{12}C \quad (1)$$

Tritium is then rapidly incorporated into water molecules. Tritium decays to helium-3 (^3He) by beta decay:

$$^3H \longrightarrow {}^3He + \beta^- \quad (2)$$

Tritium concentrations in water are typically reported as "tritium units" (TU), where 1 TU is equivalent to one ^3H atom per 10^{18} hydrogen atoms and $0.118\ Bq\,kg^{-1}$ ($1\ Bq = 1$ disintegration per second). Decay of 1 TU yields approximately $0.402\ pcm^3\,kg^{-1}$ of ^3He. The natural atmospheric production rate of ^3H is approximately 0.5 ± 0.3 atoms of $^3H\,cm^{-2}\,s^{-1}$ (1). The background ^3H concentration in meteoric precipitation before 1951 is estimated in the range between 0.5 and 20 TU, and most measurements are less than 10 TU (2) and (3, Fig. 7.2). The rate of ^3H decay and ^3He production follow these first-order rate laws:

$$^3H_t = {}^3H_0 e^{-\lambda t} \quad (3a)$$

$$^3He_t = {}^3H_0 e^{\lambda t} \quad (3b)$$

where ^3H_t and ^3He_t are the number of tritium and helium-3 atoms at time t, $^3H_0$ is the initial number of tritium atoms, and λ is the tritium decay constant ($0.05626\ yr^{-1}$). The tritium "half-life" ($t_{1/2}$), or time it takes for half of the starting tritium to decay to ^3He, is best estimated at 12.32 yr (4500 ± 8 day) (4). Figure 1 graphically shows the decay and generation behavior of ^3H and ^3He through time. The half-life is related to the decay constant by

$$\lambda = \frac{\ln 2}{t_{1/2}} \quad (4)$$

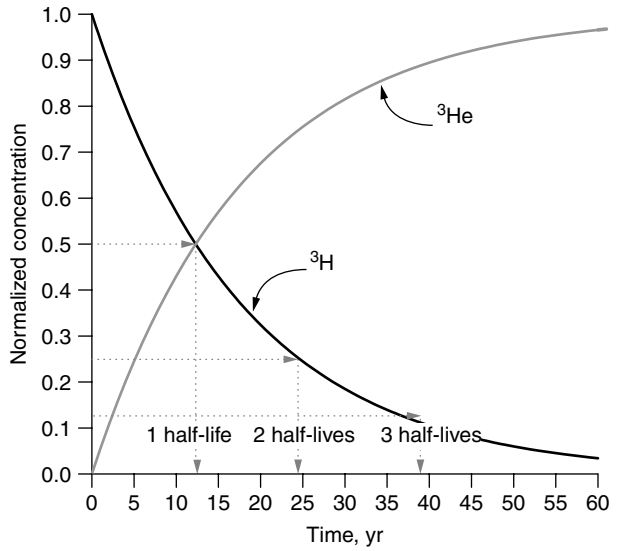


Figure 1. Tritium (^3H) decay and ^3He production through time. Values are normalized to the initial ^3H concentration ($^3H_0$).

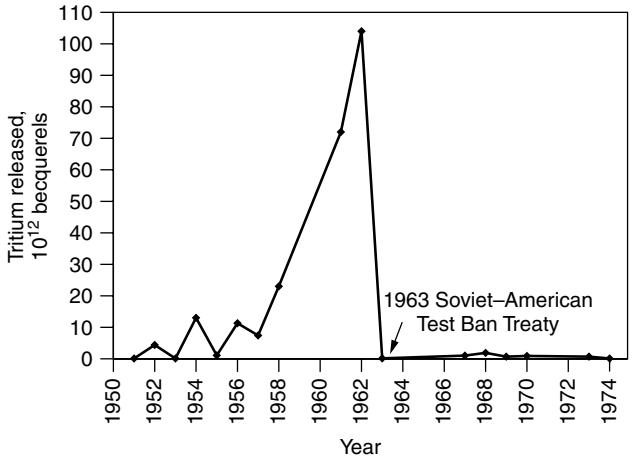


Figure 2. Anthropogenic ^3H released from atmospheric detonation of thermonuclear weapons testing (developed from data summarized by Reference 3).

During 1951, it was demonstrated that significant energy is released during hydrogen fusion to provide the basis for developing thermonuclear superbombs. Atmospheric testing (detonation) of these weapons during the next decade resulted in a dramatic increase in atmospheric ^3H concentration, until implementation of a Soviet–American atmospheric test ban treaty in 1963 (Fig. 2). Atmospheric thermonuclear weapons testing released vast quantities of high-energy neutrons that interacted with ^{14}N and led to the production of ^3H (Eq. 1). The incredible amount of ^3H produced in the atmosphere resulted in a distinct precipitation input signal of anthropogenic ^3H (Fig. 3), and a notable peak in 1963.

PRINCIPLES OF THE ^3H–^3HE DATING METHOD

The mid-1960s ^3H peak has been widely used as a direct time marker to determine groundwater ages. However, because of the relatively short half-life of ^3H, this peak has become difficult to differentiate in many systems. This is particularly true in the Southern Hemisphere where the anthropogenic ^3H in precipitation was notably lower than in the Northern Hemisphere. However, measurement of both parent ^3H and increases in its decay product, ^3He, can dramatically increase the sensitivity of the method. The "in-grown" ^3He (or ^3He produced by ^3H decay) can be equated to the initial $^3H_0$ and ^3H_t by

$$^3He_t = {}^3H_0(1 - e^{-\lambda t}) = {}^3H_t(e^{\lambda t} - 1) \quad (5)$$

Assuming that other ^3He sources are insignificant or can be accounted for and that there have been no systematic losses of tritiogenic ^3He, the relationships in Equation 5 can be rearranged, and the apparent age of the water (τ) can then be calculated from (Fig. 4)

$$\tau = \frac{t_{1/2}}{\ln 2} \ln\left(1 + \frac{^3He_t}{^3H_t}\right) \quad (6)$$

The ^3H–^3He method offers two significant advantages: (a) the method does not rely on accurate knowledge of the

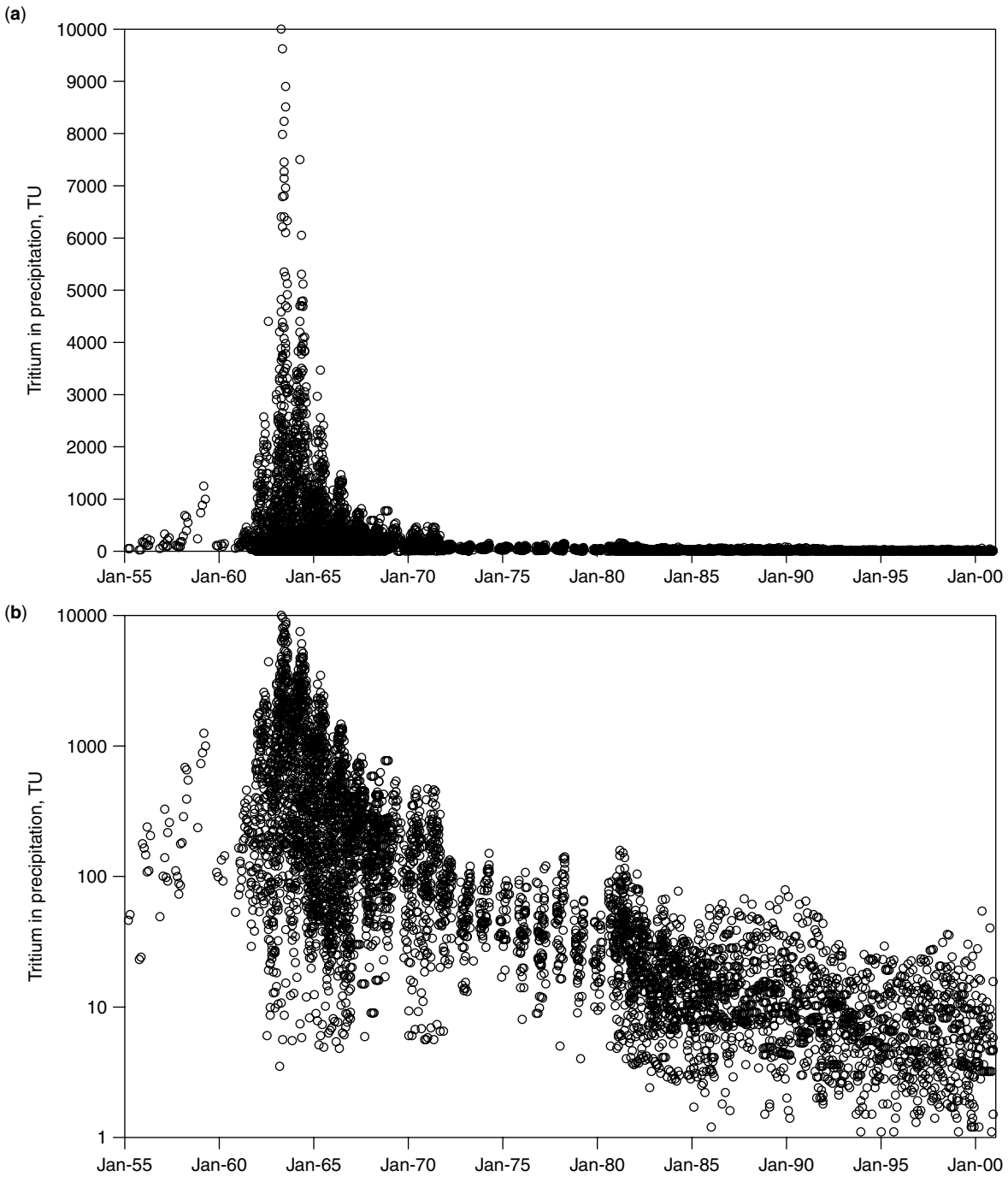


Figure 3. Tritium in precipitation (reported in tritium units, TU) measured at more than 50 locations in North America between 1955 and 2001 (top: arithmetic scale, bottom: logarithmic scale) (data obtained from Reference 5).

original ^{3}H input or identification of the mid-1960s peak, and (b) the method is generally less sensitive to analytical measurement errors (2).

The "clock" for the ^{3}H–^{3}He method begins at the seasonal water table low, where ^{3}He produced is no longer lost to the atmosphere and begins to accumulate in the groundwater. If the unsaturated zone is thick, the apparent ^{3}H–^{3}He age at the "bomb peak" signal may be significantly less than the actual time since the peak ^{3}H fallout. The difference in apparent ages can be used to estimate the travel time through the unsaturated zone. For example, Solomon et al. (6) determined an apparent ^{3}H–^{3}He age of 16 years for groundwater samples near the ^{3}H peak signal in a study at Cape Cod, Massachusetts. However, the samples were collected 30 years after the actual peak ^{3}H fallout in 1963. The difference in these age values resulted in an unsaturated zone travel time estimate of 14 years.

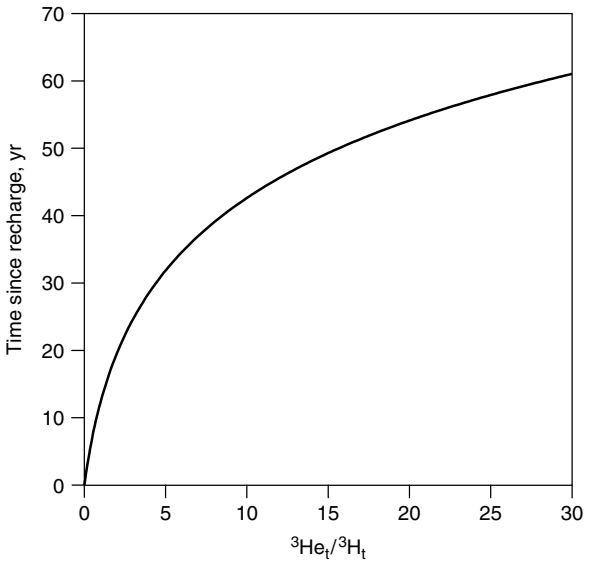


Figure 4. Calculated time since recharge from measured $^3He_t/^3H_t$ ratio (Eq. 6).

There are additional sources of ^{3}He in groundwater, and the measured ^{3}He value must be corrected for these sources before applying Eq. 6. Tritium-generated ^{3}He ($^3He_{trit}$) is determined from total measured tritium ($^3He_{total}$) by

$$^3He_{trit} = {}^3He_{total} - {}^3He_{atm} - {}^3He_{excess} - {}^3He_{crust} - {}^3He_{mantle} \quad (7)$$

where $^3He_{atm}$ is the ^{3}He concentration in solubility equilibrium with the atmosphere, $^3He_{excess}$ is the ^{3}He resulting from excess air, $^3He_{crust}$ is the ^{3}He produced in the crust, and $^3He_{mantle}$ is the ^{3}He produced in the mantle (also called primordial ^{3}He). Atmospheric ^{3}He dissolving in groundwater at the time of recharge is typically the most significant process resulting in excess ^{3}He. This process can be accounted for by considering the following (3):

- The atmospheric ^{4}He concentration is 5.24 parts per million (by volume), and the atmospheric $^3He/^4He$ ratio is 1.3×10^{-6}.
- The temperature-dependent aqueous solubility of helium (at 10 °C, the value is 4.75×10^{-8} cm^3 STP/cm^3 H_2O).
- ^{4}He is more soluble than ^{3}He in water and has a fractionation factor ($\alpha_{water-air}$) of 0.983.

Although the ^{3}H–^{3}He method is fairly insensitive to recharge temperatures, it is very sensitive to excess air, particularly for young groundwater (7). In some systems, ^{3}He from excess trapped air caused by a transient wetting front may be significant and can be identified by supersaturation of other gases, such as Ne and N_2. For most systems, subsurface generated ^{3}He ($^3He_{crust}$ and $^3He_{mantle}$) is insignificant; however, correction methods for these cases are discussed by Schlosser (8,9), Solomon et al. (2), and Cook and Solomon (7). Other potential errors in the ^{3}H–^{3}He method may be caused by diffusive loss and dispersion/mixing effects. ^{3}He diffusive loss to the atmosphere was greatest during the mid-1960 peak (due to the high concentration gradient), so this method may incorrectly calculate younger ages for groundwater below the mid-1960 peak (2). Because helium has a relatively high Henry's law constant (105.2 [dimensionless] at 25 °C) (10), care must be taken during sampling to prevent ^{3}He loss due to gas stripping.

ANALYTICAL MEASUREMENT METHODS

Tritium is typically measured by either low-level disintegration counting or by the more sensitive ^{3}He in growth method using mass spectrometry. Depending on the specific instruments and analytical procedures, ^{3}H detection limits of ~0.05–0.8 TU and analytical precision of ±2.5–5% can be achieved (9). For ^{3}He measurement, water samples are commonly collected in pinched-off copper tubes or gas-filled diffusion samplers. The helium is then isolated from all other dissolved gases and analyzed by a helium isotope mass spectrometer to resolve the $^3He/^4He$ isotopic ratio. Achievable measurement precision for the $^3He/^4He$ ratio is approximately 0.2% (9). Although approximately 40 years have passed since the mid-1960 ^{3}H "bomb peak," these analytical capabilities should permit identifying the peak signal in favorable hydrogeologic settings for several more decades (8). In most cases, analytical uncertainties result in calculated age uncertainties of less than approximately 10% (7).

CASE STUDY: COMPARISON OF THE ^{3}H–^{3}HE METHOD TO THE CFC AND ^{85}Kr DATING METHODS

Ekwurzel et al. (11) compared calculated groundwater ages for three different dating methods, including the ^{3}H–^{3}He method, in a study on the Delmarva Peninsula (approximately 15,690 km^2) located on the east coast of the United States. The Delmarva Peninsula is characterized by low topographical relief and little urban development. The hydrogeology of the area is relatively simple, consisting of low hydraulic gradients, highly permeable surficial materials, and shallow water tables. Discrete groundwater samples were collected from approximately 30 wells throughout the Delmarva Peninsula (most wells were screened across less than 1 m of the aquifer). Additionally, age dating methods were compared for a single flow system on the peninsula at Locust Grove.

Most age values calculated from the three methods agreed within approximately 2 years, indicating conservative behavior of the various tracers and reliability of the dating methods. A few wells that produced large apparent age discrepancies were located in areas of significant mixing. Dissolved N_2 concentrations from several wells with large tracer age variations (>10 years) indicated that gas stripping may have occurred in these samples. A one-dimensional advection–dispersion model, applied to estimate the effect of dispersion on the age correlation, determined that hydrodynamic dispersion effects were negligible. As stated earlier, fairly close agreement was observed among the different dating methods for

this study; however, the locations that produced significantly different tracer ages demonstrate that use of multiple methods for groundwater age dating is important because tracers are affected differently by diffusion, dispersion, sorption, degradation, gas entrapment, excess air, recharge temperature, and sampling errors. For additional case studies on the ^3H–^3He groundwater dating method, see Schlosser (9), Solomon et al. (6), Cook et al. (12), Cook and Solomon (7), and Vengosh et al. (13).

BIBLIOGRAPHY

1. Craig, H. and Lal, D. (1961). The production rate of natural tritium. *Tellus* **13**: 85–105.
2. Solomon, D.K., Schiff, S.L., Poreda, R.J., and Clarke, W.B. (1993). A validation of the $^3H/^3He$ method for determining groundwater recharge. *Water Resour. Res.* **29**: 2951–2962.
3. Clarke, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. CRC Press, New York, pp. 20, 174–188.
4. Lucas, L.L. and Unterwerger, M.P. (2000). Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Stand. Technol.* **105**: 514–549.
5. International Atomic Energy Agency. (2001). Isotope hydrology information system. The ISOHIS Database. Available: http://isohis.iaea.org.
6. Solomon, D.K, Poreda, R.J, Cook, P.G., and Hunt, A. (1995). Site characterization using $^3H/^3He$ ground-water ages, Cape Cod, MA. *Ground Water* **33**: 988–996.
7. Cook, P.G. and Solomon, D.K. (1997). Recent advances in dating young groundwater: Chlorofluorocarbons, $^3H/^3He$ and ^{85}Kr. *J. Hydrol.* **191**: 245–265.
8. Schlosser, P., Stute, M., Sonntag, C., and Munnich, K.O. (1989). Tritiogenic ^3He in shallow groundwater. *Earth Planetary Sci. Lett.* **94**: 245–256.
9. Schlosser, P. (1992). Tritium/^3He dating of waters in natural systems. In: *Isotopes of Noble Gases as Tracers in Environmental Studies*. IAEA Proceedings, Vienna, Austria, pp. 123–145.
10. Yaws, C.L. (2001). *Matheson Gas Data Book*, 7th Edn. McGraw-Hill, New York.
11. Ekwurzel, B. et al. (1994). Dating of shallow groundwater: Comparison of the transient tracers $^3H/^3He$, chlorofluorocarbons, and ^{85}Kr. *Water Resour. Res.* **30**: 1693–1707.
12. Cook, P.G. et al. (1996). Inferring shallow groundwater flow in saprolite and fractured rock using environmental tracers. *Water Resour. Res.* **32**: 1501–1509.
13. Vengosh, A., Gill, J., Davidsson, M.L., and Hudson, B. (2002). A multi-isotope (B, Sr, O, H, and C) and age dating (^3H-^3He and ^{14}C) study of groundwater from Salinas Valley, California: Hydrochemistry, dynamics, and contamination processes. *Water Resour. Res.* **38**: 1–17.

DATING GROUNDWATERS WITH TRITIUM

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INTRODUCTION

Tritium (^3H) is one of the most common radioisotopes used to identify the presence of modern groundwater recharge and estimate apparent groundwater ages (1). Tritium, a short-lived radioactive isotope of the element hydrogen, has one proton and two neutrons. Tritium emits only a very weak beta particle and has a half-life of 12.43 years. Although tritium can occur as a gas, its most common form is in water because, like nonradioactive hydrogen, radioactive tritium readily reacts with oxygen to form water, which allows groundwater to be dated. As tritium replaces one of the stable hydrogens in the water molecule, (H_2), it is referred to as the molecule HTO, or tritiated water (T_20). Similarly to water, tritium is colorless and odorless.

Tritium is produced naturally in both the atmosphere and hydrosphere of the earth when cosmic rays strike air molecules, notably by the interaction of ^{14}N with cosmic ray neutrons in accordance with the following reactions:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{3}_{1}\mathrm{H} + {}^{12}_{6}\mathrm{C}$$

and

$$^2\mathrm{H} + {}^2\mathrm{H} \rightarrow {}^3\mathrm{H} + {}^1\mathrm{H}$$

Cosmic rays interact with nitrogen (^{14}N) or with deuterium (^2H) and form tritium and carbon (^{12}C). The primary interactions occur within the upper atmosphere, and tritium falls to earth via meteoric precipitation. Atmospheric tritium is thus rapidly incorporated into water molecules allowing it to be removed from the atmosphere as rain.

The concentration of tritium in meteoric water is measured in "tritium units" (TU), where 1 TU is equal to an abundance of one atom of ^3H per 10^{18} atoms of hydrogen. This is equivalent to 7.1 disintegrations of ^3H per minute per liter of water.

ANTHROPOGENIC TRITIUM

The occurrence of tritium in the environment has been significantly changed over the years by anthropogenic influences. Tritium has several important uses; the most significant is its use as a component in the triggering mechanism in thermonuclear (fusion) weapons; very large quantities are required to maintain nuclear weapons capabilities. On May 9, 1951, the world's first thermonuclear flame reaction was ignited in a laboratory by a ^2H-^3H-^{235}U device code-named George. Following the birth of this concept, atmospheric detonation of these devices resulted in anthropogenic production of ^3H which raised concentrations in the stratosphere by several orders of magnitude. The proliferation of atmosphere testing continued throughout the mid-1950s, early 1960s, and into the 1970s. Tritium is also produced in accelerator cooling water systems or reactors, which are subjected to large proton or neutron fluxes via spallation reactions with oxygen, nitrogen, and carbon nuclei in the water systems and to a much smaller degree by radiative capture of neutrons by the deuterium nuclei in water. The tritium atom then combines with a hydrogen and oxygen atom to form tritiated water. Anthropogenic tritium has thus been formed by nuclear weapon explosions in the

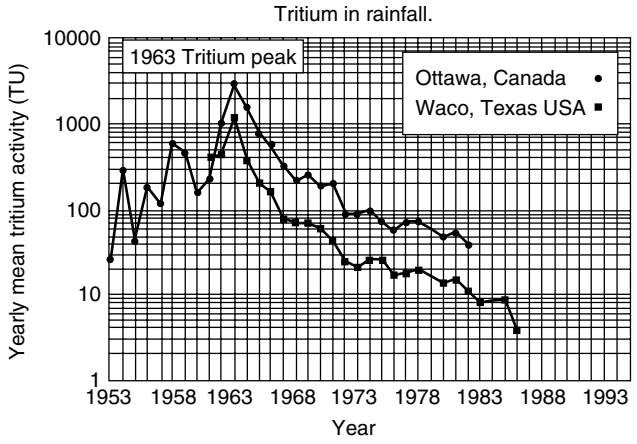


Figure 1. Tritium chart for Ottawa, Canada, and Waco, Texas, (2).

atmosphere and the operation of nuclear reactors and particle acceleration.

The longest record of atmospheric tritium measurements was initiated for precipitation in Ottawa, Canada, beginning in 1953. Atmospheric testing of nuclear devices commenced in 1952. After 1953–1954, the amount of tritium increased and reached a maximum in 1963–1964. Concentrations of ^{3}H in precipitation have decreased since the mid-1960 bomb peak, except for some small secondary peaks by China and France in 1973 and 1975. Tritium input to groundwater has subsequently occurred in a series of spikes following these periods of atmospheric testing (Fig. 1). The majority of tritium produced between the early 1950s through mid-1970s in the atmosphere has since been removed.

Other uses include various self-luminescent devices such as aircraft dials, gun sights, luminous paints, exit signs, and watches. Tritium is also used in life science research and in studies investigating the safety of new drugs.

DATING GROUNDWATER USING TRITIUM

The presence of tritium in the atmosphere from weapons testing has proved useful from several perspectives. The residual presence of nuclear-produced tritium has served as a tracer for atmospheric studies and the study of hydrologic and oceanographic processes. Tritium is considered a dating element for groundwater. By knowing the tritium concentration in precipitation and its distribution in groundwater, an apparent date for the age of the groundwater can be determined, which also allows evaluating aquifer water average transit time (T). This parameter is important because it can be used to address issues about evaluating, exploiting, and protecting water resources.

Dating groundwater can be used in ecologically sensitive coastal settings to understand the hydrogeologic setting and determine whether water is derived from surficial and/or subsurface groundwater. Oceanographers used the sharp spike in surface tritium levels over the years to measure the rate at which lower and upper ocean levels mixed. Tritium is a good marker for tracking ocean water.

Several factors affect tritium concentration in meteoric water. In the lower stratosphere, the residence time for tritium in water is between 1 and 10 years. When tritium water reaches the lower troposphere, residence time is 5 to 20 days (3). It is known that tritium concentration as meteoric precipitation in the Northern Hemisphere has fluctuated widely from less than 25 TU, prior to 1953, to more than 2200 TU in 1964 following extensive testing in the atmosphere (3). In the Southern Hemisphere, the level of bomb-produced tritium is much lower. Other factors to consider include

1. the natural production rate in the stratosphere which is estimated at 0.5 ± 0.3 atoms of ^{3}H/cm^2/s (4);
2. the decay of tritium by beta emission to stable $^{3/2}$He with a half-life of 12.26 y;
3. the seasonal injection of tritium from the stratosphere into the troposphere;
4. the presence of bomb-produced tritium; and
5. the presence of tritium produced locally by nuclear reactors and particle accelerators.

METHODOLOGY

Groundwater is dated by retrieving water samples from surface water bodies, ice or precipitation, or wells in the case of groundwater. By observing the spike in tritium levels, likely the result of atmospheric bomb testing, an age can be estimated. For example, if the spike in groundwater is determined to be 20 miles from its recharge or source area, then it could be deduced that the spike has moved 20 miles during the past 40 years, or an average rate of 0.5 miles per year.

Apparent groundwater age can be estimated directly from tritium precipitation records corrected for first-order decay. Groundwater is age dated by determining the early and late ratio of tritium in accordance with the following equation:

$$^3\mathrm{H}_{\text{early sample}} \times e^{\lambda \Delta t} / {}^3\mathrm{H}_{\text{later sample}}$$

where $\lambda = 0.0565\ \text{yr}^{-t}$ (tritium decay constant)
$\Delta t =$ the time between samples in years

A ratio greater than 1 indicates that the tritium peak has passed, or in other words, the water is older 1963. Conversely, a ratio less than 1 indicates that the peak has not yet arrived, or the water is younger than 1963.

Some amount of hydrodynamic dispersion, however, is likely to occur, which explains why natural tritium levels in precipitation are very low and reflect a secular equilibrium between natural production and the combination of decay in the atmosphere in addition to losses in the hydrosphere and ocean. Advective dispersion and diffusion are typically addressed using a mixing model that more accurately estimates groundwater ages by accounting for attenuation of tritium levels due to these processes (5). Mixing models approximate dispersion and

diffusion processes by assuming a Gaussian distribution of tritium activities.

Three kinds of models are commonly used:

1. the well-mixed or exponential model which assumes that water introduced into a system is completely and uniformly mixed with aquifer water. Thus, the water output from the system is actually representative of the aquifer waters.
2. the piston-flow model which assumes that the incoming water traverses the aquifer at constant velocity.
3. the dispersion model which assumes a dispersion phenomenon reflecting the heterogeneity of the aquifer material.

Different age waters can be distinguished. For example, tritium contents less than 2 TU typically characterize old groundwater, 2 to 10 TU may characterize mixing between old and recent water, 10 to 40 TU may characterize recent groundwater, and greater than 40 TU may characterize groundwater in close proximity to a nuclear station.

The main application of tritium is to differentiate pre-1952 water from younger water. Knowing the concentration of tritium in precipitation (the source) and its distribution in groundwater, an apparent date can be estimated.

The use of tritium to study the movement of water in the subsurface, evaluating source areas, and dating the last time subsurface water was last exposed to the atmosphere is hindered by several factors. The most important limitations are the continuing decay of nuclear-produced tritium, its unequal global distribution, and the local injection of anthropogenic tritium. For example, a tritium concentration of 30 TU may reflect late 1950s water that has decayed through three half-lives, or a 1970s water originally with 75 TU that has decayed through one half-life (6).

In many scenarios, locating the position of the mid-1960 peak is difficult due to the relatively high density of vertical sampling required, which can be expensive and impractical. Furthermore, although tritium can be used to locate the depth of the mid-1960s peak, many samples are required due to radioactive decay to locate its position. Furthermore, in waters younger than the mid-1960s, the bomb peak is not present.

DATING YOUNG GROUNDWATER USING TRITIUM/HELIUM RATIOS

Tritium is not useful for the dating relatively younger water. A way around this is the use of $^3H/^3He$ ratios. Radioactive decay of ^3H produces the noble gas helium-3 (^3He). First introduced by Tolstikhin and Kamenskiy (7), measurements of ^3H and tritiogenic ^3He define a quasi-stable tracer of initial ^3H input to groundwater and may be used to determine the position of the mid-1960s bomb peak in recharge areas and recharge rates (8–11).

Sources of helium are primarily atmospheric. Other sources include terrigenic He (R_{terr}), water in rocks that are enriched in certain elements such as thorium (Th) or Uranium (U), typically of crustal and mantle material, and samples representative of the mixing of relatively young water with old water containing R_{terr}.

Using tritium and helium concentrations, the tritium/helium age can be calculated as follows (12):

$$T_{groundwater} = t^{1/2}/\text{In } 2 \times \text{In } [1 + (^3He/^3H)]$$

where $T = 12.3$ years (the half-life of tritium)
$^3He/^3H$ = helium/tritium concentration ratio (TU)

To convert the concentration units required to evaluate this equation:

$$1\ cm^3\ STP\ g^{-1} = 4.019 \times 10^{14}\ \text{tritium units (for freshwater)}$$

This conversion can be used in conjunction with a correlation to the tritium peak method for verification.

Conditions for using this technique include the following:

1. Detectable tritium in the water sample needs to be greater than approximately 0.5 TU.
2. If R_{terr} terrigenic is present, then Ne data are also needed to define $^3He_{tri}$.
3. The $^3He/^4He$ ratio of R_{terr} must be known
4. If the amount of R_{terr} is small (i.e., <5% of the dissolved ^4He), the $^3H/^3He$ age may be insensitive to large uncertainties in R_{terr}.
5. R_{terr} must be known for samples with a large fraction of R_{terr} (i.e., within approximately 1% or better).
6. If R_{terr} cannot be defined with sufficient precision for age determination, a range in R_{terr} can be evaluated.

$^3He/^3H$ allows dating groundwater of very young ages (approximately 1 year with an uncertainty in age of approximately 0.5 years due to analytic constraints) from a single water sample. This makes $^3He/^3H$ very attractive and complements other techniques for dating groundwater. $^3He/^3H$ can be applied to dating waters that have been recharged in the past approximately 30 years, so this technique can be used for interpreting ages of water from existing domestic, industrial, and municipal production supply wells and recharge operations. Water source(s) identification, flow paths, and flow rates for a variety of purposes and objectives can also be evaluated.

From an environmental perspective, it can also be used to monitor the use of certain chemicals released into the environment such as chlorofluorocarbons (CFCs) and sulfur hexafluoride. For example, for CFCs, the $^3H/^3He$ age is defined as the time elapsed since the water was isolated from the atmosphere following recharge.

Groundwater in aquifers is generally older than expected on the basis of flow velocity. Recent studies suggest that the rate of mass exchange between aquifers and aquitards or confining layers is assumed to be small (13). The effect on age, however, does not depend on mixing rates but rather on the ratio of fluid volume in aquitards to aquifers. This is important in understanding the relationship between groundwater flow and radiometric age distribution. It means that flow

rates along an aquifer are higher than predicted by age measurements. Aquitard water is generally very old; thus, at high mixing rates, less-old water is supplied to the aquifer, and less-old water is being supplied to the aquifer because younger water is moving into the aquitard. Thus, mixing increases the age in an aquifer and also has a counterbalancing effect of decreasing the age in aquitards.

BIBLIOGRAPHY

1. Clark, I. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. Lewis, Boca Raton, FL.
2. Morrison, R.D. (2000). *Environmental Forensics, Principles & Applications*. CRC Press, New York.
3. Gat, J.R. (1980). The isotopes of hydrogen and oxygen in precipitation. In: *Handbook of Environmental Isotope Geochemistry*. P. Fritz and J.Ch. Fontes (Eds.). Elsevier, Amsterdam, Vol. 1A, pp. 21–47.
4. Graig, H. and Lal, D. (1961). The production rate of natural tritium. *Tellus* **13**: 85–105.
5. Wade, S., Leap, D.I., and Fritz, S.J. (2001). Estimating Indiana groundwater age from tritium activities. *Geol. Soc. Am. Annu. Meet.* Abstract, November 5–8, 2001.
6. Dominico, P.A. and Schwartz, F.W. (1990). *Physical and Chemical Hydrogeology*. John Wiley & Sons, New York, pp. 526–527.
7. Tolstikhin, I.N. and Kamenskiy, I.L. (1969). Determination of groundwater ages by the T-He method. *Geochem. Int.* **6**: 810–811.
8. Schlosser, P. et al. (1988). Tritium/^{3}He dating of shallow groundwater. *Earth Planetary Sci. Lett.* **89**: 353–362.
9. Schlosser, P. et al. (1989). Tritiogenic ^{3}He in shallow groundwater. *Earth Planetary Sci. Lett.* **94**: 245–256.
10. Solomon, D.K. and Sudicky, E.A. (1991). Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge. *Water Resour. Res.* **27**(9): 2309–2319.
11. Solomon, D.K. et al. (1993). A validation of the ^{3}H/^{3}He method for determining groundwater recharge. *Water Resour. Res.* **29**(9): 2951–2962.
12. Aeschbach-Herrig, W. et al. (1998). A 3H/3He study of ground water flow in a fractured bedrock aquifer. *Ground Water* **36**(4): 661–670.
13. Bethke, C.M. and Johnson, T.M. (2002). Paradox of groundwater age. *Geology* **30**(2): 107–110.

RECHARGE IN DESERT REGIONS AROUND THE WORLD

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INTRODUCTION

Arid regions are characterized by dryness, variously defined as rainfall insufficient for crops without irrigation, evaporation/evapotranspiration rates greater than precipitation, or less than 25 cm of annual rainfall. Most of the true deserts are found between 15 and 50° latitude north or south of the equator. Dry regions in the Arctic and Antarctic are not normally classified as deserts, although parts of northern Greenland and the McMurdo Sound area of Antarctica have closed basins and saline lakes and, except for temperature, would be hard to distinguish from deserts at lower latitudes (1). Middle latitude deserts in the basin interiors of the continents are characterized by scant rainfall and high summer temperatures. The trade-wind deserts, notably the Sahara of North Africa, exhibit negligible precipitation and large daily temperature ranges. Recharge rates in arid regions typically range between 3 to 4% of precipitation (2); however, a rate as low as 0.066 mm/yr or 0.033% has been measured in the Rio Grande Basin, New Mexico (3).

General

Approximately one-tenth of the land surface of the planet is arid, and an equal or slightly greater area is classified as semiarid. Arid climatic conditions profoundly affect landscape topography and depositional setting, which controls aquifer type in nonindurated deposits. Erosion and transport by wind and water result in fluvial and aeolian deposits ranging from sand dunes to valley fill deposits of stratified sand, gravel, silts, and clays. Some desert basins lack thick alluvial deposits, and groundwater is found in fractured consolidated bedrock. Carbonate aquifers exhibiting karstic features are found in some deserts and are likely vestiges of tropical climates predating current arid conditions. Regardless of the fabric of the aquifer material, it is generally true that average annual rainfall less than 12 to 25 cm may be insufficient to allow recharge to an arid region aquifer. For this reason, the sustainability of groundwater resources in arid regions is of serious concern and the focus of numerous investigations.

Historical Background

Several recharge investigations have been conducted in the southwestern United States related to water resource management and artificial recharge of arid region aquifers using waters imported from distant sources. With the construction of the California Aqueduct, the Columbia River Project (Eastern Washington State), and the Central Arizona Project, large tracts of land in the arid American west have been studied to design and engineer enhanced recharge and aquifer storage and recovery (water banking) projects (4–9).

Following environmental regulatory compliance actions in the mid 1980s, aquifer vulnerability to contamination due to agricultural and industrial practices has been the focus of several studies (3,10–12). The design of the low-level radioactive waste disposal facility in Nevada has been supported by the Amargosa Desert Research Site under the United States Geological Survey (USGS) Low-Level Radioactive Waste Program arid recharge investigations (10,13,14).

In response to recognized water resource issues related to drought, the National Science Foundation Sustainability of Semi-Arid Hydrology and Riparian Areas (SAHRA) program was initiated in 2000 to facilitate the transfer of knowledge to support the development of water resources policy. This multi-institutional/multidisciplinary program has conducted

several studies on the Rio Grande and San Pedro/Gila River Basins (Arizona), including the Semi-Arid Land Surface Atmosphere (SALSA) project to investigate the watershed-basin-scale hydrologic water balance using remote sensing tools (15).

FUNDAMENTALS OF SUBSURFACE RECHARGE

Following Potter's (10) classification, arid and semiarid regions are those whose precipitation to evaporation (P/E) ratios are smaller than 0.5 and between 0.5 and 1.0, respectively. In addition to a lower net precipitation rate, rainfalls are typically infrequent and of short duration; high-intensity seasonal storms contribute a major portion of the annual rainfall over short periods of time. Under these conditions, the shallow soil surface layer infiltration capacity may be exceeded and excess overland flow propagates rapidly to flash flooding. Even low-intensity rainfalls, can lead to significant surface runoff when desert soil crusts have formed (16).

Water focused and concentrated by topography into ephemeral washes, wadis, sabkhas, and playas provides locations of enhanced recharge in arid areas. A significant component of recharge to arid basin aquifers occurs along mountain fronts. Important aspects along the mountain front include the partitioning of rainfall and snowmelt into surface runoff, deep infiltration along fractures and faults, and vegetation-controlled evapotranspiration (17). Focused flow along mountain stream channels into the major washes in the Tucson Basin (Arizona) visibly infiltrates flood-plain sediment, and surface water commonly does not leave the watershed (18). Half the annual recharge of 9 to 10 mm/year to the Ogallala Aquifer in the southern High Plains (Oklahoma and Texas) occurs through playa floors that cover only 6% of the aquifer land surface area (19).

Arid recharge requires the downward vertical flow of water in the unsaturated zone and an excess availability of water above the evapotranspiration demand. Once infiltrated, loss mechanisms in the unsaturated zone (uptake by plant roots, evaporation, and vertical vapor flow) increase the possibility that water never reaches an underlying deep aquifer (20). The measured ratio of groundwater recharge to precipitation ranges between 2 to 3% in most arid regions. An exception has been found, however, in the coastal sabkhas of Abu Dhabi, where measured recharge was approximately 90% of the mean annual precipitation of 70 mm. This high ratio is believed to be the result of several factors: the most important is the high water table, which allows infiltration to reach the saturated zone before evaporation within the vadose zone can occur (21). Fluid pathways in the unsaturated zone are inherently complex; transport distance and time of travel are significant factors that control arid region recharge rates. Because of this, unsaturated zone techniques are generally required to estimate recharge in arid regions (11).

Vadose Zone Capillary Flow

Capillary forces, together with gravity, determine fluid flow processes in unsaturated alluvium; finer grained materials respond like sponges so that there is no free drainage, even at high water content. Capillary rise causes water to move upward against the pull of gravity and takes place in small interstitial pores under negative soil water pressures that prevent free drainage. For example, it takes 1000 days for a water particle to travel though a 10 m deep vadose zone of fine sand whose volumetric soil water content is 0.15 and whose unsaturated hydraulic conductivity is 0.15 cm/day (the hydraulic gradient below the root zone equals unity, so water flux becomes equal to the hydraulic conductivity) (19). Capillary recharge through unsaturated fine-grained alluvium is unlikely in an arid setting.

In a study of recharge in the intermittent washes in the western Mojave Desert near Victorville, California, it was found that infiltration did not occur at control sites beyond the wash where water did not accumulate. Water did not pass the root zone, and the $\delta^{18}O$ and δ deuterium isotopic composition of water retained in the shallow coarse-grained soils were consistent with removal of water by vapor transport (9). Results from Southern Nevada research indicate that soil water may be as old as 120,000 years near the bottom of the deep (240–400 m) vadose zones, which shows there has been little or no infiltration of recent precipitation (14).

Vadose Zone Macropore Flow

"Macropore" is a common name for a wide range of large pores whose diameters are generally greater than 3 mm, such as cracks in clay soils, rock fractures, fissures in sediments, polygonal pressure cracks, pipes in the indurated calcic horizon, worm holes, and old root channels. Following precipitation that produces runoff and ponding, macropores that start at the soil surface quickly become conduits for recharge. The velocity of a water particle in a macropore in the soils from the previous example is approximately 30 cm/s, and it takes only 33 s for a water particle to travel 10 m from a ponded soil surface to the water table. Macropore transport reduces evaporation losses and results in a much larger recharge rate (19).

Techniques for quantifying macropore recharge were developed in the American southern high plains semiarid alluvial fan and dune aeolian deposits, where calculated recharge flux through macropores was between 60 and 80% of the total volume of recharge that reached the water table. Using a storm model to estimate rainfall-runoff with isotope geochemistry supporting the model simulations, 95% of the total recharge was found focused into 5% of the land area where water was focused into depressions and valleys (22).

In the southern high plains of Texas and New Mexico, recharge flux averages 9 mm/year regionally or approximately 2% of precipitation. Use of stable isotopes and tritium data indicate that approximately half of the recharge occurred in the floor of playa lakes that occupy 6% of the land area; much of the remaining recharge is believed to be from macropore flow (23).

MEASUREMENT TECHNIQUES

Approaches to quantify recharge vary depending on the climate, topography, and geology of the aquifer;

processes that control the spatial distribution and volume of infiltration that recharges arid aquifers are poorly understood. For these reasons, numerous techniques are typically used, and results are compared to calibrate the analyses.

Water Balance/Modeling

Rainfall/runoff modeling is widely used to estimate recharge where recharge is calculated as a residual of the water budget. This water budget approach assumes that deep drainage below the root zone will eventually reach the water table and become recharge, sometimes neglecting the potential for deep vapor fluxes to remove water from the system. When estimated as a residual in water balance models, recharge may be in error by an order of magnitude. In a study by Gee and Hillel (24), it was recommended that quantification of drainage by lysimetry and tracer tests should be used to calibrate qualitative model estimates. Modeling efforts that ignore seasonality or transient conditions cannot simulate recharge when average annual evapotranspiration exceeds precipitation (25,26). Arid site recharge studies found significant variability under similar climatic and soil conditions, but using different plant cover and topography, estimates of recharge based on fixed fractions of annual precipitation do not reflect the seasonal plant and soil factors that control recharge.

Chloride mass-balance methods that integrate temporal and aerial distribution of groundwater recharge have been found well suited to areas of large temporal and spatial variation in recharge. For small alluvial aquifers in the wadi systems of the A'Asir and A'Hijaz mountains of western Saudi Arabia, Bazuhair (2) found that recharge varied between 3% and 4% of precipitation using this technique.

Physical Measurement

Stream gaging, seepage meters, and lysimeters provide point estimates of recharge and discharge but are not representative of the entire system (24). Streamflow and groundwater data collected in the Rillito River in the Tucson Basin was compared to microgravity measurements that showed an increase in groundwater storage within the area of the floodplain. Coupled with neutron moisture readings and environmental tracer measurements, it was found that infiltration is controlled by geology and structure, where initial depths to groundwater were greatest (27–29).

Environmental Tracers—Recharge Sources

Many of the alluvial aquifers in the Basin and Range region of the American southwest were hydrologically closed during development, resulting in readily soluble evaporate material, such as gypsum and halite, interbedded with alluvial fill. The basin fill materials are typically of late Cenozoic age and consist of thousands of feet of coarse gravel to silt and clay derived primarily from igneous and metamorphic rocks eroded from the surrounding mountains. During precipitation that is intense enough to produce runoff in ephemeral streams, recharge to the aquifer occurs near the points where stream channels leave the mountains and flow across the alluvium. Recharge from ephemeral streams generally has low dissolved solids concentrations, but as water moves downward toward the zone of saturation and down-gradient, there is extensive opportunity for interaction between water and rock. This results in a regional geochemical pattern of groundwater chemistry where more dilute water occurs near recharge areas (4). High total dissolved solids (TDS), chloride, or boron concentrations indicate low water flux and concentration by evaporation within the vadose zone or long-term residence within the saturated zone (30). Mapping of geochemical tracers within the Middle Rio Grande Basin identified spatial patterns of recharge, and focused recharge was found beneath arroyos (13).

Other tracer methods include age-dating of groundwater with historical tracers such as bomb tritium, ^{36}Cl, carbon-14, and oxygen isotope/deuterium ratios (20). On the basis of carbon-14 data, most groundwater in the regional aquifer beneath Oro Grande Wash in the Mojave Desert was recharged between 5000 and 20,000 years ago (9). In the intensely arid region of the Western Desert of Egypt, deuterium data show that modern water cannot be the source of recharge for groundwater, and it is speculated that the waters derived either from distant recharge in Chad or the Sudan or are very old Pleistocene waters from a cooler glacial time (31). Oxygen isotope ratios can determine temperature and coincidental elevation of recharge waters, allowing for differentiation between winter storm/summer storm precipitation, mountain-front recharge, and snowmelt waters (18).

In the Trans-Pecos Texas, Chihuahuan Desert, $^{87}Sr/^{86}Sr$ ratios (in combination with other chemical and isotopic data) were used to infer flow paths and residence times of recharged water. Concentrated recharge was found within regional fracture trends in carbonate rocks in the highlands, losing streams on proximal portions of alluvial fans, and irrigation return flow along well casings (32).

Environmental Tracers—Recharge Rates

Mapping of environmental tracers allows the investigator to find recharge sources, but it is often more difficult to quantify recharge rates. Artificial tracer tests of soil moisture through unsaturated, poorly sorted, horizontally stratified alluvial deposits found that transport takes place along preferential flow paths. Bromide was used as a tracer to measure the velocity of soil moisture, which ranged from approximately 55 to 275 cm per day on a test plot where water was artificially applied to natural soils (6).

Because recharged water from desert washes also spreads laterally away from the wash as depth increases, the flux of water decreases with increasing depth. In addition, arid soils are less permeable beyond the channel due to deposition of soluble salts (9); therefore, quantifying recharge rates in these settings is difficult.

Studies from the Amargosa Desert in southern Nevada, the Middle Rio Grande Basin in north-central New Mexico, and the Palouse Catena of the Columbia River regional aquifer in southeastern Washington were used to compare tracer-based recharge estimates with water-balance models. Mean annual precipitation at the three study areas was approximately 0.1, 0.25, and 0.5 m per

year, respectively. Estimates of groundwater recharge were derived from vadose zone profiling of chloride, stable isotopes, and tritium and compared. The geochemical chloride profiles suggested that recharge rates are in approximate equilibrium with current climatic conditions. This was corroborated by isotopic and hydraulic data; however, chloride profiles at the driest sites suggested features that could be interpreted as relicts of past wetter conditions (13,25,26,33).

Mapped geochemical and isotopic data reflect recharge from basin margins and from the Rio Grande River in the Middle Rio Grande Basin, New Mexico. Isotopically depleted waters were some of the oldest waters in the basin and represent water recharged in the area of the Jemez Mountains during the last glacial period about 20,000 years ago. Younger waters, about 7,000 years old, were also mapped along the basin margins. Radiocarbon ages were used to estimate modern and paleorecharge rates, and recharge rates during the last glacial period were estimated to be at least six times greater than the modern radiocarbon-based recharge (34).

INCIDENTAL RECHARGE

Arid land recharge may include incidental recharge due to environmental pollutant releases, irrigation return flow, canal seepage, sewage effluent seepage in dry washes, and seepage from surface impoundments such as stormwater retention ponds. The evidence for irrigation and industrial-related recharge includes the presence of pesticides, caffeine, pharmaceuticals, and other chemical pollutants in groundwater (20,35), although it should be recognized that some contaminant chemicals may be transported through the subsurface by nonaqueous means. Treated municipal wastewater released into ephemeral, effluent-dependent stream channels is an important source of recharge in some regions (36). The Santa Cruz River in south-central Arizona contributes 6.0 acre-feet/day/mile to the subsurface, or approximately 80% of the flow volume results in recharge (37).

SUMMARY

Hydrologic processes in arid or semiarid lands are distinctly different from those in humid climates and exhibit wide variation in magnitudes and type of recharge. Precipitation that results in focused flow and ponding allows macropore transport of recharge, whereas loss mechanisms in the unsaturated zone allow unsaturated water or vapor flux to occur in either vertical direction, depending on surface conditions. Recharge studies use a combination of approaches, such as thermal and geophysical techniques, geochemical tracers, radioisotopes, and unsaturated zone modeling calibrated against streamflow and groundwater level information to characterize this complex hydrologic process (28). Extremes in temperature and precipitation in arid regions necessitate focused consideration of the amount and distribution of recharge to the aquifers so as to manage limited water resources adequately.

BIBLIOGRAPHY

1. Davis, S. and DeWiest, R.J.M. (1966). *Hydrogeology*. John Wiley & Sons, New York.
2. Bazuhair, A.S. and Wood, W.W. (1996). Chloride mass-balance method for estimating ground water recharge in arid areas; examples from western Saudi Arabia. *J. Hydrol.* **186**(1–4): 153–159.
3. Daniel B. Stephens & Associates, Inc. (1996). *Estimation of Infiltration and Recharge for Environmental Site Assessment*. American Petroleum Institute, Albuquerque, NM, Health and Environmental Sciences Department, Publication Number 4643.
4. Hem, J.D. and Robertson, F.N. (1987). Hydrogeochemistry of ground water recharge in alluvial aquifers, Southern Arizona. *Symp. Proc., 3rd Symp. Artificial Recharge Groundwater in Arizona*. May 20–21, 1987. Salt River Project, Phoenix, AZ, pp. 30–51.
5. Drost, B.W., Whitman, K.J., and Gonthier, J.B. (1990). *The Geologic Framework of the Columbia Plateau Regional Aquifer System, Washington, Oregon, and Idaho*. U.S. Geological Survey, Water-Resources Investigation Report 87–4238.
6. Graham, D.D. (1991). Results and significance of an unsaturated-zone tracer test at an artificial-recharge basin, Tucson, Arizona. *Symp. Proc., 5th Bienn. Symp. Artificial Recharge Groundwater*, May 29–31, 1991. Salt River Project, Phoenix, AZ, pp. 30–51.
7. Rockhold, M.L., Fayer, M.J., Kincaid, C.T., and Gee, G.W. (1995). *Estimation of Ground Water Recharge for the Performance Assessment of a Low-Level Waste Disposal Facility at the Hanford Site*. Battelle Pacific Northwest Laboratory, Richland, WA.
8. Watson, M. (1999). *Final Technical Memorandum, Identification of Candidate Recharge Areas and Pilot Test Sites, Farmington Groundwater Recharge/Wetlands Feasibility Study*. U.S. Army Corps of Engineers.
9. Izbicki, J.A., Michel, R.L., and Martin, P. (2000). Chloride and tritium concentrations in a thick unsaturated zone underlying an intermittent stream in the Mojave Desert, Southern California. *Conf. Proc. Nat. Recharge Groundwater Symp.*, June 2, 2000, Tempe, AZ, pp. 1–8.
10. Potter, L.D. (1992). Desert characteristics as related to waste disposal. In: *Deserts as Dumps? The Disposal of Hazardous Materials in Arid Ecosystems*. C.C. Rwith and B.M. Thomson (Eds.). Univ. of New Mexico Press, Albuquerque, NM, pp. 21–56.
11. Scanlan, B.R., Tyler, S.W., and Wierenga, P.J. (1997). Hydrologic issues in arid, unsaturated systems and implications for contaminant transport. *Rev. Geophys.* **35**(4): 461–490.
12. Desconnets, J.C., Taupin, J.D., Lebel, T., and Leduc, C. (1997). Hydrology of the HAPEX-Sahel Central Super-Site: Surface water drainage and aquifer recharge through the pool system. *J. Hydrol.* **188–189**(1–4): 155–178.
13. Stonestrom, D.A. (1999). What do environmental tracers say about patterns of ground water recharge, past and present? Examples from the Amargosa Desert, Rio Grande Basin, and Palouse Catena. *Geological Society of America, 1999 Annu. Meet., Abstracts with Programs—Geological Society of America*, Oct. 25–28, 1999, p. 87.
14. Tyler, S.W. (1999). Ground water recharge in arid regions: Questions about today and the past? (Abstract) Ground water supply issues in the next century. *NGWA National Convention and Exposition*, Dec. 3–6, 1999, p. 7.

15. Goodrich, D.C., Chehbouni, A., Goff, B., MacNish, B., Maddock, T., Moran, S., Williams, D.G., and Watts, C. (1998). *An Overview of the 1997 Activities of the Semi-Arid Land-Atmosphere (SALSA) Program*. American Meteorological Society. Special Symposium on Hydrology. Phoenix, AZ.
16. Abu-Awwad, A.M. and Sharanawi, M.R. (1997). Water harvesting and infiltration in arid areas affected by surface crust: Examples from Jordan. *J. Arid Environ.* **37**: 443–452.
17. Wilson, J.L. and Guan, H. (2004). *Mountain-Block Hydrology and Mountain-Front Recharge*. F.M. Phillips, J.F. Hogan, and B. Scanlon (Eds.). Water Resources Monograph Series. American Geophysical Union, Washington, DC.
18. Eastoe, C.J. (2003). Locating recharge zones with isotopes. *Southwest Hydrol.* **January/February**: 22–23.
19. Hendrickx, J.M.H. and Walker, G.R. (1997). Recharge from precipitation. In: *Recharge of Phreatic Aquifers in (Semi-) Arid Areas*. I. Simmers (Ed.). Vol. 19, International Association of Hydrogeologists, Balkema, Rotterdam, the Netherlands, pp. 19–114.
20. Scanlon, B.R. (in press). *Evaluation of Methods for Estimating Basin Scale Recharge in Semiarid and Arid Regions. Recharge and Vadose Zone Processes: Alluvial Basins in the Southwestern United States*. F.M. Phillips, J.F. Hogan, and B. Scanlon (Eds.). Water Resources Monograph Series. American Geophysical Union, Washington, DC.
21. Sanford, W.E. and Wood, W.W. (1999). A large recharge/precipitation ratio on the coastal sabkhas of Abu Dhabi. *Geological Society of America, 1999 Annu. Meet.*, *Abstracts with Programs—Geological Society of America*, Oct. 25–28, 1999, pp. 214–215.
22. Wood, W.W., Rainwater, K.A., and Thompson, D.B. (1997). Quantifying macropore recharge: Examples from a semi-arid area. *Ground Water* **35**(6): 1097–1106.
23. Wood, W.W. and Sanford, W.E. (1995). Chemical and isotopic methods for quantifying ground water recharge in a regional, semiarid environment. *Ground Water* **33**(3): 458–468.
24. Gee, G.W. and Hillel, D. (1988). Groundwater recharge in arid regions: Review and critique of estimation methods. *Hydrological Processes* **2**(3): 255–266.
25. Walvoord, M., Phillips, F.M., Tyler, S.W., and Hartsough, P.C. (2002). Deep arid system hydrodynamics, Part 2: Application to paleohydrologic reconstruction using vadose-zone profiles from the Northern Mojave Desert. *Water Resour. Res.* **38**(12): 1291. doi: 10.1029/2001 WR000825.
26. Walvoord, M. and Phillips, F.M. (in press). Deep arid system hydrodynamics, Part 3: Vegetation control on desert-floor recharge. *J. Hydrol.*
27. Pool, D.R. and Wellman, J. (1998). Streamflow infiltration and ground-water recharge along Rillito Creek in response to the El Nino-related precipitation in 1992–93 and in 1998. *11th Annu. Symp. Arizona Hydrological Society*, September 23–26, 1998, Tucson, AZ.
28. Hoffman, J.P. (1999). Recharge processes studied in Rillito Creek, Tucson, Arizona. *12th Annu. Symp*. Arizona Hydrological Society, Pinetop-Lakeside, AZ, September 9–11, 1999.
29. Bailey, M.A., Hoffmann, J.P., and Ferre, P.A. (2000). *Investigation of Subsurface Temperature Variations to Quantify Infiltration in an Ephemeral Stream, Tucson, Arizona*. Geological Society of America, *Abstracts with Programs—Geological Society of America*, Nov. 9–18, 2000, p. 185.
30. Hoffman, J.P. and Steinfampf, W.C. (1999). A study of recharge processes in an ephemeral stream in Tucson, Arizona. *Proc. 9th Bienn. Symp. Artificial Recharge of Groundwater*, Tempe, AZ, June 10–12, 1999, pp. 49–55.
31. Landis, G.P. et al. (1997). Reconnaissance hydrogen isotope geochemistry of Egyptian ground waters. *Ann. Geol. Surv. of Egypt* **20**(Part II): 655–673.
32. Sharp, J.M. and Uliana, M.M. (1998). Regional groundwater flow in a semi-arid region—controls of fracture systems in carbonate units. *Geological Society of America Symp.*, Toronto, Canada. Presentation and Abstract.
33. Walvoord, M., Plummer, M.A., Phillips, F.M., and Wolfsberg, A.V. (2002). Deep arid system hydrodynamic, Part 1: Equilibrium states and response times in thick desert vadose zones. *Water Resour. Res.* **38**(12): 1308. doi: 10.1029/2001 WR000824.
34. Plummer, L.N. (2002). Environmental tracers and how they are used to understand the aquifer. In: *Ground Water Resources of the Middle Rio Grande Basin*. J.R. Baroline and J.C. Cole (Eds.). U.S. Geological Survey Circular 1222, pp. 82–83.
35. Seiler, R.L., Zaugg, S.D., Thomas, J.M., and Howcroft, D.L. (1999). Caffeine and pharmaceuticals as indicators of waste water contamination in wells. *Ground Water* **37**(3): pp. 405–410.
36. Sinclair, K. (1999). *City of Moses Lake, Dunes Municipal Waste Water Treatment Plant, Class II Ground Water Inspection*. Washington State Department of Ecology, Environmental Assessment Program. Water Body No. WA-41-9289GW. Olympia, WA.
37. Wilson, L.G., DeCook, K.J., and Neuman, S.P. (1980). *Regional Recharge Research for Southwest Alluvial Basins*. Water Resources Research Center, University of Arizona, Tucson, AZ.

HYDROLOGIC FEASIBILITY ASSESSMENT AND DESIGN IN PHYTOREMEDIATION

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SUMMARY OF PRACTICAL IMPLICATIONS

Several design considerations for phytoremediation are based on the capability of trees to remove contaminated water from aquifers. These capabilities depend upon the amount of water that can be withdrawn, the vertical distribution of contaminants, and flow patterns in the aquifer. For each of these, an example field site is given where methods were applied to quantify the characteristics. These include a model of forest evaporation for estimating the balance between precipitation and evapotranspiration, a simple model of recharge-driven plume diving, and the use of groundwater flow modeling for assessing various features of the groundwater flow.

ASSESSMENT AND CHARACTERIZATION OF PHYTOCONTAINMENT

To clean up a contaminated site, characterizing the type and extent of pollutants at the site and developing a

conceptual remediation plan are essential. A proficient plan covers the expected effectiveness of the remedial technology, projection of the time required to achieve cleanup, and cost. The best way of assessing these factors is to use models to determine the capability of the existing or projected vegetation to contribute to the control and cleanup of the site. No other method has proven applicable and useful for projecting future scenarios, especially for selection and design.

Phytohydraulic containment (1) of contaminated groundwater depends on the evapotranspiration rate exceeding the flow rate of groundwater from the water table down to the lowest extent of the contaminated plume. Phytodegradation and phytotransformation require that the contaminants be in contact with the plants, rhizosphere microorganisms, and any associated exogenous enzymes, all of which can degrade or transform pollutants. Because roots grow from the surface downward to the water table and remain in the capillary zone in most cases, the main factor influencing the effectiveness of phytoremediation is the ability of the plants to draw contaminated water to the roots. Two critical elements are the rate and amount of water withdrawn directly from the aquifer (*versus* soil water from precipitation) and the vertical distribution of contaminants. In other cases to be illustrated in this chapter, plant control of infiltration will limit leaching from contaminated soil. Thus, the local water balance is the vital basis for the assessment and design of phytoremediation to control and remove soil and shallow groundwater contaminants.

The physiologies of vegetation at a site, local hydrology and geology, and the chemical characteristics of the contaminants control the leaching and uptake of contaminated water. The capabilities to transpire large amounts of water, to put roots into the capillary or phreatic zones, and to tolerate stress from other plants and wildlife, contaminants, disease, and occasional lack of nutrients and water are the vital plant attributes for phytocontainment and treatment. The local hydrology involves meteorology (precipitation, wind speed and direction, and air temperature); interception; surface conditions that control runoff *versus* infiltration; percolation through the vadose zone; quantity of flow and direction; and change in storage in the surficial aquifer. The local soil stratigraphy, porosity and hydraulic conductivity of different layers, and hydraulic gradient are the important hydrogeologic factors. The dominant chemical characteristic is the extent of sorption and uptake.

The art of using vadose and groundwater models and measurements to assess and design phytohydraulic control and treatment is progressing rapidly. Hong et al. (1) used modeling to guide the field design of a methyl *tertiary*-butyl ether (MTBE) phytoremediation application in Houston, Texas. They simulated the saturated and unsaturated zones and established that deep-planted (approximately 5 meters or 15 feet) hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN-34' 'Imperial Carolina') trees could control this shallow methyl *tertiary*-butyl ether plume after full canopy development. Field studies are underway to confirm the projections. Quinn et al. (2) estimated the effects of hybrid poplars (*Populus trichocarpa* × *Populus deltoides*) planted to a depth greater than 8 meters (25 feet) into a confined aquifer at Argonne National Laboratory near Chicago, Illinois. Simulations with the U.S. Geological Survey standard groundwater model MODFLOW and the associated particle tracking code indicate that a high degree of containment should be achieved after tree canopy closure. Extensive parts of the trichloroethylene contaminated confined aquifer are expected to be dewatered, or nearly so, on a seasonal basis. Eberts et al. (this book) and Hirsch et al. (this book) along with this chapter, complete a summary of the pioneering work with vadose and phreatic zone modeling to assess and design phytocontainment and treatment systems based on evapotranspiration. Landmeyer (3) reviews some of the measurement techniques that may be useful in phytocontainment and treatment assessments. Ferro et al. (4) reviews measurement and assessment techniques (not involving modeling) applied at a petroleum hydrocarbon contaminated site in Ogden, Utah.

This chapter presents three field examples that illustrate important design considerations for the application of phytoremediation to shallow aquifer contamination. The first case presents a method for estimating the effective evapotranspiration rate for a site in Joliet, Illinois. The second case illustrates the need for vertical characterization of plumes in general by introducing a clear-cut example of a landscape feature that causes plume diving. Hydrogeologic features that cause plumes to migrate deeper into aquifers work against phytoremediation because of the increased evapotranspiration required to control the plume. The second case study also reveals that conventional monitoring approaches that use long-screened wells have a great potential for missing plumes or underestimating the length. The third case explores a proposed phytoremediation system at a site in Florida where a contaminant plume dived upon emerging from under a paved area. Methods to control the vertical location of the plume and potential application of phytoremediation are assessed using the U.S. Geological Survey modular groundwater flow model, MODFLOW (5).

AVERAGED TRANSPORT THROUGH THE VADOSE ZONE

Joliet Army Ammunition Plant

Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) plumes were found in the shallow aquifer at the Joliet Army Ammunition Plant. Figure 1 shows the area in a 1:7200 scale aerial photograph of the site. Of primary interest was a forested area along the banks of Prairie Creek. In this area of the site, there is a possibility either of naturally occurring phytoremediation by existing trees or of enhancing phytoremediation by planting new trees. Either option depends upon the capability of the trees to remove contaminants from the shallow aquifer. The objective of the work at the Joliet plant was to assess the potential for net withdrawal of water from the aquifer.

The photograph reveals some of the irregular nature of the forest cover in this area. A significant fraction of the forested area consists of a lower density of forest cover where lower evapotranspiration rates would be expected.



Figure 1. Aerial photograph (1:7200) of the Joliet Army Ammunition Plant site showing Prairie Creek and the forested area overlying the contaminated aquifer. Note that the side of the photograph is oriented north and south.

A vegetation survey conducted at the site showed that the lower density forests contained a number of dead or dying trees. Thus, the role of the existing vegetation in phytoremediation of the contaminant plume depends on the influence of the forest cover and the capability to continue extracting water in the future over this section of the groundwater flow path. Because of the relatively low quality of the existing vegetation, replanting with young trees [hybrid poplars (*Populus* spp.) or willows (*Salix* spp.)] or native prairie grasses might provide a more sustainable treatment system.

Evapotranspiration Estimates

Several equations have been developed for estimating evapotranspiration. The most applicable for this analysis is the Penman-Monteith equation (6). This equation is based on a site energy budget. The budget is based on (1) calculation of all the short- and long-wave energy available for evaporation at the plant canopy, and (2) water vapor diffusing out of the leaves, controlled by the surface or stomatal resistance, and then out into the atmosphere, controlled by aerodynamic resistance (7). The equation for evapotranspiration ET in millimeters per day is as follows

$$ET = \frac{1}{\lambda}\left[\frac{\Delta A + \rho_a c_p \dfrac{D}{r_a}}{\Delta + \gamma\left(1 + \dfrac{r_s}{r_a}\right)}\right] \quad (1)$$

where λ is the latent heat of vaporization equal to $2.501 + 0.002361\ T_w$ in million joules per kilogram, in which T_w is the water temperature at the interface with the air; Δ is the gradient of the saturated vapor pressure in kilopascals per °C; A is the available energy in million joules per square meter per day; ρ_a is the density of moist air in kilograms per cubic meter equal to $3.486P_a/(275 + T_a)$, in which P_a is atmospheric pressure in kilopascals and T_a is air temperature in °C; c_p is the specific heat of moist air equal to 1.013 kilojoules per kilogram per °C; D is the vapor pressure deficit in kilopascals at a reference height; r_a is the aerodynamic resistance in seconds per meter; γ is the psychrometric constant in kilopascals per °C equal to $c_p P_a/(1000\varepsilon\lambda)$, in which ε is the ratio of the molecular weight of water vapor to that of dry air or 0.622; and r_s is the surface resistance of the land cover in seconds per meter that also includes the effect of vegetation. [See Shuttleworth (7) for a description of the reference grass or crop method to estimate relative resistance of a different vegetative land cover.] Most of these variables are strongly related to the meteorological conditions of the site, affirming that the feasibility and success of phytocontainment is very site specific.

A practical approach (7) for estimating evapotranspiration, based on the energy balance and aerodynamic effects, uses generalized long-term climatic data to approximate evapotranspiration. For the evaluation at the Joliet site, existing climatic data were used to estimate evapotranspiration. In the U.S., the Solar and Meteorological Observation Network, SAMSON (8), provides hourly climate observations recorded for a 30-year period (1961 to 1990) from 239 stations located around the country. The data from SAMSON include (1) hourly precipitation (rainfall and snowfall) amounts, (2) air temperature, (3) percent cloud cover, (4) solar radiation, and (5) relative humidity. These data provide the means to estimate averaged hourly, daily, monthly, or annual evaporation amounts for locations in all parts of the U.S. For Joliet, the nearest SAMSON station is located at Chicago. The complete hourly SAMSON file for this station consists of approximately 38 megabytes of data. Practical use of these data in Equation (1) requires post processing to generate, in this case, monthly rainfall and climatic estimates from the 28-year-long record for the Chicago station.

Tables 1 and 2 give a summary of the processed SAMSON data for the Chicago station. These values were used in Equation (1) to generate the forest evapotranspiration estimates given in Table 3. The net extraction, defined here as the potential evapotranspiration less the rainfall, gives an estimate of the amount of water that the forested area near Prairie Creek can remove from the aquifer. For the months of December through March, the net extraction is assumed to be zero because average temperatures were less than 4.4 °C (40 °F). Thus, in the warmer months of the year, the estimated evapotranspiration exceeds the amount of water available from rainfall. Net extraction ranges from 222 to 348 millimeters per month. These correspond to 2.4×10^5 to 3.7×10^5 gallons per acre per month.

Table 1. Monthly Storm Statistics Determined from the SAMSON Database for the Chicago Station

Month	Average Interarrival Time (days)	Average Depth (Millimeters)	Average Storm Duration (hours)	Average Number of Storms
January	1.70	2	0.133	18.0
February	1.59	2	0.123	16.3
March	1.55	3	0.140	19.3
April	1.39	4	0.128	20.3
May	1.69	5	0.113	17.1
June	3.07	6	0.099	15.9
July	2.21	7	0.100	14.2
August	2.13	8	0.105	14.5
September	1.99	6	0.106	14.9
October	2.07	4	0.125	14.5
November	1.72	4	0.143	17.7
December	1.55	3	0.144	19.3

Table 2. Monthly Temperature and Relative Humidity Statistics Determined from the SAMSON Database for the Chicago Station

Month	Average Temperature (°C)	Minimum Temperature (°C)	Maximum Temperature (°C)	Average Dew Point Temperature (°C)	Average Relative Humidity
January	−5.83	−32.2	17.8	−10.19	0.72
February	−3.33	−25.0	21.7	−7.86	0.71
March	2.82	−22.2	30.6	−2.49	0.70
April	9.21	−13.3	32.8	2.17	0.65
May	15.16	−4.4	33.9	7.70	0.64
June	20.47	3.3	39.4	13.10	0.66
July	23.12	5.6	38.9	16.53	0.68
August	22.14	5.0	37.8	16.17	0.71
September	18.01	−1.1	36.1	12.10	0.71
October	11.59	−7.2	32.2	5.35	0.69
November	4.67	−17.2	24.4	−0.19	0.73
December	−2.66	−31.7	21.7	−6.74	0.76

Table 3. Monthly Estimated Evapotranspiration, Rainfall, and Net Extraction Estimates Determined from the SAMSON Database for the Chicago Station and the Forest Evapotranspiration Equation (1)

Month	Estimated Evapotranspiration (Millimeters Per Day)	Estimated Evapotranspiration (Millimeters)	Monthly Precipitation (Millimeters)	Net Extraction (Millimeters)	Net Extraction (Gallons Per Acre)
January	4.87	151	42.7		
February	6.21	174	34.7		
March	9.88	306	66.6		
April	11.34	352	92.3	259	2.8×10^5
May	12.22	379	86.4	293	3.1×10^5
June	14.80	444	95.7	348	3.7×10^5
July	13.85	429	99.0	330	3.5×10^5
August	12.27	380	118	262	2.8×10^5
September	10.42	313	90.6	222	2.4×10^5
October	8.62	267	63.1	204	2.1×10^5
November	5.75	173	77.7	95	0.4×10^5
December	5.50	171	65.2		

The estimated amount of water evaporated and transpired in excess of the rainfall amount was assumed to be drawn from the aquifer. This analysis assumed, however, that the trees can draw water from the aquifer without hydraulic limitation. The depth to the aquifer and the low hydraulic conductivity of the aquifer materials limit the actual rate of withdrawal. Another limitation was the variable density of vegetation in the forest. Dead or dying trees reduce the amount of water extracted from the aquifer. This analysis suggested that in the absence

of site-specific evapotranspiration measurements, which would quantify how the existing vegetation actually draws water from the aquifer, there is the potential for the trees to create a net withdrawal of water from the Joliet surficial aquifer during the summer months. Nevertheless, additional site investigation and performance monitoring of any phytoremediation remedy is necessary. These feasibility and application procedures require collection of site-specific climatic and hydrogeologic data to verify and adjust the forecasts from Equation (1). Sap-flow measurements and sampling of tissues from trees are necessary to provide verification of remediation efficacy.

VERTICAL CHARACTERIZATION OF CONTAMINANT DISTRIBUTIONS

Typical Characteristics of Surficial Aquifers

With a positive potential for withdrawal of water from an aquifer, there are at least two important additional considerations. First is the vertical location of contaminants in the aquifer. Before being able to assess the prospects for removal, accurate delineation of contamination is required. The following example describes a case where accurate vertical delineation was used to reveal, in addition to the distribution of contaminants, landscape features that were responsible for diving of the plume (9). Because the contaminants move with the water, the location of aquifer recharge is also an important consideration for phytoremediation to be successful. This case indicates clearly that phytoremediation, which is dependent upon the capability of trees to remove water from the top of an aquifer, requires an understanding of the vertical distribution of the contaminants. The second consideration is the depth to which water is removed from the surficial aquifer. At each site, these recharge and discharge zones are important determinants of the groundwater flow. The importance of characterizing recharge, evapotranspiration, and discharge is illustrated in a second example where phytoremediation was considered to remediate a chlorinated solvent plume. See the section "Feasibility Investigation for Phytohydraulic Containment and Treatment."

Vertical dimensions that are small relative to the length of the flow system characterize many aquifers. In order to better visualize the stratigraphy or vertical distribution of contaminants, however, commonly drawings are vertically exaggerated, which visually exaggerates the importance of vertical variations. Aquifers and some contaminant plumes can extend over distances of kilometers at least, whereas the thickness is of the order of meters. This results in ratios of length to thickness on the order of 100:1. For analysis of the flow at water tables or in surficial aquifers, the approach taken by Dupuit and Forchheimer (10) recognizes the two orders of magnitude difference in scale. The approach also uses the assumptions that the head in the aquifer is depth-independent (vertical potentials) and that the discharge is proportional to the slope of the water table (Darcy's equation).

Two more observations are significant. First, because the hydraulic conductivity of a confining layer is orders-of-magnitude lower than that of an aquifer, flow in the confining layer tends to be almost vertical (11). Thus, because of the typical scale, the flow in the aquifer is nearly horizontal as a consequence of vertical potentials and nearly vertical in confining units as a consequence of permeability distributions. Conceptually, the three-dimensional character of flow has been reduced to aquifers with planar flow and confining units with vertical flow. The second important observation concerns the apparent dilution of contaminant plumes that is commonly characterized by aquifer dispersivity. In tabulating dispersivity, Gelhar et al. (12) stated that vertical dispersivities in aquifers were not often measured, but that available data suggested that the values of vertical dispersivity were two orders-of-magnitude lower than longitudinal dispersivity. Therefore, the dilution of plumes over the thickness of the aquifer is likely to be minimal when compared to longitudinal dispersion. The conventional explanation for the difference in dispersivities is that sediments resulting from depositional systems have a preferential orientation—that of the water that deposited the sediments. The practical implication is that transport of contaminants perpendicular to main direction of deposition is minimized.

The conclusions drawn from these observations are that water entering the aquifer vertically is turned so that flow is nearly horizontal. This follows from the Dupuit observations. As recharge accretes along the length of the flow path, more and more water is added to the aquifer. Because of continuity and limited vertical dispersivity, this water is added to the top of the aquifer and contaminant plumes appear to "dive" or move deeper into the aquifer. Likewise, when removed from a surficial aquifer due to evapotranspiration, water is removed from the top and a contaminant plume would appear to rise back to the water table. Such flow characteristics are similar in concept to the classic work of Toth (13) but consistent with the scaling observations of Dupuit and Forchheimer.

At some sites, unlined drainage ditches, leaking water mains and sewer pipes, irrigation, and the flow pattern in the aquifer can determine the vertical distribution of contaminants. Where recharge is the likely cause of diving, the amount of water that infiltrates into the area above the plume, and the amount that this recharge contributes to flow in the aquifer determine where and how much diving will take place.

Plume Diving: East Patchogue, New York

A gasoline release at an East Patchogue, New York, underground storage tank (*i.e.*, UST) facility created large benzene, toluene, ethylbenzene and xylene (BTEX), and methyl *tertiary*-butyl ether (MTBE) plumes. The plumes were detected because the contaminants showed up in a private water supply well, located 1200 meters (4000 feet) down gradient from the source. The well screen was about 15 meters (50 feet) below the water table, where much of the methyl *tertiary*-butyl ether mass was located. The site investigation started at this point and proceeded up gradient to identify the source.

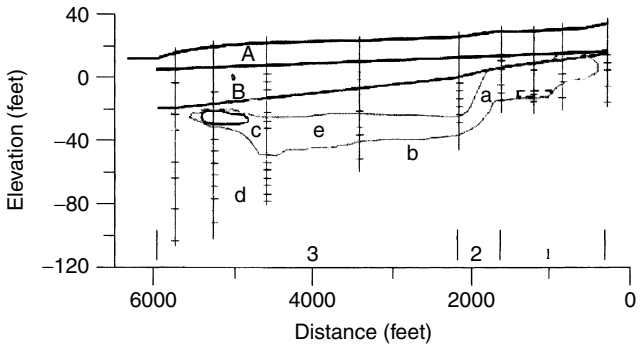


Figure 2. Vertical section through the xylene, benzene, and methyl *tertiary*-butyl ether plumes at East Patchogue, New York. A leaking tank was located at the right-hand edge of the drawing and the flow is to the left. The aquifer was divided into three recharge zones labeled 1, 2, and 3 below the plumes. In zones 1 and 3, the recharge was 559 millimeters per year (22 inches per year), whereas zone 2 recharge dominated by a gravel pit was 1120 millimeters per year (44 inches per year). The water table is marked "A" and the predicted top of the plumes by "B" (see www.epa.gov/athens/onsite for how the top of the plumes was derived). The plume labels are xylene: a—concentrations of 1000 micrograms per liter; benzene: b—100 micrograms per liter and c—1000 micrograms per liter; and methyl *tertiary*-butyl ether: d—100 micrograms per liter and e—1000 micrograms per liter. Note that 1 foot is equal to 0.3048 meter.

Because of the importance of the aquifer for drinking water supply, the State of New York undertook an extensive investigation of the site that included vertical characterization of the plumes. Multilevel samplers with 15-centimeter (6-inch) screens at 1.5-meter (5-foot) intervals were used. A resulting vertical section through the plume showed that BTEX and methyl *tertiary*-butyl ether tended to dive into the aquifer with distance from the source (Fig. 2). Furthermore, a significant amount of diving occurred as the benzene and xylene plumes passed under a gravel pit. At East Patchogue, the maximum depth of the hydrocarbon plumes reached 7.62 meters (25 feet) below the water table.

By studying the well logs and performing a detailed hydraulic characterization of the aquifer with a borehole flowmeter, vertical migration controlled by stratigraphy was ruled out because the hydraulic conductivities varied by less than a factor of two over the aquifer. Weaver et al. (14) present an Internet calculator for plume diving in simple aquifer systems (www.epa.gov/athens/learn2model) that is based on a mass balance and Dupuit-Forchheimer flows in aquifers (15). The calculator reproduces the upper bound on the contaminant distribution by accounting for enhanced recharge from the gravel pit (Fig. 2). Because of the lack of stratigraphic evidence for preferential flow paths and the ability of the model to reproduce the observed plume diving, recharge-driven plume diving is the likely reason for the observed vertical distribution of the contaminants at East Patchague (9).

This example sheds light not only on how recharge pushes the plume downward, but also what happens when water discharges from aquifers. Where water comes up at discharge points, so will the contaminants: along wetlands, streams, rivers, lakes, or the ocean. The ocean is the expected destination of the methyl *tertiary*-butyl ether plume at East Patchogue, where the groundwater discharges into Great South Bay, adjacent to the southern shore of Long Island. The groundwater and contaminants move upward as the plume approaches the discharge point at the bottom of the Bay.

Despite the low vertical dispersivity, contaminant distributions still, of course, vary over the vertical. This was seen in the East Patchogue plume where the maximum concentration at each sample location was higher than the average taken over the entire plume thickness. With conventional sampling techniques, there is effective averaging over the length of the well screens used. With no knowledge of the underlying vertical contaminant distribution, the well screen might be placed anywhere relative to the contaminant distribution. This could easily lead to well screens that sample part of the contaminant distribution and part clean water. The resulting concentrations will be between undetectable and the maximum for the location [(14); see the average borehole concentration calculator that is a part of the OnSite system at www.epa.gov/athens/onsite for a specific example]. Therefore, the same hydrologic characterization of a plume determines the feasibility for phytohydraulic containment and treatment, and also cost effectively dictates when and where the cleanup should be monitored.

FEASIBILITY INVESTIGATION FOR PHYTOHYDRAULIC CONTAINMENT AND TREATMENT

The Orlando Naval Training Center is one of thousands of U.S. Department of Defense facilities contaminated with chlorinated solvents. The plume is shallow and within the rooting depth of proven phytoremediation approaches using tree planting. The Training Center has been closed and the Navy is cleaning up and preparing the site to be turned over to the City of Orlando. As such the Naval Southern Command in Charleston, South Carolina has pilot tested a number of innovative remediation methods. One of the methods investigated was the use of phytoremediation to cost effectively clean up the plume. For this purpose, the EPA National Exposure Research Laboratory in Athens, Georgia was requested by the Navy to establish guidelines for determining the feasibility of applying phytocontainment and treatment and to apply those guidelines at the Orlando Naval Training Center.

The initial phase involved (1) designating appropriate characterization data for an assessment, (2) selecting the appropriate flow and transport models from a multimedia context, (3) vegetation surveys for indigenous phytoremediation potential (conducted by Navy forester), (4) pioneering sap-flow measurements of existing trees and extrapolation to stand-level estimates of existing evapotranspiration for assessments, (5) projecting improved evapotranspiration from replanting, and (6) assessing chlorinated solvent degradation rates in various media by vegetation and microorganisms. This section reports

on the selection and application of appropriate models for assessment of the feasibility of phytocontainment and treatment. Existing stand assessments of evapotranspiration and projections were conducted by the U.S. Forest Service Coweeta Hydrologic Laboratory (16) based on sap-flow measurements and extrapolation and projection methods as described in Vose et al. (this book). Nzengung (17) collected vegetation from the site, soil and aquifer cores, and wetland and lake sediments to determine the level of ongoing attenuation. These laboratory incubations provide expected rates and kinetics of degradation and transformation of tetrachloroethylene and trichloroethylene that contaminate the site.

This section covers all other important components of a feasibility investigation—selecting and setting up a groundwater model, and parametrizing that model to simulate the effects of existing and projected vegetation, and runoff and infiltration control. Depth of the plume capture is used as the criteria for projecting the likelihood of using vegetation to capture and treat the plume. As a result, these projections are conservative because the transformation and degradation resulting from contaminant reactions in lake and wetland sediments and from plant enzymatic processes have not been fully assessed to date.

The Orlando Naval Training Center in Florida has a plume of chlorinated solvents that has resulted in detection of significant amounts of vinyl chloride in adjacent Lake Druid shown in Fig. 3. Lake Druid is also bordered by a number of residences and represents a valuable esthetic and recreational asset to adjoining residents.

Site Assessment and Apparent Plume Diving

A groundwater plume of chlorinated ethenes originated at the site of a laundry and dry cleaning facility. Prior to the closing in 1994, hazardous materials and water contaminated with chlorinated solvents were released to the groundwater from the surge tank beside Building 1100, and from spills of tetrachloroethylene and trichloroethylene in the facility. The contaminated groundwater plume flowed from the site of the former laundry underneath and into the nearby Lake Druid. The site plan shows that the source area is contained within an area of very high impervious cover. This consists of the buildings, paved driveways, and parking lots. Immediately down gradient from the parking lot is an unlined drainage ditch. The ditch that receives runoff from the parking lot and buildings on the site runs perpendicular to and crosses the plume that emerges from beneath the pavement. Beyond a narrow grassy area lies a densely wooded area that borders Lake Druid, where the plume discharges. Located nearly over the top of the plume is a creek that feeds the lake. Much of the wooded area is a seepage wetland.

Figure 4 shows the distribution of the chlorinated ethene contaminants taken over a vertical section of the

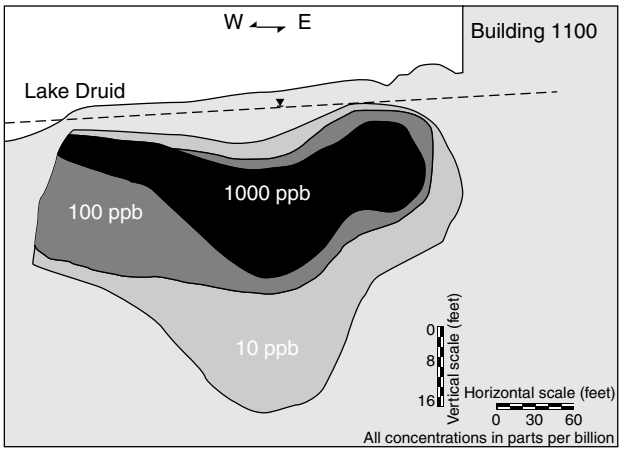


Figure 4. Vertical section of chlorinated ethene plume at Orlando Naval Training Center. Lake Druid is on the left and the contaminant source on the right. Note that 1 foot = 0.3048 meter and ppb is the concentration in micrograms per liter.

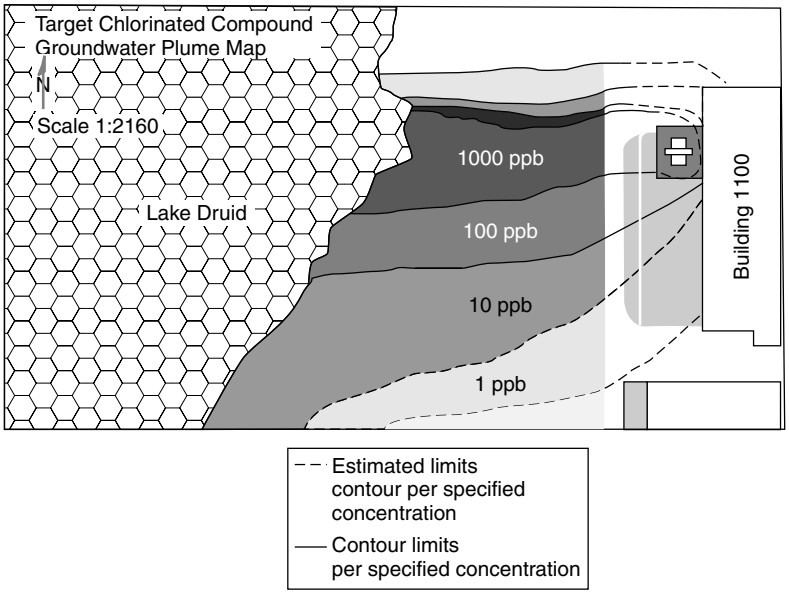


Figure 3. Site map of the Orlando Naval Training Center showing the Building 1100 source area and the shoreline of Lake Druid. The light shading surrounding Building 1100 delineates impervious parking lots and roads. Note that ppb is the concentration in micrograms per liter.

aquifer spanning the distance from the former laundry to the lakeshore. The data were obtained using a direct push probe operated on a 0.6-meter (2-foot) interval. These results show that the concentrations are low in the upper part of the aquifer, once the plume is down gradient of the ditch. In these locations the depth of uncontaminated water having undetectable amounts of chlorinated ethenes ranges up to 2.4 meters (7 feet) below the water table. The horizontal distance spanned by the diving portion of the plume is approximately 67 meters (220 feet). Thus the plume moves deeper into the aquifer upon emergence from the paved area and upon passing under the unlined ditch.

Model Application for Orlando Naval Training Center

The effects of recharge and discharge on the groundwater flow at Building 1100 were simulated with two models. First, the simple screening model for plume diving was applied (14). The model assumes that flow occurs between two points with fixed heads, the aquifer is a single uniform layer, and the flow system can be described by a set of one-dimensional segments. These assumptions are satisfied for a screening analysis of the Orlando Naval Training Center plume, although other details of the flow system require the use of a numerical model. This consideration led to the application of MODFLOW with particle tracking for a more detailed evaluation.

The screening-level plume diving calculation allows determination of the vertical displacement of the plume generated by the supply and withdrawal of water from the aquifer. The simple model was used to assess the amount of diving that would occur as the plume passed under the unlined ditch. With an estimated average annual rainfall of 1400 milliliters (55 inches) at Orlando, the amount of water that could run off into the ditch is very large. Estimates based on the area of the pavement surrounding the source ranged up to the equivalent of 38000 millimeters per year (1500 inches per year) concentrated in the ditch. The actual amount of infiltration through the ditch was not determined for this study. However, the leakage through the ditch would be a function of the transient depth of water, soil properties, soil antecedent moisture content, and the vegetation in the ditch. The online calculator (www.epa.gov/athens/onsite) was used to determine how much water would be required to infiltrate through the ditch to cause the observed diving of the plume. The purpose of this exercise was to determine if the observed plume diving could be attributed to reasonable recharge amounts ranging from the rainfall rate of 1400 milliliters (55 inches) to the estimated runoff amount of 38000 millimeters per year (1500 inches per year). Figure 5 shows the results from infiltration amounts of 1400 milliliters per year (55 inches per year) and 2800 millimeters per year (110 inches per year). Thus, if the ditch recharges double the average annual precipitation to the aquifer from the impervious area, this amount can account for the observed plume diving. This amount of water 2800 millimeters per year (110 inches per year) is less than 10 percent of the maximum estimated flow in the ditch and thus forms a plausible explanation for the vertical distribution of the contamination observed at the site. In the upper portion of the aquifer, there is no evidence for stratigraphic preferential flow paths and density-driven plume diving is not evident because the plume dives only after emerging from below the pavement.

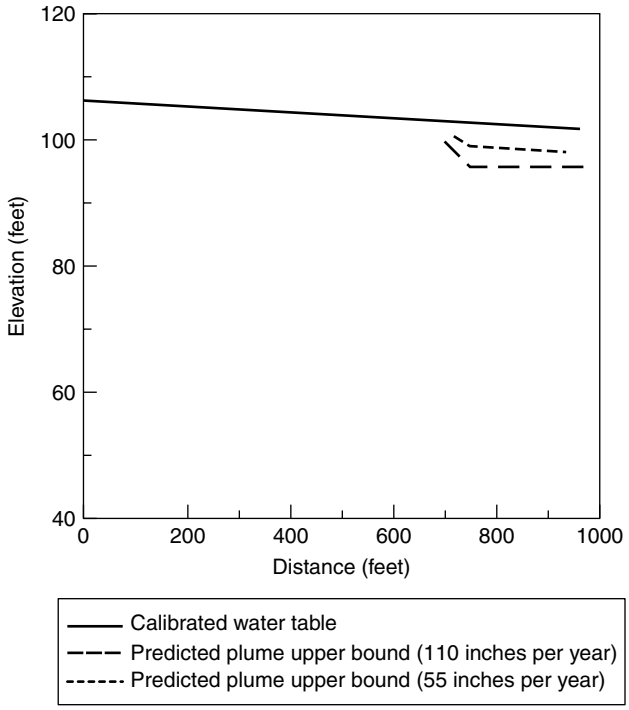


Figure 5. Predicted plume diving using the OnSite plume diving calculator (www.epa.gov/athens/onsite) and two estimates of infiltration through the unlined ditch. Note that 1 foot is 0.3048 meter and 1 inch is 25.4 millimeters.

Numerical Modeling

The U.S. Geological Survey modular groundwater flow (MODFLOW) code with particle tracking was used to perform more detailed simulations of the site. These simulations provided a more precise determination of the vertical and horizontal distribution of flow and a tool with which to evaluate the various design alternatives. Some of the parameters used in the model were taken from a previous modeling study (18) that was not focused on the plume and Lake Druid. Halford (18) calibrated the model to regional flow conditions. Calibrated parameters for hydraulic conductivity, porosity, and aquifer and layer thicknesses from Halford (18) were used in the current model. Boundary conditions were taken to match observed water levels collected around the site and consistent with the large-scale flows simulated by Halford (18). The need for site-scale water levels constrained the modeled flow domain to the area immediately surrounding Lake Druid. For an adequate assessment of the potential effects of vegetation, the area around Lake Druid and Building 1100 was modeled in more detail, both horizontally and vertically. To provide sufficient vertical delineation of the plume, the model simulations were based on 12 layers to adequately resolve the lake bathymetry. The refinements provided sufficient resolution to explore the factors that

control the vertical movement of the contaminants moving from Building 1100 to Lake Druid.

The amount of transpiration from either the existing vegetation or by any proposed plantings was difficult to estimate. A generalized estimate of 1300 millimeters per year (51 inches per year) was available from the Florida Agricultural Extension Service for central Florida. An estimate of 500 millimeters per year (20 inches per year) was determined for nearby orange groves (19). Finally, a site-specific estimate of 200 to 300 millimeters per year (8 to 12 inches per year) was made by Vose and Elliot (16) for the existing mature trees over the down gradient end of the plume. The estimate was made by measuring the sap-flow rate in nine trees in spring, summer, and fall. The estimate included only mature trees and did not account for the understory vegetation. Vose and Elliot (16) believed that this might not be too severe a limitation because the understory may be cycling shallow soil moisture, and they cite studies that show that understory transpiration can offset reduced overstory transpiration in open stands. The potential evapotranspiration at full stocking of the stand was 600 to 900 millimeters per year (24 to 35 inches per year), a higher value because of the relatively sparse distribution of the existing mature trees (also see Vose et al. this book). With the estimated precipitation of 1400 millimeters per year (55 inches per year) in central Florida, the estimated evapotranspiration ranges from 14 to 93 percent of that value. The lower values reflected the site-specific measurements.

These values suggested that in any case there was no strong driving force for removal of water from the aquifer by the vegetation. The generalized or regional estimate of evapotranspiration of 1300 millimeters per year (51 inches per year) came close to balancing precipitation. With the site-specific estimate of 200 to 300 millimeters per year (8 to 12 inches per year) accounting for some of the precipitation, the remainder would evaporate, contribute to soil moisture, or run off.

The MODFLOW results reproduced the presumed flow pattern in the cross section of the aquifer (Fig. 6). The simulated downward flow just down gradient of the paved area accurately reflects the observed plume (Fig. 4). The 12-layer representation of the aquifer allows adequate representation of the bathymetry of the lake in order to properly resolve the pattern of groundwater flow to the bottom of the lake. The discharge pattern was consistent with measurements of the attenuated plume emerging into the lake (data not shown in this chapter). The significance of these simulations was that the recharge and discharge patterns of the aquifer alone, can explain the vertical distribution of the contaminants (Fig. 4). Furthermore, the use of 12 thin layers to represent the surficial aquifer is unusual [see for example (18)] but necessary to represent a plume in this hydrogeologic setting.

These observations lead to the following strategies for phytoremediation at the site. First, the prospects for the trees transpiring sufficient water to pull the contaminant plume up to the root zone for treatment is too unlikely for phytoremediation alone to be considered as an adequate

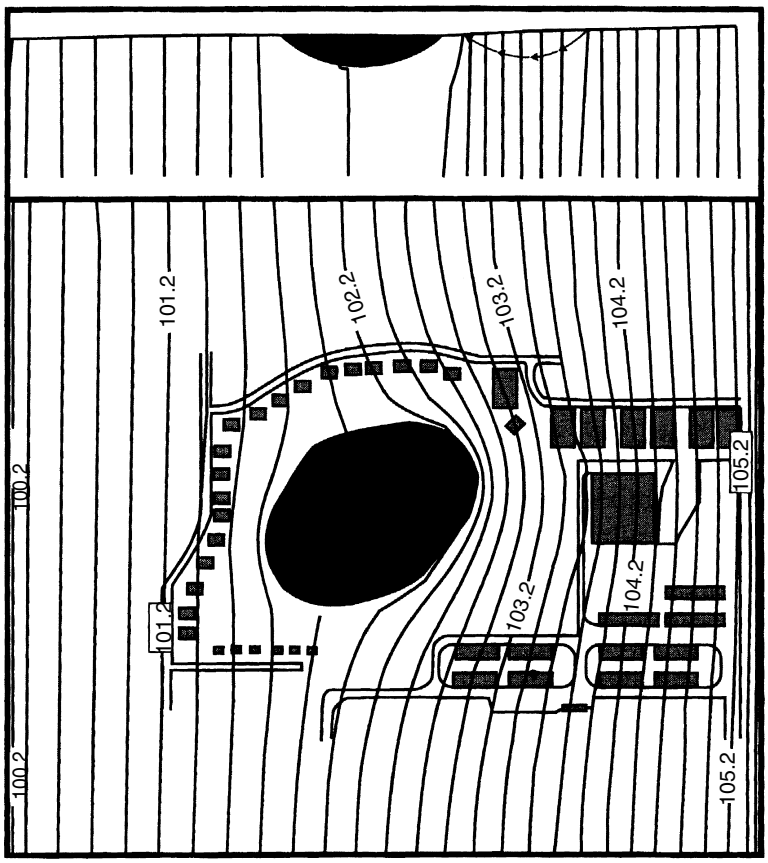


Figure 6. MODFLOW simulation of part of the Orlando, Florida U.S. Naval Training Center showing the effects of infiltration through the unlined ditch and upwelling at the shoreline. The upper panel represents a vertical section through the source and Lake Druid. The nearly vertical lines represent constant head contours, which correspond to the contours (labeled in feet above mean sea level; note that 1 foot is 0.3048 meter) on the plan view shown in the lower panel. The arrows in the upper panel represent a flow path from the unlined ditch to a discharge point along the shoreline. The scale is approximately 1:8280. The sides of the lower panel are vertically oriented north (top) to south (bottom).

cleanup remedy. This follows from the fact that the existing vegetation, extracting at least of 200 millimeters per year (8 inches per year), has not contained the existing contaminant plume.

Because the transpiration of trees alone cannot contain the plume, clearly the combined effects of replanted trees and natural attenuation in the seepage wetland and lake sediments needed to be investigated next. Nzengung (17) found significant potential for microbial and enzymatic degradation of chlorinated solvents in the wetland and lake sediments, thus requiring a refined hydraulic analysis. The refined analysis established that enhanced evapotranspiration would pull some of the plume upward into the seepage wetland and probably achieve better attenuation. This next investigation established more contact with a wider range of shallow rooted aquatic and wetland plants at the lakeshore without threatening the health of the existing wetland (Medina et al. this book). Nevertheless, the quantification of attenuation rates (17) was deemed too uncertain to forecast whether this enhanced natural attenuation would be sufficient without a field pilot investigation. These pilot investigations are currently (2003) underway. Because forecasting was not possible for the enhanced natural attenuation option, other supplemental design scenarios were also investigated. These included diversion of the surface runoff (from the impervious parking lots and roofs) from the unlined ditch to alleviate some plume diving, and planting more trees through the parking lot cover and over the source to contain the plume. Because of the ecological sensitivity of the seepage wetlands, an investigation of alternative planting was useful to avoid any temporary disruption of the wetland with supplemental planting if possible, especially to avoid planting alien species that are of regulatory concern to the State of Florida.

Simulations of eliminating the localized recharge to the aquifer at the edge of the parking lot established that most but not all of the downward movement of plume below the water table would be eliminated. However, some infiltration through the down gradient tree and shrub cover would continue because rainfall in this humid area exceeds potential evapotranspiration (Vose et al. this book). In addition, this sandy aquifer has high conductivity that limits contact of the plume with roots, wetland soils, and lake sediments, even under the best of conditions.

Finally, if trees were planted over the source zone, the simulations demonstrate that transpiration could remove water from the upper part of the aquifer despite the hydraulic conductivity. With the proper selection of trees that transform and degrade chlorinated solvents, some of the contaminated water could be treated, leaving less for natural attenuation. This could have the effect of removing contaminants from the aquifer, before the plume enters wetland soil and lake sediments. The MODFLOW results show that upward gradients would be established through the upper 7 meters (23 feet) of the aquifer if the evapotranspiration rate was 800 millimeters per year and through the upper 10 meters (30 feet) of the aquifer if the evapotranspiration was 1300 millimeters per year. These amounts exceed the site specific measured values of 200 to 300 millimeters per year (16) because the observed values were net values that integrated the effect of the trees working against infiltration. The higher values used in the model were selected because recharge was assumed to be zero due to the presence of the pavement. Forcing the trees to draw water from the aquifer exclusively over the source area maximized the impact on the contaminated portion of the aquifer by maximizing the withdrawal of water from the source zone. Overall, runoff diversion, tree planting over the source, and enhanced natural attenuation in the seepage wetland and nearer the lakeshore have the potential to manage contamination at this site but the uncertainty in enhanced attenuation requires a field pilot test to be sure this is the best remedy for this particular plume.

FEASIBILITY AND DESIGN IMPLICATIONS

Design of phytoremediation systems requires delineation of contaminant plumes and the parameters governing flow and transport in shallow aquifers. Because trees remove water and contaminants from the aquifer, estimates of evapotranspiration are needed to design phytocontainment systems. For the Joliet Army Ammunition Plant, the estimates were based on a forest evaporation model (7) using the Penman-Monteith equation (6) with climate data from the U.S. SAMSON database. From these readily available data, the feasibility of phytoremediation can be assessed.

Vertical delineation of contaminant plumes is best accomplished with short-screened or point sampling that eliminates (1) mixing of clean and contaminated water caused by screen placement that is only partly contained within the plume, and (2) averaging of concentration over long well screens. Both of these sampling effects or artifacts cause contaminant concentrations to be underestimated. Further, if the horizontal and vertical boundaries of the plume are not accurately defined, then transport processes are not correctly determined and phytoremediation potential can not be accurately assessed.

Sampling at the Orlando Naval Training Center revealed that the chlorinated solvent plume was depressed once the plume emerged from below the paved parking lot located adjacent to the source. Because of the presence of an unlined ditch adjacent to the parking lot, the plume dived due to localized recharge from the bottom of the unlined ditch. This plume characteristic was quantified with two models. These models included a simplified analytical solution of flow and a three dimensional numerical model of the site (MODFLOW) to simulate groundwater flow. Like the field data, the numerical model needed to be sufficiently resolved in the vertical to simulate the vertical distribution of flow and the bathymetry of the lake. Thus, a greater-than-usual number of layers were required for this phytocontainment assessment.

Both of these models showed that with reasonable rates of recharge and evapotranspiration and using some regional scale MODFLOW parameters, the observed plume diving could be accounted for just from the hydraulics of flow in the aquifer. Thus, the application of phytoremediation to this site was established as critically dependent upon the localized pattern of flow in the aquifer.

The analysis of the Naval Training Center site shows that the localized plume characteristics must be known to plan the locations for tree planting or design other remedial options for the site.

At the Naval Training Center, observations and simulations show that the contaminated water discharges to Lake Druid. Thus, the shoreline vegetation has the potential to intercept and treat the contaminated aquifer water. This interception of the groundwater flow is dependent upon evapotranspiration and all other characteristics of flow in the aquifer. Other elements of a remedy at this site include plume control by eliminating runoff from the parking lot to the unlined ditch. This would have the effect of preventing some of the downward migration of the contaminants. The depth of contamination at the source, however, is approximately 10 meters (34 feet). The depth of contamination is due to the location of the sump and the denser-than-water nature of the contaminants. If trees were planted and successfully grown at the source, then some of the contaminated water would migrate upward. The effectiveness of this source control depends upon the evapotranspiration rate that could be achieved by the trees and by the continued prevention of recharge in the parking lot.

Overall, runoff diversion, source phytocontainment, and phyto-enhancement of natural attenuation may be sufficient to remediate this site over a long period (until the nonaqueous phase is completely dissolved). However, due to the uncertainty in extrapolating treatment and attinuation kinetics, field pilot studies are necessary. These pilot investigations are underway at the Orlando site and other source removal remedies have been tested.

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BIBLIOGRAPHY

1. Hong, M.S. et al. (2001). Phytoremediation of MTBE from a groundwater plume. *Environ. Sci. Technol.* **35**(6): 1231–1239.
2. Quinn, J., M.C. Negri, R.R. Hinchman, L.P. Moos, and J.B. Wozinak (2001). Predicting the effect of deep-rooted hybrid poplars on the groundwater flow system at a large-scale phytoremediation site. *Int. J. Phytoremed.* **3**(1): 41–60.
3. Landmeyer, J.E. (2001). Monitoring the effect of poplar trees on petroleum-hydrocarbon and chlorinated-solvent contaminated ground water. *Int. J. Phytoremed.* **3**(1): 61–85.
4. Ferro, A., J. Chard, R. Kjelgren, B. Chard, D. Turner, and T. Montague (2001). Groundwater capture using hybrid poplar trees: evaluation of a system in Ogden, Utah. *Inter. J. Phytoremed* **3**(1): 87–104.
5. McDonald, M.G. and A.W. Harbaugh (1988). *A modular three-dimensional finite-difference ground-water flow model*. U.S. Geological Survey Techniques of Water Resources Investigations Book 6, Chapter A1.
6. Jensen, M.E., R.D. Burman, R.G. Allen, eds. (1990). *Evapotranspiration and Irrigation Water Requirements*. Manual No. 70. American Society of Civil Engineers, New York.
7. Shuttleworth, J. (1993). Evaporation. In: *Handbook of Hydrology*. D.R. Maidment (Ed.). McGraw-Hill, New York, pp. 4.1–4.53.
8. U.S. Department of Commerce (1993). *Solar and Meterological Surface Observation Network 1961–1990*. National Climatic Data Center (http://www.ncdc.noaa.gov).
9. Weaver, J.W., J.T. Haas, and J.T. Wilson (1996). Analysis of the gasoline spill at East Patchogue, New York. In: *Proceedings of Non-Aqueous Phase Liquids (NAPLs) in Subsurface Environment: Assessment and Remediation*. L. Reddi (Ed.). American Society of Civil Engineers, Washington, DC, November 12–14, pp. 707–718.
10. Bear, J. (1972). *Dynamics of Fluids in Porous Media*. Dover, New York.
11. Charbeneau, R.J. (1999). *Groundwater Hydraulics and Pollutant Transport*. Prentice Hall, Upper Saddle River, New Jersey, pp. 593.
12. Gelhar, L.W., C. Welty, and K.R. Rehfeldt (1992). A critical review of data on field scale dispersion in aquifers. *Water Resour. Res.* **28**(7): 1955–1974.
13. Toth, J., (1963). A theoretical analysis of groundwater flow in small drainage basins. *J. Geophys. Res.* **68**: 4375–4387.
14. Weaver, J.W., C.B. Sosik, and J.W. Washington (2001). *OnSite: the online site assessment tool*. U.S. Environmental Protection Agency National Exposure Research Laboratory. Athens, Georgia. (www.epa.gov/athens/onsite) (In review).
15. Strack (1984). Three-dimensional streamlines in Dupuit-Forcheimer flow. *Water Resour. Res.* **20**(7): 812–822.
16. Vose, J.M. and K.J. Elliot (1999). *Preliminary estimates of transpiration at the Naval Training Center, Orlando, Florida: results from phase I*. Report by the U.S. Department of Agriculture Forest Service Coweta Hydrologic Laboratory, Otto, North Carolina.
17. Nzengung, V.A. (2000). *Data on phytotransformation and natural attenuation processes for the degradation of perchloroethene (PCE) and trichloroethene (TCE): data specific for the Orlando Naval Training Center (NTC), Orlando, Florida, task 1 to 4 (separate reports)*. Contract report. Contract #: UKC019 (QT-RT-99-002122), U.S. Environmental Protection Agency National Exposure Research Laboratory, Athens, Georgia.
18. Halford, K.J. (1998). *Assessment of the potential effects of phytoremediation on ground-water flow around area C at Orlando Naval Training Center, Florida*. U.S. Geological Survey Water Investigations Report 98–4110.
19. Summer, D.M. (1996). *Evapotranspiration from successional vegetation in a deforested area of the Lake Wales Ridge*, Florida, U.S. Geological Survey Water-Resources Investigations Report 96-4244, 37 pp.

READING LIST

Pennington, J.C., D.W. Harrelson, M. Zakikhani, D. Gunnison, J. Clarke, C.J. McGrath, H. Fredrickson, J.H. May, E. Perkins, C.A. Hayes, and D. Ringelberg (1998). *Feasibility of using natural attenuation as a remedial alternative for explosives-contaminated groundwater at site L1*. Joliet Army Ammunition

Plant, Joliet, Illinois. U.S. Army Corps of Engineers, Waterways Experiment Station Technical Report EL-98-8, Vicksburg, Mississippi.

Vogel, T., K. Huang, R. Zhang, M.Th. van Genuchten (1996). *The HYDRUS code for simulating one-dimensional water flow, solute transport, and heat movement in variably-saturated media*. U.S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture. Research Report 140, Riverside, California.

WELL DESIGN AND CONSTRUCTION

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INTRODUCTION

Wells are used to collect groundwater from alluvial fresh water aquifers, saline water from brackish water aquifers, and seawater from beach shore aquifers. Wells are relatively simple to build, and the source water they collect is pretreated via slow filtration through the subsurface granular geologic formations in the area of source water extraction. Therefore, source water from wells is usually of better quality in terms of solids, silt, oil and grease, natural organic contamination, and pathogen content compared to source water collected from open surface water (i.e., river, lake, or ocean) intakes.

Key well performance characteristics are yield, static and pumping water levels, and cone of depression. Well yield indicates how much water can be withdrawn from a given well for a preset period of time. Well yield is typically measured in cubic meters per second (m^3/s) or cubic feet per second (cfs) for large wells and in liters per second (lps) or gallons per hour (gph) for small wells. Pumping and static water levels are the groundwater levels in the well when pumping from the well is on and off, respectively. When a well is operational, the surface of the groundwater level in the aquifer takes an inverted cone shape due to directional water flow toward the well. This inverted shape is called a cone of depression (Fig. 1).

Well type, size, and capacity are determined by a hydrogeologic investigation which typically includes the following key steps:

1. Complete a preliminary geologic survey to identify if the selected site is generally suitable for constructing of subsurface water intake.
2. Drill-test to collect samples of the aquifer formation deposits for visual classification and grain-size distribution analysis.
3. Install one or more test wells and observation wells, and conduct a pumping test to determine the site-specific hydraulic characteristics of the aquifer for subsurface system design and determination of the intake system yield.
4. Collect an adequate amount of samples of the source water and analyze sample water quality, with special emphasis on the content of iron, manganese, barium, strontium, silica, radon, carbon dioxide, arsenic, and hydrogen sulfide in the source water. If the aquifer water quality is under the influence of a surface water source (i.e., river, lake, ocean) whose quality and quantity vary seasonally, then complete year-round intake water quality sampling to determine seasonal fluctuations of source water quality.
5. If the subsurface intake system requires multiple collection facilities (wells, or infiltration galleries/river bank filtration facilities), then complete a computer model analysis to establish the response of the production aquifer to pumping and the potential impact of groundwater collection on adjacent fresh or saline water aquifers, which could interact with the water supply aquifer.

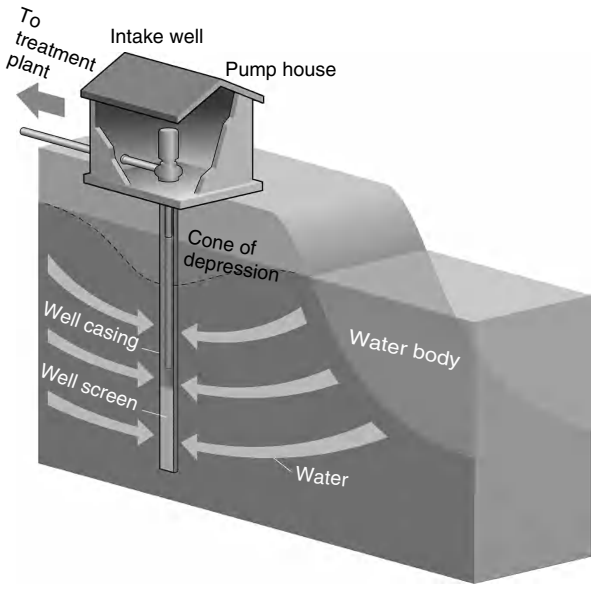


Figure 1. Vertical intake well.

The key factors that determine if the use of subsurface intake is practical or/and economical are the type of the water source aquifer (confined vs. unconfined); the aquifer permeability (hydraulic conductivity), which is a measure of the velocity of water movement through the ground (typically measured in m/s); the average specific yield (productivity) of the aquifer (in m^3/day per linear meter of riverbank or seashore along which the collector wells are located); the thickness of the production aquifer deposits; and the existence of nearby fresh or brackish water aquifers, which could be negatively impacted by the intake well operations or may have a measurable effect on intake well water quality. A confined aquifer (also often referred to as an artesian aquifer) is a water saturated geologic formation between two layers of low permeability (i.e., bedrock) that restrict the vertical movement of the groundwater in or out of the aquifer. Confined aquifers are often contained by the surrounding geologic formations and are pressurized therefore, collecting water from such aquifers may not require pumping. Unconfined aquifers are groundwater saturated formations whose upper surface (commonly referred to as the water table) fluctuates over time. Aquifer water table fluctuation is driven by recharge from surface runoff (rain or snowmelt)

or fluctuation of the water table of the surface waterbody (river, lake, etc.) connected to the aquifer.

Unconfined alluvial aquifers located along riverbanks are commonly used for freshwater supplies. Confined or semiconfined aquifers yield the most suitable source of water for brackish water desalination systems (1). Aquifers that favor the construction of wells are coarse-grained, porous, and highly permeable geologic formations (i.e., sand, gravel, and limestone) connected to a riverbed (for freshwater intakes) or the ocean floor (for seawater intakes) whose specific yield (transmissivity) exceeds 1,500 m^3/day/m and whose water carrying zone is at least 6 meters (20 feet) deep (2). The higher the aquifer permeability, transmissivity, and thickness, the larger the well yield the aquifer can support.

WELL SITE SELECTION

Once an aquifer of suitable yield has been identified, the location of the actual field is to be selected. Whenever possible, the well field should be located perpendicularly to the main direction of groundwater flow (i.e., along the banks of a nearby river). The most suitable location for collecting a large amount of river water is on a river island or within a meander. If significant clogging of the riverbed is expected, then the wells should be located closer to the riverbanks.

In addition, a potable water well field has to be sited away and uphill from potential contamination sources such as septic tanks, landfills, industrial plants, and underground fuel storage tanks. Most states regulate the location of private potable water wells and require locating wells at least 15 to 30 meters (50 to 100 feet) away from septic systems.

INTAKE WELL TYPES AND KEY DESIGN CRITERIA

Intake wells are typically vertical or horizontal water collectors drilled into the source water aquifer. Vertical intake wells are usually less costly than horizontal wells, but their yield is relatively small, typically, 0.004 to 0.044 m^3/s (0.1 to 1.0 MGD). Therefore, vertical wells are typically used for supplying relatively small quantities of water usually less than 20,000 m^3/day (5 MGD).

Vertical Intake Wells

Vertical intake wells consist of the following key elements: a casing, well screen, filter pack, well seal, and surface seal. Many wells have submersible or vertical turbine pumps installed inside the well casing (Fig. 1). A well casing is a steel or nonmetallic (typically, fiberglass) pipe which lines the well borehole to protect the well from caving in. Most state standards require steel casings for freshwater supply wells and specify the thickness of the casing. The diameter of the casing has to house the well intake pump and provide ample room for pump service. The diameter of the well casing is determined mainly by the well screen size and yield, but the well borehole diameter has to be at least 0.1 meters (4 in.) larger than the well casing to accommodate the installation of the well seal. Usually, the well casing diameter is between 200 and 1200 mm (8 and 48 in.), and the well depth is typically less than 75 meters (250 feet).

The well screen is the intake portion of the well and is a sieve-like structure that has slotted or perforated openings. The well screen is located at a depth corresponding to the water carrying zone of the aquifer. Screen depth, size of openings, diameter, and length are key well performance design criteria. These well parameters are selected to maximize a well's safe yield; control well entrance velocity; and to avoid excessive entrance of sand and other particulates, which have a negative impact on well useful life and water quality. The performance of the well screen is enhanced by a gravel (filter) pack, which consists of clean, uniform, and well rounded gravel and sand placed between the borehole wall and the well screen to prefilter the groundwater entering the well. Typically, the gravel pack depth extends at least 1 meter (3 feet) above the well screen. A well seal is installed above the filter pack to prevent soil and contaminants from entering the well screen area. The well seal is a cylindrical layer of cement, bentonite, or clay placed in the annulus of the well between the well casting and the borehole. Typically, the well seal extends at least 0.6 meters (2 feet) above the top of the gravel pack and usually through the elevation of the soil frost zone. The aboveground portion of the well is finished with a concrete surface seal. The surface and well seals protect the well from surface runoff contamination and support the casing.

A detailed methodology for sizing well screen diameter, length, openings and capacity, and for selecting the grain size of the material for the gravel pack is presented elsewhere (3). This source also provides information on determining the thickness of the gravel pack around the well screen, the permissible approach velocity of the water stream converging to the well, and ultimately the design capacity of a new well or the maximum capacity of an existing well.

Once constructed, vertical well performance has to be monitored frequently to secure long-term performance and identify early signs of potential malfunction and failure. The most common causes of well failure are borehole collapse, corrosion of the casing, improper or defective construction techniques, growth of organisms within the well borehole, and formation of mineral concentrations or crusts in the open-hole or screened section of the well borehole.

Horizontal Collector Wells

Horizontal (Ranney) collector wells consist of a caisson that extends below the ground surface and has water well collector screens (laterals) projected horizontally from inside the caisson into the surrounding aquifer (Fig. 2). The well screens in the collector wells are placed horizontally, but a higher rate of source water collection is possible than that of vertical wells, which allows, collecting the same intake water quantity with fewer wells.

Individual horizontal intake wells are typically designed to collect from 0.0044 to 1.75 m^3/s (0.1 to 40.0 MGD) of source water per well. The largest 1.75 m^3/s (40 MGD) horizontal collector wells in the United States were installed on the banks of the Platte River in 1990

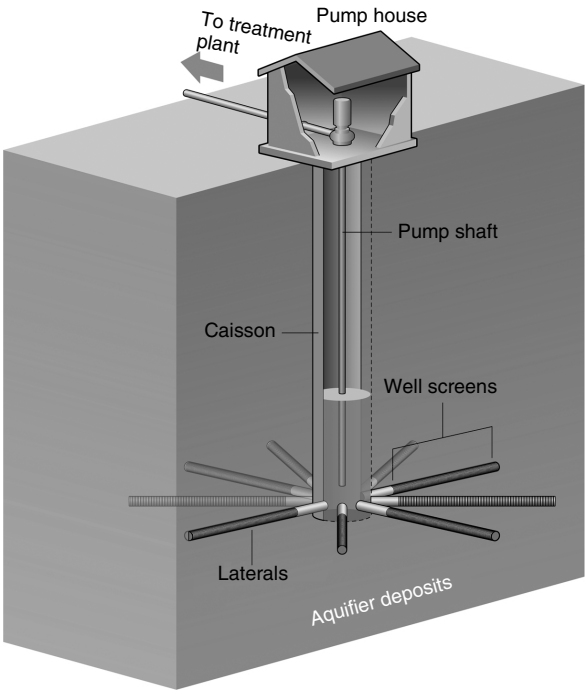


Figure 2. Horizontal collector well.

for water supply to the City of Lincoln, Nebraska. In the United States, utilities use horizontal collector wells whose laterals are located directly under the riverbed.

The caisson of the horizontal collector well is constructed of reinforced concrete of 2.7 to 6.0 m (9 feet to 20 feet) inside diameter and a wall thickness of approximately 0.5 to 1.0 meters (1.5 to 3.0 feet). The caisson depth varies according to site-specific geologic conditions, ranging from approximately 10 meters to over 45 meters (30 to 150 feet).

The number, length, and location of the horizontal laterals are determined by a detailed hydrogeologic investigation. Typically, the diameter of the laterals ranges from 0.2 to 0.3 meters (8 to 12 inches) and their length extends up to 60 meters (200 feet). The size of the lateral screens is selected to accommodate the grain size of the underground soil formation. If necessary, an artificial gravel-pack filter can be installed around the screens to suit finer grained deposits. Usually, one well has 2 to 14 laterals.

When horizontal wells are used for fresh or brackish groundwater intake, the caisson is extended above the floodplain elevation for this location to protect the pumping equipment, electrical, and instrumentation and control equipment from flooding. When used as seawater beach wells, especially for smaller size applications, Ranney-type wells can be constructed watertight at or below grade to minimize their visual impact on the shoreline. In large intake capacity applications, horizontal beach wells are typically coupled so that the intake pump station is installed above the well caisson. The well intake pump station can be designed with submersible pumps to minimize noise. However, for medium and larger size wells, most frequently vertical turbine pumps are used because these pumps usually have higher energy efficiency and require less power. A more detailed description of horizontal collector well design and construction is presented elsewhere (4).

Infiltration Galleries

Infiltration galleries are riverbank or seashore filtration systems that are typically implemented when conventional horizontal or vertical intake wells cannot be used because of unfavorable hydrogeologic conditions. For example, they are suitable for intakes where the permeability of the underground soil formation is relatively low, or for river or seashore filtration, where the thickness of the beach or the onshore sediments is insufficient to develop conventional intake wells.

Infiltration galleries consist of an excavation trench which is filled with filtration media of size and depth similar to that of the granular media filters used for conventional water treatment plants. Vertical or horizontal collector wells are installed at equal distances (usually 30 to 60 meters) inside the filter media. Typically the capacity of a single collection well is 0.009 to 0.09 m^3/s (0.2 to 2.0 MGD).

A common type of infiltration gallery is a horizontal well collection system that has a single trench (Fig. 3). The media in the wells are configured in three distinctive layers: a bottom layer of sand of approximately 2 to 3.5 meters (6 to 10 feet), followed by a 1.2 to 2 meter (4 to 6 feet) layer of graded gravel pack surrounding the horizontal well collector screens, topped by a (6 to 9 meter) (20- to 30-foot) layer of sand. Horizontal well collector screens are typically designed for an inflow velocity of 3 cm/s (0.1 ft/s) or less.

Infiltration galleries can be designed either similarly to conventional rapid sand filters (if the natural source water movement, such as river flow or ocean water wave motion, can provide adequate flushing of the infiltration gallery media contact surface with the waterbody) or can be constructed as slow sand filtration systems, which have at least a 9-meter (30-feet) layer of sand overlying the collection well screens. Infiltration galleries are usually 15 to 20% more costly to construct than conventional vertical or horizontal intake wells, and therefore, their use is warranted only when the hyrogeologic conditions of the intake site are not suitable for conventional intake wells.

Riverbed/Seabed Filtration Intake Systems

These intake systems consist of a submerged, slow sand medium filtration system (filtration bed) located in a riverbed or in the near-shore surf zone of the ocean floor (Fig. 4). The filtration bed is connected to a series of intake wells located on the shore via tunnels or horizontal collector pipes.

The filtration bed is sized and configured using design criteria similar to those for slow sand water treatment plant filters. The filter bed depth is typically between 0.9 m and 1.2 m (3 to 4 ft). The gravel supporting the filter bed's sand is 0.15 to 0.5 m (0.5 to 1.5 ft) deep. The design surface loading rate of the filter medium is typically between 0.05 and 0.2 m^3/m^2h (0.2 and 0.8 gpm/sq ft). Similar to slow sand filters, a mat of natural organic materials is formed on the surface of the filtration bed. This mat enhances removal of organics and fine particles from the source

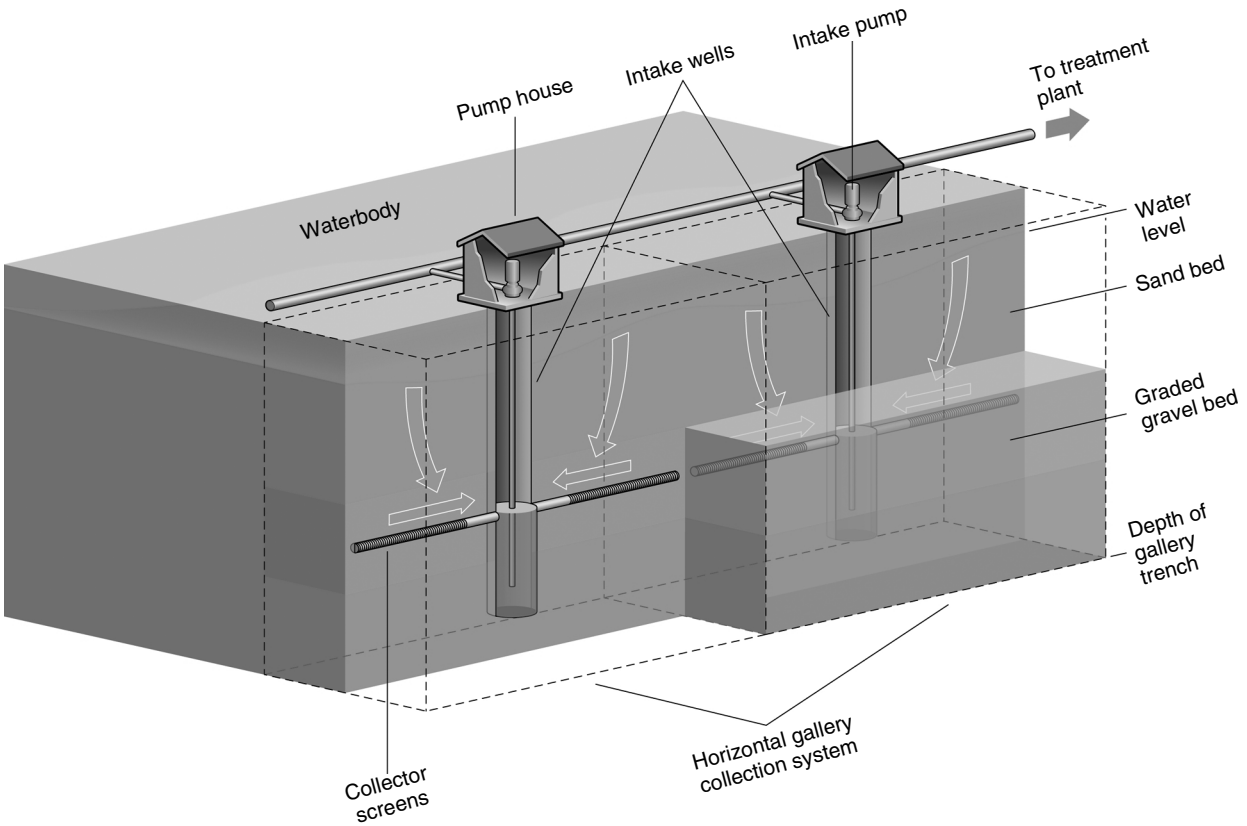


Figure 3. Infiltration gallery.

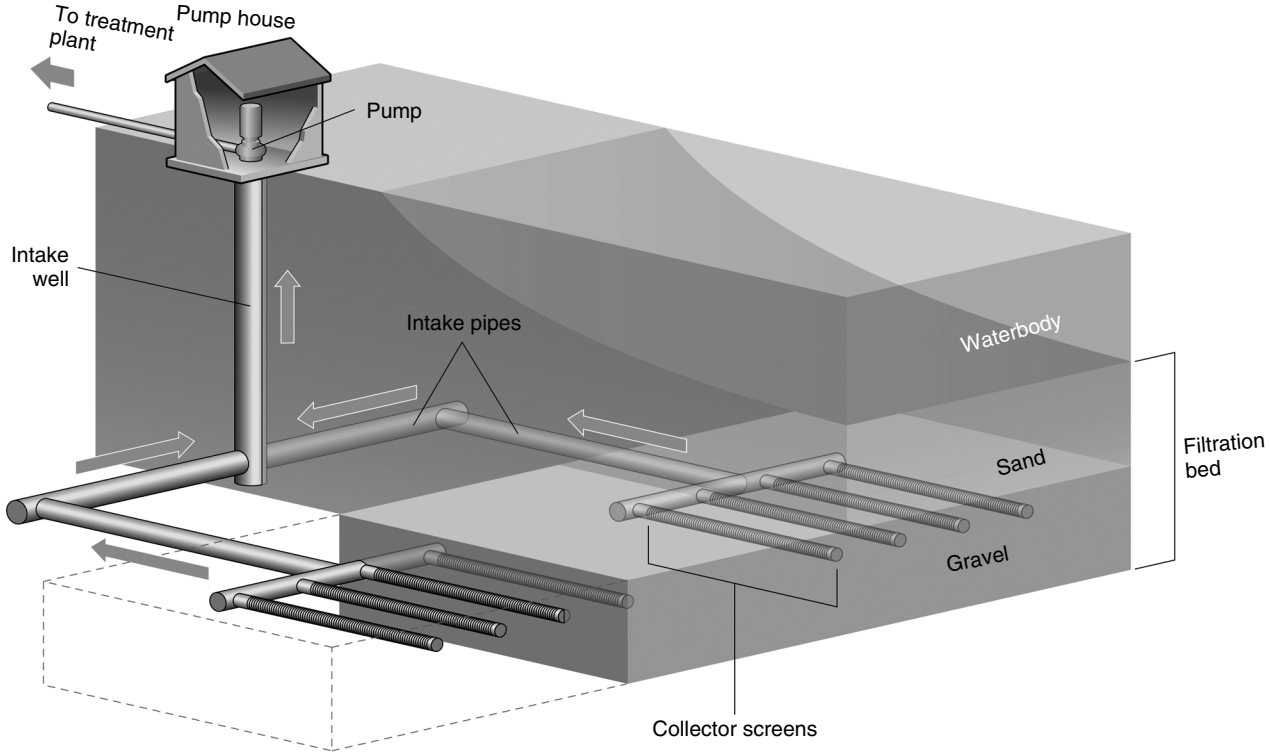


Figure 4. Riverbed/seabed filtration intake system.

water. The surface filtration mat is often removed from the surface of the filtration bed by naturally occurring seasonal scouring, such as river flooding or storms. When the mat is removed and some of the filtration bed sand is lost over time, the sand medium has to be replaced to its original depth to maintain filtration bed efficiency.

An alternative riverbed filtration system, which consists of a soft-soil tunnel constructed in the sand and gravel aquifer, whose well screens extend horizontally from the tunnel under the river, has been designed on the Ohio River for the Louisville Water Company in Kentucky (2). The riverbed filtration system consists of twenty-three 61-meter (200-ft) long laterals located at an equidistance of 79.3 meters (260 ft) in the riverbed, connected to the collection tunnel of a total length of 1830 meters (6000 ft). The laterals are 0.3 m in diameter, and the riverbed serves as a natural slow sand filtration system. The experience gained at Louisville indicates that the maximum water yield of this system is 0.22 to 0.31 m^3/s (5 to 7 MGD) per 305 m (1000 feet) of riverbank length.

The largest seawater desalination plant with a seabed intake system currently under construction is the 0.58 m^3/s (13.2 MGD) Fukuoka District RO facility in Japan. This plant is planned to be operational in late 2005. The Fukuoka seawater desalination plant seabed intake area is 30,000 m^2 (312,000 sq ft).

Typically, riverbed and seabed filtration intakes are the costliest well intake systems. Their construction costs are approximately 1.2 to 2.3 times higher than those of conventional intake wells (5).

BIBLIOGRAPHY

1. Missimer, T.M. (1999). Raw water quality—the critical design factor for brackish water reverse osmosis treatment facilities. *Desalination and Water Reuse* **9**(1): 41–47.
2. Chittaranjan, R., Melin, G., and Linsky, R. (Eds.). (2002). *Riverbank Filtration—Improving Source Water Quality*. Kluwer Academic, Dordrecht, the Netherlands, p. 24.
3. Williams, E.B. (1981). Fundamental concepts of well design. *Ground Water* **19**(5): 527–542.
4. Hunt, H.C. (1996). Filtered seawater supplies—naturally. *Desalination and Water Reuse* **6**(2): 32–37.
5. Wright, R.R. and Missimer, T.M. (1997). Alternative intake systems for seawater membrane water treatment plants. *Proc. Int. Desalination Assoc. Conf.*, Madrid, Vol. 3, pp. 407–422.

PHYSICAL PROPERTIES OF DNAPLs AND GROUNDWATER CONTAMINATION

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The physical behavior of dense nonaqueous phase liquids (DNAPLs) can broadly be divided between two classes based on melting point. Polynuclear aromatic hydrocarbons (PAHs) have melting points that are at the lowest, 80 °C (for naphthalene). Consequently, PAHs are solids at the temperatures typical in the subsurface; thus, the potential for migration through the soil column or groundwater systems is limited. Cosolvents can make PAHs soluble and mobile; however, the PAH solutions (when dissolved by petroleum hydrocarbons) are typically lighter than water and do not behave as DNAPLs. The second class of DNAPLs are chlorinated solvents. These compounds are liquids at normal subsurface temperatures, making them extremely mobile in unsaturated and saturated zone soils. Here we discuss those and other properties that make contamination by chlorinated solvents one of the most ubiquitous and recalcitrant of groundwater problems. A good overview of chlorinated solvent characteristics and remediation is included in Pankow and Cherry (1).

The introduction of chlorinated solvents was perceived as a great innovation for safety and an improvement in the quality of the degreasers. Prior to that introduction, distilled mineral spirits were the only available solvents. Explosions and fires from mineral spirits were a constant threat and occurrence causing death and injury. In today's climate where risk is evaluated in terms of one event in a million cancer risk, there are numerous lives saved through the use of chlorinated solvents. One of the most common chlorinated solvents is tetrachloroethene, also called perchloroethene (PCE) or "perc." This solvent is mostly associated with dry cleaner leaks. Another commonly used industrial degreaser, trichloroethene (TCE), has been found at many industrial facilities.

The properties that make chlorinated solvents so problematic with regard to groundwater contamination include density, solubility, viscosity, surface tension, and dehydration.

Chlorinated solvents are significantly denser than water. The density values in g/cm^3 (water is 1.00) are:

1,1-Dichloroethane (1,1-DCA)	1.18
1,1-Dichloroethene (1,1-DCE)	1.22
Trichloroethane (TCA)	1.34
Trichloroethene (TCE)	1.46
Tetrachloroethene or perchloroethylene (PCE)	1.62

Upon release into the environment, DNAPLs sink through the vadose zone, through the water table, and, over the long-term, through aquitards. A release of chlorinated solvents will travel downward or laterally until it has been exposed to a volume of soil sufficient to retain the released DNAPLs in pore spaces within the soil matrix.

Due to high density, chlorinated solvents can flow upgradient to the groundwater flow along the down dip surface of an aquitard. The most problematic phenomenon caused by high density chlorinated solvents is the dimple effect. Upon release, chlorinated solvents will travel to an aquitard and seek the lowest point on the surface of that aquitard. It is unlikely that any given stratigraphic unit acting as an aquitard is perfectly planar; it will have small to large dips, depressions, and dimples. Each of these can act as a reservoir for DNAPLs. These reservoirs will be outside an advective flow regime set up by a "pump and treat" groundwater system. The only means

of transport from these reservoirs is through diffusion, which is effective enough to cause significant dissolved phase contamination, but not effective enough to offer timely remediation.

Chlorinated solvents are soluble in water. Values in mg/L are:

1,1-DCA	5100
1,1-DCE	400
TCA	700
TCE	1100
PCE	200

These levels of solubility represent significant potential for groundwater transport of released chlorinated solvents in the dissolved phase.

Most chlorinated solvents are less viscous than water. Values in centiposes (water is 1.00) are:

1,1-DCA	0.51
1,1-DCE	0.36
TCA	0.90
TCE	0.57
PCE	0.93

The low viscosity makes chlorinated solvents extremely mobile in the vadose zone; they can readily flow through flow channels that may be as small as a human hair.

The surface tension of chlorinated solvents with respect to water has significant impact on the manner in which chlorinated solvents penetrate the capillary fringe zone and then migrate through the saturated zone. Water has a high surface tension of 73 dyn/cm; chlorinated solvents have surface tensions in the range of 20–40 dyn/cm. When free phase chlorinated solvents migrate to the capillary fringe, they will be held up until a head is built up sufficient to overcome the capillary retention of the water. The capillary retention is directly proportional to the interfacial tension and inversely proportional to the pore throat radius and liquid density. The smaller the pore size, the greater the head required to displace entrained water. This can result in significant lateral spreading of a DNAPLs release above the capillary fringe in fine grained soils.

Another effect of surface tension forces involves how surfaces in larger pore spaces are wetted. The tendency of one fluid to replace another on a surface is termed wettability.

As broad rules, the following apply:

- In soil, water is the wettting fluid with respect to solvents or air.
- Solvents are wetting fluids in air, but not in the presence of water.
- With respect to carbonaceous soil components, solvents are wetting in the presence of air or water.

Free phase chlorinated solvents have the capacity to dehydrate clays, causing cracking and further migration through what at first analysis appears to be impermeable layers. Bentonite pellets used to seal wells in areas contaminated with DNAPLs may not work, due the failure of the bentonite to swell in those conditions. DNAPLs can also migrate through previously installed and sealed wells via the same mechanism.

All of the above phenomena impact the fate and transport of DNAPLs to and through groundwater systems. Those physical properties also manifest themselves by the nature of a given release. The release of a large volume of DNAPLs in a short period of time causes rapid migration laterally as well as downward through the vadose and saturated zone that overcomes any small permeability differences. This leaves a significant volume of residual contamination entrained in the zone of passage. Conversely, DNAPLs release that occurs slowly over a long period of time will travel through narrow channels representing the most permeable path through the subsurface. Small differences in permeability will be exploited under these conditions. Under slow release conditions, less of the DNAPLs is entrained within the soil matrix: the overall potential for vertical migration is greater, more DNAPLs will penetrate to a greater depth, and the potential to impact groundwater is also greater.

Subsurface “dimples”—slight depressions or irregularities at the top of an underlying aquitard where DNAPLs may collect—have been observed. These features are difficult to locate.

The overall effect of the physical properties described above, particularly where the “dimple” effect is manifest, may make timely remediation of groundwater contaminated with DNAPLs impossible. In those instances, the most economic method of protecting health will lie in municipal or point of use treatment systems for the recovered groundwater.

BIBLIOGRAPHY

1. Pankow, J.F. and Cherry, J.A. (1996). Dense chlorinated solvents, and other DNAPLs. In: *Groundwater: History, Behavior, and Remediation*. Waterloo Press, Guelph, Ontario, Canada, p. 522.

WATER DOWSING (WITCHING)

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‘Water dowsing’ is the supposed ability to locate underground water using a simple handheld device such as a forked stick, bent wires, or a plumb bob. ‘Dowsing’ is the general term applied to ‘divining’ for objects or materials concealed beneath the ground. Divining, or divination, implies a supernatural intervention and has been practiced for at least 2000 years for a variety of purposes. Water dowsing is also known as water witching.

To dowse for water, the ‘diviner’ walks along the ground holding the device, which then ‘responds’ to the presence of an ‘underground stream.’ The traditional European divining rod is a forked hazel twig, which is grasped in both hands and bent under tension; the ends held horizontal and point, forward. Only a slight involuntary movement on the part of the operator is then needed to make the

twig jerk downward. Other such methods in use are two pieces of bent wire, one in each hand, which then cross to indicate the 'underground stream,' or a plumb bob, which begins to rotate.

The concept relies on the hypothesis that groundwater occurs in streams, similar to surface water. A diviner can then trace the path of an 'underground stream' from the surface. He may pick up several streams and indicate where they cross. A successful bore or well must be sunk exactly on the stream, or failure will be justified by having missed the 'stream.' Some diviners also claim to be able to detect the salinity of the underground water, or the depth of the water table, water-bearing strata or fracture, and the likely well yield.

There is vast literature on dowsing, and modern texts can be found in 'New Age' bookshops. Water witching is carried out in all hydrogeologic environments, ranging from extensive shallow aquifers, where success is assured, to fractured rock terrains in which success rates are poor. However, scientifically constructed tests always produce statistically random results, often to the chagrin of the diviner, who may have a real belief in his ability to dowse for underground water. Water witchers often have experience and local knowledge that aids them in selecting of favorable areas before actually applying the technique to locate an exact drilling site.

Dowsing with a forked twig was first mentioned in 1556 by Georgius Agricola in his descriptions of mining practices in the Harz Mountains of central Germany where the diving rod was being used supposedly to locate mineral veins (Fig. 1). Agricola mentions that the material for the twig was selected for different minerals, for instance, hazel for silver and ash for copper. Agricola is scathing about the practice, referring to dowsers as cunning manipulators and to the faith among common miners 1.

The practice of water dowsing spread through Europe in the seventeenth century, and then to North America and Australasia, where it is a widely held belief among farmers. The first mention of divining applied to water was apparently to locate a well for a convent in Spain (from a life of Saint Theresa, in Ref. 2, p. 171) in 1568. However, Arthur J. Ellis (3), who comprehensively reviewed the history of water witching, suggested that the practice gained wider credence from the activities of Baron and Baroness de Beausoleil in the early 1600s. The Beausoleils traveled through mining areas, even visiting



Figure 1. Use of divining rods in prospecting for ore 1. (From Agricola, De re metallica, German edition, 1580).

America, and the Baroness apparently used divining to discover the Chateau Thierry mineral water in France. After this, the divining rod seems to have been exclusively applied to locating groundwater, no doubt because of the interest in mineral water at the time and the high success rate of water wells in northern Europe. Connection with witchcraft led to the name water witching, which is used exclusively in North America.

BIBLIOGRAPHY

1. Agricola, G. (1912). *1556, De re metallica libri XII*, 1st Ed. Frobenius, Basel, p. 538 (English translation by H.C. Hoover and L.H. Hoover, The Mining Magazine, London), p. 640.
2. Barrett, W.F. (1911). *The So-Called Divining or Dowsing Rod. Psychical Research*. Home Library series, ch 12, pp. 167–186.
3. Ellis, A.J. (1917). *The Divining Rod—A History of Water Witching*. United States Geological Survey, Water-Supply Paper 416.

SUBSURFACE DRAINAGE

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The basic reason for agricultural lands to be affected by waterlogging and salinity is the inadequacy of the natural drainage system to handle the water that reaches the land either by natural or artificial means. Under such situations, an artificial drainage system has to be provided. The meaning of land drainage varies in different regions and contexts. A geographer or a surface hydrologist may use it to mean the pattern of natural watercourses in a hilly area. A pedologist may think in terms of the permeability of a poorly drained or well-drained soil. In Peru, engineers interpret drainage as reconstruction of natural waterways rather than removal of water. In Canada, it may mean reclamation of marshland for agricultural or urban development. In Holland, a Dutch farmer may use it for the installation of drainpipe in the soil. Thus, in different areas, this term implies different meanings and objectives. If the land use is primarily agricultural then land drainage could be defined as the establishment and operation of a system by which the flow of water from the soil is enhanced, so that agriculture can benefit from the subsequently reduced or controlled water level in the soil. Agricultural land drainage aims at reclaiming and conserving land for agriculture, to increase crop yields, to permit cultivating more than one crop in an area, and to reduce the cost of production

INTRODUCTION

There are no hard and fast lines between the objectives of different kinds of agricultural drainage, but broadly there are two types of drainage, surface drainage and subsurface drainage. Surface drainage is the removal of excess water from the land surface to create more favorable conditions for plant growth. Subsurface drainage is the removal or control of groundwater and/or removal or control of salts using water as the vehicle. The excess water may be from precipitation, water applied in irrigation, losses from conveyance channels and storage systems, and water that has seeped from groundwater in upper reaches. It is the drainage of excess water from the land surface at a rate that will prevent long periods of ponding without excessive erosion, so that crops would have favorable moisture conditions. Any drain or well-designed system to control or lower the groundwater is considered subsurface drainage. It can be broadly classified in two categories as (1) horizontal drainage and (2) vertical drainage. The other category of drainage frequently referred to nowadays is biodrainage. The objective of this article is to discuss various aspects of subsurface drainage. The main focus will be on horizontal drainage hereafter referred to as subsurface drainage. Vertical drainage and biodrainage will also be discussed briefly later.

HISTORICAL PERSPECTIVE

Agricultural drainage to improve crop production is an age-old concept that has been used with profitable results for quite some time in the past with different orientations and variations. Even though agricultural drainage is discussed in ancient Greek history, its development in different parts of the world is not very well known. In Greek civilization, some areas were reclaimed by systems of ditches. Drainage of humid and semi-humid areas started in the tenth century and extended to different parts of Europe in the sixteenth and seventeenth centuries. Herodotus has referred to the oldest instance of drainage in 400 B.C. by the Egyptians in the Nile Valley. In the United Kingdom, the earliest work is traced to the thirteenth century when Romney marsh was reclaimed, but the major work was carried out about 250 years before. In the United States, the first tile drains were laid by John Johnson of New York for a total length of 56 km. Due to the import of tiling machines in 1848 more than 100 tile factories existed in Illinois, Indiana, and Ohio. By 1882, about 43,230 km of tile drains were installed in Indiana alone. The Bureau of Reclamation had constructed about 4990 km of drains in 1931. By this time, subsurface drains had been installed extensively in most of the states in the United States.

In India, the problem of waterlogging and soil salinity were observed in village Munak in the former Punjab as early as 1855. Due to the construction of large canal systems, salinity was observed in several areas. In the Ganges canal, salinity was observed in 1876, and in lower Chenab canals, it was observed after these canals opened in 1892. The first subsurface drainage experiment was laid out in India in 1873, although it was not considered successful. In Punjab, a Waterlogging Board was constituted in 1925. In 1928, Inglis and Gokhale established that subsurface drainage is effective in lowering the water table at the Baramati farm.

The earliest drainage method consisted of making drains from stones. With the use of stones, the old method of drainage by open trenches was abandoned. Another

method of draining permanent pastures was through turf drains the remains of which can still be seen in many fields in the mid lands in the United Kingdom. Some of these even had useful lives of 100 years. Besides turf drains, other varieties of drains were plug drains principally used in arable lands, straw drains used extensively in the heavy land districts, and brushwood drains made from fagots or bundles of brushwood, which were placed at in the bottom of deep trenches. Then, came brick drains followed by U-tiles or horseshoe drains. The last to come were cylindrical brick tiles or clay tiles, which have now been replaced by PVC perforated/corrugated pipes.

HORIZONTAL SUBSURFACE DRAINAGE

Buried pipes, pipeless drains, or deep open ditches are commonly used to drain lands in this kind of drainage. Pipe drains consist of a system of tiles or pipes such that excess water enters in lateral lines through the joints between two tiles or perforations in the pipes and flows towards collector/main drains. Pipeless drains, called mole drains, are cylindrical channels artificially made in the subsoil by a mole plow. When the cost of regular pipe drains becomes too high due to close spacing, mole drains are used. The principles and hydraulics of mole drains are similar to those of pipe drains. It is a temporary method of drainage because moles deteriorate in a few years and have to be remade frequently. Deep open ditches, if constructed close enough, can work similarly to pipe drains or mole drains to lower the water table and remove excess water. Practically, open ditches are difficult to maintain and cause a lot of inconvenience to men, animals, and farm equipment that cross them.

SUBSURFACE DRAINAGE THEORIES

A number of mathematical solutions have been proposed to describe water table behavior and to evolve drainage criteria for appropriate design of drainage systems, using steady-state or transient flow conditions in horizontal or sloping aquifers. The solutions have been obtained by employing experimental, analytical, or numerical approaches. These solutions help to evolve drainage criteria that help in determining the drainage rate and spacing for a preselected suitable depth of drains, depending on soil characteristics and water table height midway between drains. The basic objective of evolving drainage criteria is to attain and maintain an optimum or a reasonably permissible value of average water table depth and root zone that is either free from salts or has electrical conductivity below the tolerance limit of the plants to get the maximum net benefit. Some of the theories are presented here.

Steady State

In this situation, recharge due to rainfall or irrigation is assumed constant and equal to the discharge from drains, such that water table does not change with time. This criterion describes the quantity of water to be removed in a given period of time under conditions of given water table height above the drain level. This criterion is generally applicable in flat areas of a humid region, where low intensity, long duration rainfall occurs in winter and spring. By selecting appropriate soil water hydrologic parameters, it can also be used for arid salt-affected lands. Based on this theory, Colding (1), Rothe (2), Kozeny (3), and Hooghoudt (4) obtained the same relationship independently. Hooghoudt (5), based on the Dupuit–Forchheimer assumptions, proposed an equation for computing of drain spacing as

$$L^2 = \frac{4Kh_0(2d + h_0)}{q} \tag{1}$$

where L is the drain spacing, K is the hydraulic conductivity of the soil, d is the depth to an impermeable layer below the drain axis, q is the rate of recharge, and h_0 is the height of the water table above the drain axis at the midpoint between the drains. It is more appropriately applicable only when the depth to impermeable layer d is relatively small compared to h. For comparatively large values of d, the flow to drains will tend to be radial. To account for the extra resistance caused by radial flow, Hooghoudt introduced the concept of equivalent depth (d_e), such that d is replaced by d_e. In such cases, Equation 1 may be written as

$$L^2 = \frac{8K_b d_e h_0 + 4K_a h_0^2}{q} \tag{2}$$

In this equation, K_a and K_b are the hydraulic conductivities of the soil above and below the drain, levels. The first term pertains to flow below the drains and the second term indicates flow above the drains.

Ernst (6) extended Hooghoudt's approach to make it applicable to stratified soils that have a slowly permeable top layer. He assumed horizontal and radial flow resistance in his analysis. His solution is simple, but the presence of the geometry factor in the solution makes it slightly cumbersome for practical applicability. Nomographs developed by Van Beers (7) made Ernst's solution simpler for practical purposes.

Kirkham (8) obtained an analytical solution for a problem similar to Hooghoudt's, using potential theory and ignoring the flow above the drains. Later on Kirkham (9) reported that, if vertical flow in the upper region is also taken into account, the solution becomes

$$h = \frac{qL}{K}\left(\frac{1}{1 - q/K}\right)F_k \tag{3}$$

where

$$F_k = \frac{(L - d\sqrt{2})^2}{8dL} + \frac{1}{\pi}\ln\left(\frac{d}{r\sqrt{2}}\right) + f(d, L)$$

r is the radius of the subsurface drain, and $f(d, L)$ is a function of d and L, which was evaluated from an infinite series, which introduced a reduction in flow depth. The new reduced depth, d_e, was called equivalent depth and was defined as $L/8F_k$.

Wessling (10) analyzed the solution given by Hooghoudt (5) and Kirkham (9) and concluded that both solutions gave almost identical results within a 5% variation. Lovell and Youngs (11) calculated water table heights above drains using a number of steady-state equations and found that it could be computed with sufficient accuracy for smaller as well as for larger depths of the impermeable barrier. At intermediate depths, the solutions led to large uncertainties in the estimates. It was also noticed that among all drainage equations, Hooghoudt's equivalent depth equation, when used with an optimum drain radius obtained by a hodographic analysis for finite soil depths, gave reasonable values of lateral drain spacing which were within the known limits of uncertainty.

Unsteady State

This theory is generally used in areas that have a high intensity of rainfall or in arid lands where the rise in the water table due to frequent irrigation needs to be lowered by drainage. It describes the fall of the water table required within a certain period after the water table has risen near the land surface due to instantaneous recharge. Most of the unsteady-state theories relate to the study of groundwater flow in a homogeneous, isotropic, unconfined aquifer lying over a horizontal impermeable layer and are characterized by Dupuit–Forchheimer assumptions based on the Boussinesq (12) partial differential equation, which is

$$h\frac{\partial^2 h}{\partial x^2} + \left(\frac{\partial h}{\partial x}\right)^2 = \frac{f}{K}\frac{\partial h}{\partial t} \tag{4}$$

where K is the hydraulic conductivity of the aquifer, h is the height of the phreatic surface above the impermeable layer, and f is the drainable porosity (dimensionless). Equation 4 is a nonlinear second-order partial differential equation. Solutions of nonlinear or linearized forms of this equation for appropriate boundary conditions representing different physical flow conditions have been obtained in the past by a number of researchers. There are three physically identified commonly occurring flow situations: (1) a falling water table between two level drains, (2) a falling water table between two bilevel drains, and (3) a water table between two drains/canals fluctuating due to recharge or evapotranspiration.

Falling Water Table between Two Level Drains. Boussinesq (13) obtained an exact analytical solution of Eq. 4 with initial conditions $h(L/2, 0) = h_0$ and boundary conditions $h(0, t) = h(L, t) = 0$, assuming drains located at the impervious layer. His solution, which describes the temporal and spatial variation of a falling water table in nondimensional form, can be written as:

$$\frac{h}{h_0} = \frac{1}{\left(\dfrac{9Kh_0t}{fL^2} - 1\right)} \tag{5}$$

where h_0 is the initial midpoint of the water table height, h is the water table height after lowering it from an initial value of h_0 in time t, and L is the spacing between two drains.

Glover (14) also obtained the same solution for Eq. 4 as given by Boussinesq (13). Dumm (14) assumed an initially horizontal groundwater table at a certain height above the drain level because of instantaneous recharge due to rainfall or irrigation. Equation 4 was linearized by assuming that the free water surface has a small slope enabling h, associated with $(\partial^2 h/\partial x^2)$, to be replaced by D, average depth of flow, and neglecting $(\partial h/\partial x)^2$ by considering that it is very small. Equation 4 is thus reduced to

$$\frac{\partial^2 h}{\partial x^2} = \frac{f}{KD}\frac{\partial h}{\partial t} \tag{6}$$

Assuming that the initial water table is horizontal and zero end conditions, a Fourier series solution for falling water table heights midway between the drains was obtained as

$$h\left(\frac{L}{2}, t\right) = \frac{4h_0}{\pi}\sum_{n=1,-3,5}^{\infty}\frac{1}{n}e^{-\frac{n^2\pi^2 KDt}{fL^2}} \tag{7}$$

Dumm (15) assumed that the initial water table was a fourth-degree parabola and obtained the solution for the boundary conditions used by Glover (14). The only difference between Eq. 8 and his solution was the shape factor which was replaced by 1.16 instead of a value of $4/\pi$.

Brooks (16) presented a solution to the nonlinear Boussinesq equation describing unsteady flow toward equally spaced drains above a horizontal impermeable barrier in the form of a perturbation series. Van Schilfgaarde (17, 18) derived an exact solution to Boussinesq's Equation 4 for the boundary conditions when drains did not reach the impermeable layer. He also applied a convergence correction to the solution of the drainage problem and finally obtained an equation for drain spacing as

$$L = 3A\left[\frac{K(d_e + h)(d_e + h_m)t}{2f(h_m - h)}\right]^{\frac{1}{2}} \tag{8}$$

where

$$A = \left[1 - \left(\frac{d_e}{d_e + h_m}\right)^2\right]^{\frac{1}{2}}$$

d_e is the equivalent depth of an impervious layer below the drain, and h_m is the maximum water table height above the drain level. The results of this solution compared with those obtained from the Glover–Dumm (14) solution differed by the order of 10 to 40%.

Role of Evapotranspiration in Drainage Design

Work was also carried out by Brooks (16), Moody (19), Pandey and Gupta (20), Singh et al. (21, 22), and Nikam et al. (23) to include the contribution of other processes, mainly evapotranspiration, in lowering the water table. Both steady and nonsteady approaches have been used.

Falling Water Table Between Two Bilevel Drains. De Boer and Chu (24) developed an unsteady-state theory

for a bilevel drainage system using the Bouwer and Van Schilfgaarde (25) approach. They suggested using a bilevel drainage system because by having deep and shallow drain lines on an alternate basis, the excavation and digging cost would be reduced substantially and thus a bilevel drainage system would be economical compared to a conventional level drainage system. Studies were also carried out by Chu and De Boer (26), Sabti (27), Verma et al. (28), and Upadhyaya and Chauhan (29).

Fluctuating Water Table. Kraijenhoff van de Leur (30) studied the effect of constant steady-state recharge during the drainage process instead of an instantaneous recharge, as assumed by Dumm. The governing equation and initial and boundary conditions are written as

$$\frac{\partial^2 h}{\partial x^2} + \frac{R}{Kd} = \frac{f}{KD}\frac{\partial h}{\partial t}$$
$$h(x, 0) = 0, \qquad 0 < x < L$$
$$h(0, t) = h(L, t) = 0, \quad t > 0$$

where R is the recharge rate per unit area. The height of the water table midway between parallel drains at any time t is given as

$$h(L/2, t) = h_t = \frac{4}{\pi}\frac{R}{f}J \sum_{n=1,3,5}^{\infty} \frac{1}{n^3}(1 - e^{-\frac{n^2 t}{J}})$$

where $J = fL^2/\pi^2 KD$.

This equation is not used for routine drain spacing computations; however, it is useful for hydrologic studies such as estimating water table fluctuation or drain discharge variation with time for a given recharge pattern.

Maasland (31) also analyzed the problem of water table fluctuations in response to constant recharge, intermittent constant recharge, and intermittent instantaneous recharge independently and almost at the same time as Kraijenhoff van de Leur (1958) using similar and a few different boundary conditions.

NUMERICAL SOLUTIONS

Dass and Morel-Seytoux (32) solved the one-dimensional nonlinear Boussinesq equation by Galerkin's finite element technique for three initial water table conditions. They observed that Galerkin's method was applicable to any initial water table profile. Studies were also carried out by Marino (33), Singh and Jacob (34), Singh and Rai (35), Skaggs (36), Pandey et al. (37,38), and Sewa Ram et al. (39).

Drainage of Sloping Lands

When wetness is prolonged, subsurface drainage and hillside seeps are an acute problem in many parts of the world such as the pre-Alps in Switzerland and adjacent countries and the tea gardens of Assam, India, where drainage of sloping lands is considered quite an important problem.

Because of saturation of the soil, the growth of plantations and trees is retarded, and there is difficulty in new afforestations and plantations. In the southern Appalachian Mountains, such problems were experienced for which elaborate experimental studies were carried out to study storm flow response on sloping forested watersheds. The theoretical analysis of this problem has also been difficult and is a classical hydrologic issue. Some notable works may be mentioned as those of Werner (40), Schmid and Luthin (41), Wooding and Chapman (42), Luthin and Guitjens (43), Chauhan et al. (44), Childs (45), Jaiswal and Chauhan (46), Sewa Ram and Chauhan (47), and Upadhyaya and Chauhan (48).

DESIGN CRITERIA FOR HORIZONTAL DRAINS

Steady-State Criteria

This criterion is generally applicable in flat areas of humid regions, where low intensity, long duration rainfall occurs in winter and spring. In this situation, recharge due to rainfall or irrigation is assumed constant and equal to the discharge from drains such that the water table height does not change with time. This criterion describes the quantity of water to be removed in a given period of time under conditions of given water table heights above the drain level. In this criterion, drain discharge is matched to provide a clear root-zone depth above the midpoint of the water table. Such a criterion can be expressed as for example, a drain discharge of 7 mm per day when the water table depth is at the midpoint of two drains at 50 cm below the ground level. Hooghoudt's equation has generally been recommended for designing drain spacing in homogeneous soils because of its simplicity and ease of use. For layered soil or for soil that has a slowly permeable top layer, the Ernst equation (6) has been recommended because it takes radial flow into account in the total flow.

Unsteady-State Criteria

This criterion is generally used in areas of high intensity storms that occur quite commonly or in irrigated lands which requires establishing a rate of fall of the midpoint of the water table between two horizontal drains to match the sensitivity of a selected crop that can sustain a high water table for a limited period. The Glover–Dumm equation is recommended for use by the United States Bureau of Reclamation. According to this criterion, the water table should drop from the ground surface to at least 30 cm below in 24 hrs and to 50 cm below in 48 hrs (49). When the water table rises to some 15 cm below the ground surface, it should drop to 35–40 cm below in 1 day (50).

Equivalence Between Steady-state and Nonsteady State Criteria. Steady-state criteria are comparable to the falling water table criteria. For the drainage criterion consisting of a discharge rate of 0.007 m/day, when the water table depth is 0.50 m, the hydraulic head (h) will be 50 cm if the drain depth is 1 m. If the water table rises to the surface, both the discharge rates and hydraulic head will

increase by two times and become 0.014 m/day and 100 cm, respectively. For a clay soil whose drainable porosity is 4 to 5%, this would result in a drop of the water table from the ground surface to about 30 cm below in 1 day which corresponds to the U.S. standard.

Vertical Drainage

Vertical drainage and conjunctive use of canals and groundwater is another good way of lowering the water table and providing subsurface drainage. With good quality groundwater, it is an excellent practice. On one hand, it lowers the water table and, on the other hand, through the same process, it also provides irrigation for increasing the production of agricultural crops. However, it is important to understand the different issues involved. Sometimes, the objective of vertical drainage is steady-state lowering of water tables in the root zone for growing crops due to overlapping of drawdown caused by pumping closely spaced wells. In other words, it is similar to the well-known well point system. Such a system is used for building foundations or other structures in high water table areas where rapid lowering of water tables is required for short periods. Such a system would not only be structurally costly but would also involve high recurring energy costs. Such a system does not seem to be practicable for growing agricultural crops. Thus, lowering of water tables should be considered in terms of total withdrawal on a long-term basis instead of transient lowering in a short period for growing crops that require lowering of 0.3–0.5 m in 1 to 2 days, as for maize or soybean.

De Ridder (51) and Attia and Twinhof (52) recommend the technical feasibility of tube well drainage only based on the geometry of the aquifer, hydraulic parameters, the thickness and hydraulic resistance of the clay cap, the groundwater quality, and the rate of recharge. According to them, well drainage enables lowering the groundwater to a much greater depth than gravity drainage. Where deeper layers of substrata are more pervious than layers near the surface, pumping from these layers may reduce the artesian pressure that is often present, and create a vertical downward flow through the upper layers. If the pervious strata are found at a depth of 5 m or more, well drainage can be applied successfully, if the transmissivity of the aquifer is fairly high. If the aquifer is semiconfined, an additional criterion would be the value of the hydraulic resistance of the upper clay layer. The energy requirement is another consideration that should be looked into for well drainage. Unlike gravity drainage, well drainage is not economically feasible in small areas because too large a portion of the water drained consists of foreign water. Well drainage may also not be feasible in areas where artesian pressure is too high.

In a case study of SCARPS in Pakistan by Awan (53), tube wells were installed to lower the water table and provide more water for intensive agriculture and to reduce salinity. Large capacity tube wells were installed near the outlets to feed one or two watercourses. A large number of problems were faced from vertical drainage. The operational and maintenance costs were quite heavy. There were problems of spares making tube wells remain idle. Eighty percent of the total budget went to electricity bills leaving little money for maintenance. Several disputes cropped up among the farmers who were supplied water from the same watercourse. The authorities were forced to shift the policy in the sweet water zone from large public tube wells to the private sector. In a later study, Smedema and Zimmer (54) also favored private investments in the freshwater zone, which seemed quite successful. It was also observed that providing horizontal drainage instead of tube well drainage could have reduced the salinity of the drainage effluent.

Even in the Australian Wakool drainage project of about 57,000 ha, affected lands had water tables within 2 to 3 m of the surface. An attempt to lower the water table by using 52 tube wells faced similar problems, as in SCARPS in Pakistan. The high capital and growing operating and maintenance costs affected the economic value of the scheme, and it seemed unlikely that a scheme of such a magnitude could ever be built again for Australian agriculture.

Biodrainage

Biodrainage is being propagated as a method of subsurface drainage. It is an economical method of drainage, it improves the ecology of the area, and it is environmentally friendly. It provides costly wood and biomass useful for many purposes. It can transpire water from the groundwater table in good amounts. A large range of plants tolerant to salinity can be grown in waterlogged, salt-affected lands. However, it is important to identify appropriate situations where this method can be effective and useful. It is unfair to assign it an objective, which it cannot achieve, and then misinterpret the approach. The issue to be examined is whether meeting the shortage of food production is a pressing need now or in the future in developing countries and, if so, how can biodrainage be used to reclaim waterlogged and salt-affected lands for food production. If there is no immediate necessity to increase food production, then it could be a good alternative to put all such areas under trees. However, if the priority favors food production, then it has to be seen whether forest or tree crops can lower water tables at a fast enough rate to grow maize/soybean or other crops without the ill effects of waterlogging. Even if plants can lower the water table at a fast rate, one would have to look for a proper cropping system. It needs to be seen whether one can grow food crops simultaneously with tree crops and maintain a deep enough water table. Alternatively, one will be required to grow tree crops for a few years, and, after the water table has been lowered, then one can grow grain crops; this has to be properly understood and practically planned. Similarly, it is understandable that many agricultural, horticultural, and other tree crops can tolerate salinity of different levels. But, whether it is practicable to reclaim a saline soil whose electrical conductivity is more than 50 dS/m, through tree crops, so as to make it suitable for growing agricultural crops, needs to be explored.

According to Smedema (55) there are three situations for biodrainage: waterlogged landscape depressions, areas along a canal to intercept canal seepage, and growing plants to act as parallel field drainage. In the first, instead of installing a pumped well for drawing down the water

table, the drainage improvement could be done by planting trees, shrubs, or other vegetation. In the second, in place of an interceptor drain practised in the past at the toe of the embankment of a canal, drainage conditions could be improved by planting a strip of suitable vegetation. In the third, biological line sinks (strips of planted trees/shrubs) can be used instead of conventional parallel field drainage systems such as ditches or pipe drains. Such a system could also work as a typical windbreak for a more favorable microclimatic environment. According to Smedema (55) this is generally not a realistic option, when common crops are facing severely waterlogged conditions. However, biodrainage under certain conditions has merit according to which it may be confined to growing tolerant species under not too extreme waterlogging conditions. The scope of biodrainage seems to be more favorable in an arid zone where drainage surpluses are small in relation to evapotranspiration rates (1 to 2 mm/day vs. 10 mm/day). The claims of using biodrainage to cope with salinity do not seem to be supported by experimental evidence from Australia and California. Biodrainage without any physical drainage is more likely in the long run to lead to a harmful buildup of root-zone salinity.

PRESENT STATUS AND SCOPE OF DRAINAGE

Land drainage in the past has played an important role in the modernization of rain-fed and irrigated agriculture throughout the world. Drainage of European agricultural lands, where improved drainage was needed in as much as 25% of agricultural land, helped Europe to attain self-sufficiency in food production. Nearly 70% of this land has been put under subsurface drainage during the last 30 years. Drainage development in the United States, helped by other technologies, created one of the most efficient production systems. As half of wetlands were converted into cropped land, drainage developments since 1960 are being influenced by changing environmental ethics because there is more emphasis on protecting wetlands. In spite of this, even in the United States, about 10 to 20 mha of cropland still need drainage. Out of a total agricultural area of 18.65 mha in the United Kingdom, besides presently drained lands, a further 3.5 mha still require drainage. Considerable experience in design and construction of drainage systems has been gained in Russia. The total area of drained land exceeds 1 mha. More than half of the land is under subsurface drainage.

According to Smedema, the world's total cropped land area stands at 1450–1500 mha of which 250 mha (70%) is provided with irrigation facilities. Of this cropland, 150–200 mha (10–15%) have drainage facilities. Of this about a 50 mha area is irrigated, and the remaining 100–150 mha are rain fed. All of the latter are in Europe and North America. It is estimated that 250–300 mha of rain-fed cropland still needs drainage of which 25–30 mha would be a reasonable medium-term program to cover the humid tropic lands of Southeast Asia. The current rate of drainage development is estimated at 0.5–1.09 mha/year.

Drainage, it is predicted, will increase food production in the irrigated area by 1–1.5% and in the rain-fed area by 0.5–1%. The global average will be about 1%. The need for drainage of irrigated lands consists of surface drainage and subsurface drainage to combat waterlogging and salinity. A medium-term (25 years) drainage plan would cover 10–15 mha surface drainage and 2–3 mha of subsurface drainage. All of this is located in developing countries.

BIBLIOGRAPHY

1. Colding, L.A. (1872). Om louene for vandets be voegelse I jorden. Danske vidensk. Selsk. Skr. 5 *Raekke Natur Vog math. Afd.* **9B**: 563–621 (Copenhagen).
2. Rothe, J. (1924). Diestrangent fernung bei Dranungen Landw. *Jahrb*. **59**: 453–490.
3. Kozeny, J. (1932). Hydrologische grandlagaen des Dranuer suches. *Trans. 6th Comm. International Society of Soil Science.* **A**: 42–67.
4. Hooghoudt, S.B. (1936). Bepaling van den doorlaatfactor van den grond met behulp van pompproeven (z.g. boorgatenmethode). *Verslag Landbouwk. Onderzolk*. **42**: 449–541.
5. Hooghoudt, S.B. (1940). Bijdragen tet de Bennis van eenige natuurheundige grootheden van den grond, 7, Algemeene beschsuwing van het probleem. Van de detail ontwatering en de infiltratic door middle van parallel loopende drains, greppels slooten, en kanalen. vaersl. *Landiouwk. Ond*. **46**: 515–707.
6. Ernst, L.F. (1956). Calculation of steady flow of ground water in vertical cross section. *Netherlands Journal of Agriculture Science* **9**: 126–131.
7. Van Beers, W.F.J. (1965). Some nomographs for the calculation of drain spacings. *Int. Inst. Land Reclaim. Improve. Bull.* No. 8, Wageningen, p. 45.
8. Kirkham, D. (1958). Seepage of steady rainfall through soil into drains. *Transactions American Geographical Union* **39**(5): 892–908.
9. Kirkham, D. (1960). An upper limit for the height of the water table in drainage design formula. *Trans. 7th International Congress for Science* **I**: 486–492.
10. Wessling, J. (1964). A comparison of the steady-state drain spacing formulas of Hooghoudt and Kirkham in connection with design practices. *Int. Land Water Manage. Res. Tech. Bull.* 34, Wageningen.
11. Lovell, G.J. and Youngs, E.G. (1984). A comparison of steady state land drainage equation. *Agricultural Water Management* **9**: 1–21.
12. Boussinesq, J. (1877). Du movement non permanent des eaux souterraines. *Essai Sur la theorie des eaux courantes*, Memoires presents par divers savants a l'. Academie des Sciences de institut de France, 23, 1, Paris, France, p. 680 (Note en Basde 252–260).
13. Boussinesq, J. (1904). Recherches theoriques sur l'ecoulement des nappes d'eau infiltree's dans le sol et sur le debit des sources. *Journal de Math. Pures et Appl.* Series 5, Tome X (in French) pp. 5–78.
14. Dumm, L.D. (1954). Drain spacing formula: New formula for determining depth and spacing of subsurface drains in irrigated lands. *Agricultural Engineering* **35**(10): 726–730.
15. Dumm, L.D. (1960). Validity and use of the transient concept in subsurface drainage. Paper presented at American Society of Agricultural Engineers meeting held at Memphis, pp. 4–7.
16. Brooks, R.H. (1961). Unsteady flow of groundwater into drain tile. *Amer. Soc. Civil Eng., Proc.* **87**(IR2): 27–37.
17. Schilfgaarde, J. (1963). Design of tile drainage for falling water tables. *Amer. Soc. Civil Eng. Proc.* **89**(IR2): 1–17.

18. Schilfgaarde, J. (1965). Transient design of drainage systems. *Amer. Soc. Civil Eng. Proc.* **91**(IR3): 9–22.
19. Moody, W.T. (1966). Nonlinear differential equation of drain spacing. *Journal of Irrigation and Drainage Division, ASCE* **92**(IR2): 1–9.
20. Pandey, R.S. and Gupta, S.K. (1990). Drainage design equation with simultaneous evaporation from soil surface. *ICID Bulletin* **39**(1): 19–25.
21. Singh, K.M., Singh, O.P., Ram, S., and Chauhan, H.S. (1992). Modified steady state drainage equations for transient conditions in subsurface drainage. *Agricultural Water Management* **20**(4): 329–339.
22. Singh, K.M., Singh, O.P., Chauhan, H.S., and Ram, S. (1996). Comparison of subsurface drainage theories for drainage of waterlogged saline soils of Haryana state, India. *Applied Engineering in Agriculture* **8**(5): 653–657.
23. Nikam, P.J., Chauhan, H.S., Gupta, S.K., and Ram, S. (1992). Water table behaviour in drained lands: effect of evapotranspiration from the water table. *Agricultural Water Management* **20**: 313–328.
24. De Boer, D.W. and Chu, S.T. (1975). Bi-level subsurface drainage theory. *Transactions of the American Society of Agricultural Engineers* **18**(4): 664–667.
25. Bouwer, H. and Van Schilfgaarde, J. (1963). Simplified method of predicting fall of water table in drained lands. *Transactions of the American Society of Agricultural Engineers* **6**(4): 228–291,296.
26. Chu, S.T. and DeBoer, D.W. (1976). Field and laboratory evaluation of bi-level drainage theory. *Transactions of the American Society of Agricultural Engineers* **19**(3): 478–481.
27. Sabti, N.A. (1989). Linear and nonlinear solution of the Boussinesq equation for the bi-level drainage problem. *Agricultural Water Management* **16**: 269–278.
28. Verma, A.K., Gupta, S.K., Singh, K.K., and Chauhan, H.S. (1998). An analytical solution for design of bi-level drainage systems. *Agricultural Water Management* **37**: 75–92.
29. Upadhyaya, A. and Chauhan, H.S. (2000). An analytical solution for bi-level drainage design in the presence of evapotranspiration. *Agricultural Water Management* **45**: 167–184.
30. Kraijenhoff Van de Leur, D.A. (1958). A study of non-steady ground water flow with special reference to a reservoir coefficient. *De Ingenieur* **70**: 87–94.
31. Maasland, M. (1959). Water table fluctuations induced by intermittent recharge. *Journal of Geophysical Research* **64**(5): 549–559.
32. Dass, P. and Morel-Seytoux, H.J. (1974). Subsurface drainage solutions by Galerkin's method. *Journal of Irrigation and Drainage Division* **100**(IR1): 1–15.
33. Marino, M.A. (1974). Water table fluctuation in response to recharge. *Journal of Irrigation Drainage Division, ASCE* **100**: 117–125.
34. Singh, S.R. and Jacob, C.M. (1976). Numerical solution of Boussinesq equation. *Journal of the Engineering Mechanics Division, Proceedings of ASCE* **102**(EM5): 807–823.
35. Singh, R.N. and Rai, S.N. (1989). A solution for the nonlinear Boussinesq equation for phreatic flow using an integral balance approach. *Journal of Hydrology* **109**(3/4): 319–323.
36. Skaggs, R.W. (1991). Modelling water table response to subirrigation and drainage. *Transactions of the American Society of Agricultural Engineers* **34**(1): 169–175.
37. Pandey, R.S., Bhattacharya, A.K., Singh, O.P., and Gupta, S.K. (1992). Drawdown solutions with variable drainable porosity. *Journal of Irrigation and Drainage Engineering* **118**(3): 382–396.
38. Pandey, R.S., Bhattacharya, A.K., Singh, O.P., and Gupta, S.K. (1997). Water table drawdown during drainage with evaporation/evapotranspiration. *Agricultural Water Management* **35**: 61–73.
39. Ram, S., Jaiswal, C.S., and Chauhan, H.S. (1994). Transient water table rise with canal seepage and recharge. *Journal of Hydrology* **163**: 197–202.
40. Werner, P.W. (1957). Some problems in non-artesian ground water flow. *Transactions American Geophysical Union* **38**(4): 511–518.
41. Schmid, P.A. and Luthin, J.N. (1964). The drainage of sloping lands. *Journal of Geophysical Research* **69**: 1525–1529.
42. Wooding, R.A. and Chapman, T.G. (1966). Groundwater flow over a sloping impermeable layer, 1. Application of the Dupuit-Forchheimer assumptions. *J. Geophys. Res.* **71**: 2895–2902.
43. Luthin, J.N. and Guitjens, J.C. (1967). Transient solutions for drainage of sloping land. *Journal of the Irrigation and Drainage Division, Proceedings of American Society of Civil Engineers* **93**(IR3): 43–51.
44. Chauhan, H.S., Schwab, G.O., and Hamdy, M.Y. (1968). Analytical and computer solution of transient water table for drainage of sloping land. *Water Resources Research* **4**(3): 673–679.
45. Childs, E.C. (1971). Drainage of ground water resting on sloping bed. *Water Resources Research* **7**(3): 1256–1263.
46. Jaiswal, C.S. and Chauhan, H.S. (1975). A Hele-Shaw model study of steady state flow in an unconfined aquifers resting on a sloping bed. *Water Resources Research* **II**(4): 596–600.
47. Ram, S. and Chauhan, H.S. (1987). Analytical and experimental solutions for drainage of sloping lands with time varying recharge. *Water Resources Research. American Geophysical Union* **23**(6): 1090–1096.
48. Upadhyaya, A. and Chauhan, H.S. (2001). Falling water tables in a horizontal/sloping aquifer. *Journal of Irrigation and Drainage Engg. ASCE* **127**(6): 376–384.
49. Kidder, E.H. and Lytle, W.F. (1994). Drainage investigation in plastic till soils of Northeastern Illinois. *Agr. Eng.* **39**: 384–386.
50. Neal, J.H. (1934). Proper spacing and depth of tile drains determined by the physical properties of the soil. *Minnesota Agr. Exp. Sta. Tech. Bull.* 101.
51. De Ridder, N.A. (1973). Drainage by means of pumping from wells pp. 223–237; *Theories of Field Drainage and Watershed Runoff*. Vol. II. *Drainage Principles and Applications; ILRI*. Wageningen, the Netherlands.
52. Attia, F.A.R. and Twinhof, A. (1989). Feasibility of tube well drainage in nile valley. pp. 303–326 Chapter 13 *Land Drainage in Egypt*. M.H. Amer and de Ridder (Eds.). Cairo, p. 377.
53. Awan, N.M. (1991). *Salinity control and reclamation project, a case study in 'Approaches to Integrated Water Resource Management in Humid Tropics Arid and Semi Arid Zones in Developing Countries' compiled by Maynara*. M. Hufschmidt, Janusz, Kindler.
54. Smedema, B. and Zimmer, D. (1994). *Vertical drainage and conjunctive use. GRID ISSN. 1021-268X*, pp. 7–8.
55. Smedema, B. (Dec. 1997). Biological drainage myth or opportunity? *GRID Iptrid Network Magazine*, p. 9.
56. Smedema, L.K. (2000). Global needs and challenges, the role of Drainage in today's world. *Proc. 8th ICID International Drainage Workshop*, 31st Jan–4th Feb, New Delhi, Vol. 1–1.

DRAWDOWN

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According to Wilson and Moore (1), drawdown is the lowering of the water level in a well as a result of withdrawal. Drawdown data are collected to evaluate the performance of the well and to determine the aquifer's hydraulic character (transmissivity). Drawdown measurements also provide information on the well efficiency and performance. For example, measurements can be used with well discharge data to detect deterioration of the well screen.

The drawdown in a pumping well is the sum of head loss factors (2). Some of the factors are natural processes, head loss in the aquifer, loss in the damage zone (well drilling), well development, and turbulent loss in the filter zone. The damage zone consists of drilling debris, filter cake, and drilling fluid.

When water is withdrawn from a well, the initial discharge is from casing storage and from aquifer storage near the well bore. As withdrawal continues, water is withdrawn at greater distances from the well. The cone depression or drawdown expands and deepens more slowly with time because an increasing amount of stored water is available from each foot of expansion of the cone (3). The cone of depression will continue to enlarge until the following conditions are met (4):

1. It intercepts a body of water (stream, lake, or wetland) that supplies enough water to equal the pumping rate.
2. Enough recharge from precipitation occurs within the cone of depression's influence to equal the pumping rate.
3. Leakage occurs from overlying or underlying aquifers to equal the pumping rate.

The cone of depression around a well is controlled by the transmissivity of the aquifer. In aquifers of a low transmissivity (10,000 gpd/ft_2), the cone is deep and has steep sides and a small radius. In aquifers of high transmissivity (100,000 gpd/ft_2), the cone is shallow and has a large radius

Slichter in 1899, Thiem in 1906, and Theis in 1935 (5) introduced the equations to predict drawdown. The transmissivity of the aquifer determines the shape of the drawdown curve.

The following is a list of key terms associated with well drawdown (6):

Static level— water level of a well that is not affected by the withdrawal of ground water.

Pumping level— the level of water in the well during pumping.

Well yield— the discharge of a well or rate at which a well yields water either by pumping or free flow.

Specific capacity— an expression of the productivity of a well obtained by dividing the rate of discharge by the drawdown in the well. It should be described on the basis of the number of hours of pumping prior to the time the measurement is made because it generally decreases with time as drawdown increases.

Well efficiency (well hydraulics)— defined as the ratio of actual specific capacity to theoretical specific capacity. Actual specific capacity is related to drawdown in the well and theoretical specific capacity. Well efficiency is determined by a step drawdown test.

Step drawdown test— In this test, the well is pumped at several (three or more) successively higher pumping rates, and the drawdown at each rate is recorded. The test is usually conducted during 1 day. The discharge is kept constant through each step.

Getting access to the well to take drawdown measurements is sometimes difficult. Ideally, you can gain access through a pipe intended for measurements. Measurements of drawdown in wells can be obtained by one of the following methods (7):

1. wetted steel tape
2. air-line submergence method
3. electrical tape
4. pressure transducer

Wetted Steel Tape

Before the 1960s, most water level measurements were made with a steel tape (most likely a 100- or 200-foot Lufkin tape). It is typically used for depths up to 90 feet. Electrical methods and pressure transducers in part have replaced tapes. However, the steel tape still has applications today, for example, to calibrate pressure transducers. To use the wetted tape method, the hydrologist will need a steel measuring tape, a weight, and carpenter's chalk. Before the tape is lowered down the well, the lower 1 to 2 feet or so of the tape is coated with carpenter's chalk. Problems that may be encountered using this method are moisture on the well casing, cascading water, and oil (leaking from pump lubrication). In some cases, this method can be very inaccurate. For example, if the water level is below the well screen, water flowing into the well can wash the chalk off the tape.

Electrical Tape

Most electrical tapes are marked every one-tenth foot. An electrical probe is lowered into the water, which completes an electrical circuit, and this sounds a buzzer or light.

Pressure Transducer

The transducer probe measures the column of water above the probe. It is very useful in aquifer tests where the water level changes rapidly with time.

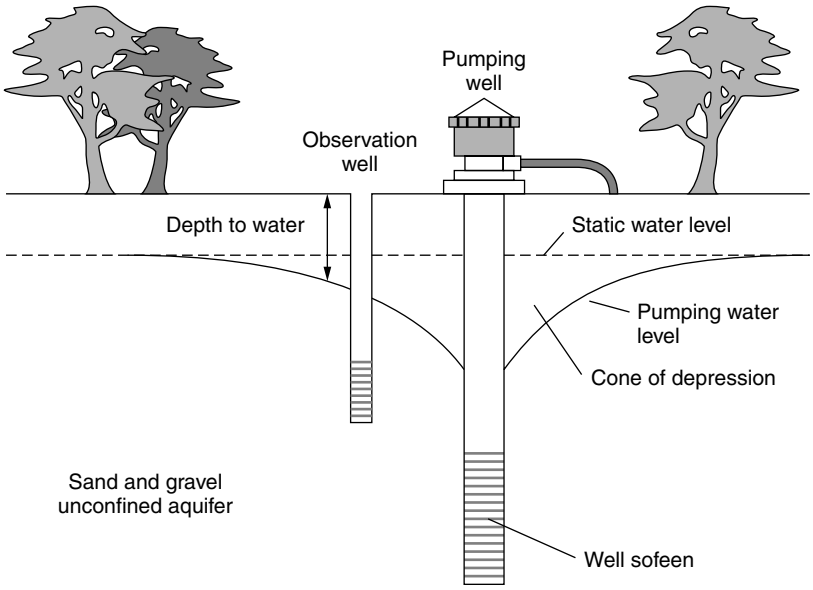


Figure 1. Diagram of a well (6).

Specific capacity tests can be used to determine the amount of water a well will yield. In this test, the pumping rate and drawdown (water-level changes) are monitored for a set period of time. The first step is to measure the initial water level in the well. Commonly, a well is pumped at several successively increasing rates for uniform periods (typically 1 hour) to establish a rate that can be maintained for long-term pumping. The well is then pumped at a steady rate and the water-level changes are monitored at the pumped well. Water levels should also be monitored in at least one observation well 2 to 20 meters (6 to 65 feet) from the pumped well. The water level will decline quickly at first as water is removed from the well, then more slowly as the rate of flow into the well approaches the pumping rate. The ratio of the discharge rate (Q) to the water-level change (drawdown, dd) gives the well's specific capacity, or $\mathrm{Sc} = Q/\mathrm{dd}$. For example, if the discharge rate is 6 liters per second (L/s) [100 gallons per minute] and drawdown is 3 meters (10 feet), the specific capacity of the well is 2 L/s per meter (10 gpm/ft) of drawdown. Once the specific capacity and the available amount of drawdown are known, the yield of the well can be determined from the formula $Q = \mathrm{Sc} \times \mathrm{dd}$. An estimate of the transmissibility in an unconfined aquifer can be obtained by multiplying the specific capacity by 2000.

A step-drawdown test evaluates the performance of the well. Well performance can be affected by resistance to flow in the aquifer itself; partial penetration of the well screen, incomplete removal of mud from the gravel envelope, or invasion of fines into the envelope; and blockage of part of the screen area. The well should be developed prior to the test by using a surge block and/or pumping until the well discharge is clear. In this test, the well is pumped at several (three or more) successively higher pumping rates, and the drawdown for each rate is recorded. The test is usually conducted during 1 day. The discharge is kept constant through each step. The test measures the change in specific capacity. The data provide a basis to choose the pump size and rate for the aquifer test and for long-term production.

BIBLIOGRAPHY

1. Wilson, W. and Moore, J. (1998). *Glossary of Hydrology*. American Geological Institute, Alexandria, VA, p. 248.
2. Roscoe Moss Company. (1990). *Handbook of Ground Water Development*. Wiley-Interscience, New York, p. 493.
3. Theis, C.V. (1938). The significance and nature of the cone of depression in ground water bodies. *Econ. Geol.* **35**:889–902.
4. Driscoll, F.G. (1986). *Groundwater and Wells*. Johnson Division, UOP Inc.
5. Theis, C.V. (1935). The lowering of the piezometer surface and the rate and discharge of a well using ground water storage. *Trans. AGU* **16**: 519–524.
6. Moore, J.E. et al. (1995) *Groundwater-a Primer*. American Geological Institute, Alexandria, VA, p. 53.
7. Moore, J.E. (2002). *Field Hydrogeology, a Guide for Site Investigations and Report Preparation*. Lewis, Boca Raton, FL, p. 195.

WATER LEVEL DRAWDOWN

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INTRODUCTION AND DEFINITIONS

Contrary to the popular image of caverns and underground rivers, ground water is the water that fills or saturates the soil in a specific location. *Water level drawdown* describes the effect on the actual or potential water surface of removing water from a well, trench, or sump. The water table is the interface between this saturated water/soil zone (or aquifer) and an unsaturated water/soil zone. The

concept of an aquifer can be easily seen by filling a jar with rocks. Water can then be poured into the jar to fill up the empty spaces between the rocks. The level of the water in the jar is analogous to the subsurface water table, and the volume saturated with water is the aquifer. If one then placed a straw in the middle of the jar and began to pull out water, the water table would become depressed in a cone shape around the straw similar to the depression in the water level of a sink as the water goes down the drain. This depression in the water table is known as the cone of depression. The vertical difference, at any given point, between the original (or static) water level and the water surface formed by the cone of depression is called the *drawdown*.

The goal of this article is to provide an understanding of the key terms and concepts associated with drawdown and an introduction to the uses of drawdown in groundwater hydrology. The meaning of drawdown varies slightly between unconfined and confined (artesian) aquifers.

DRAWDOWN IN UNCONFINED AND CONFINED AQUIFERS

Depending upon whether an aquifer is unconfined or confined, drawdown is discussed in terms of either the water table or the piezometric surface, respectively (Fig. 1).

Unconfined aquifers have no impermeable layer between the water table and the ground surface. They can also be called "free" or "water table" aquifers. The water table in these aquifers is in direct contact with the atmosphere through the pores of the unsaturated soil above, and the water table is in balance with the air pressure. These aquifers are influenced by the infiltration of storm water and are also more easily contaminated through the infiltration of chemicals from surface spills.

For unconfined aquifers, the static water level is the height of the water in the well before pumping (Fig. 2). This is often calculated by measuring the depth to the water

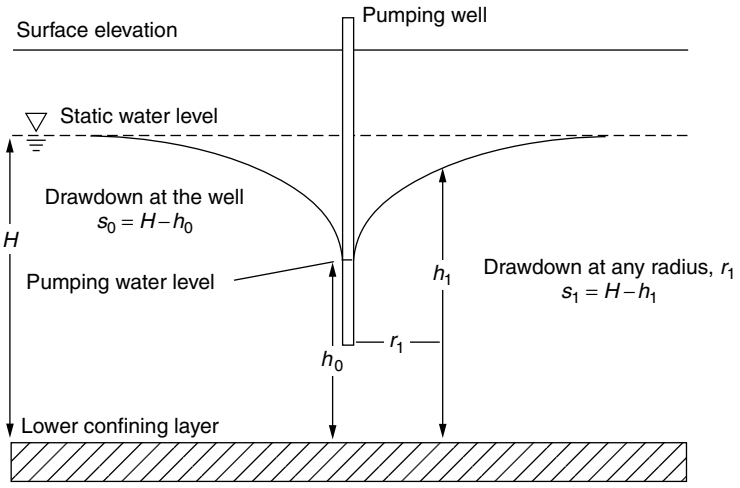


Figure 1. Drawdown in an unconfined aquifer.

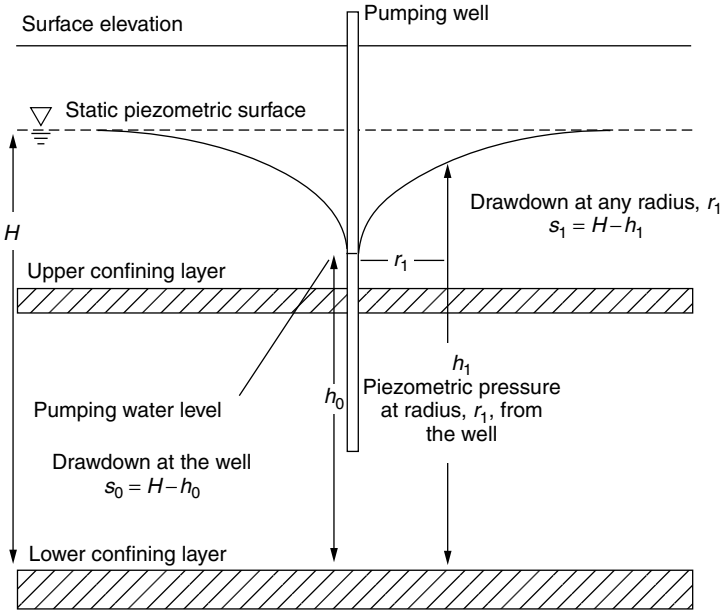


Figure 2. Drawdown in a confined (artesian) aquifer.

from the surface elevation. It can be given as "depth-to-water" or, sometimes, can be given as an elevation compared to mean sea level (MSL). In groundwater equations, it is expressed by a capital "H" and is measured, not from the surface down, but from the lower confining layer up. It is a measurement of pressure or head. So, if the depth to water is 26 feet and the surface elevation is 686 feet above MSL, the static water level is at 660 feet above MSL. If boring logs show that the lower confining level is at an elevation of 585 feet, then $H = 75$ feet $(660 - 585 = 75)$.

Confined (or artesian) aquifers have a confining layer, an impermeable bed, between the aquifer and the ground surface. As a result, the water in confined aquifers is often under pressure. Artesian springs are one result of this phenomenon. If a well is drilled into a confined aquifer, the water level in the well will rise to the height of the pressure in the aquifer. Artesian springs occur when the water pressure is such that the water rises to the surface through a fracture in the confining layer. This height, or head, is the *piezometric* level at the well. A combination of all piezometric or *potentiometric* heights throughout a confined aquifer is the *piezometric surface*. The piezometric surface is what the water table would be if there were no upper confining layer.

In confined aquifers, the static piezometric surface is the piezometric surface measured before pumping begins. It is expressed in the same terms as the static water level and is also measured as a pressure, or head, from the lower confining layer.

The pumping water level in a well is a water level in the well during pumping. Like the static water level or static piezometric surface, the pumping water level is measured from the lower confining bed and is a pressure or head in feet or meters. It is usually designated by a lower case "h."

The difference between the static level and pumping level at the well is the *drawdown* at the well. It is usually designated by s_0. Observation wells can be placed at various distances or radii from the pumping well to observe the drawdown at these locations. The difference between the static level and the pumping level at any radius, r_1, from the well is the drawdown, s_1, and it is the difference between H and the pumping water level, h_1, at that radius.

If all the pumping levels could be viewed in cross section, they would form a curve, the *drawdown curve* similar to these shown in the two figures. Drawdown in three dimensions is an inverted cone known as the *cone of depression*. The cone of depression defines the distance at which drawdown occurs as a result of the pumping of the well in question. This distance is known as the *radius of influence* of the well, and the area circumscribed by this radius is known as the *area of influence*.

IMPORTANCE AND USE OF DRAWDOWN INFORMATION

The measurement of drawdown is very useful to the study of the hydraulic characteristics of an aquifer. To understand this importance, it is first necessary to review the basic equilibrium equations for both unconfined and confined aquifers. The equation for an unconfined aquifer is

$$Q = \frac{\pi K(H^2 - h^2)}{\ln\left(\frac{r_i}{r_w}\right)} \tag{1}$$

where
Q = pumping rate
K = coefficient of permeability
H = saturated thickness at the radius of influence (static water level)
h = saturated thickness at the well
r_i = radius of influence
r_w = radius of the well

The equation for a confined aquifer is

$$Q = \frac{2\pi KM(H - h)}{\ln\left(\frac{r_i}{r_w}\right)} \tag{2}$$

where
M = thickness of confined aquifer
H = piezometric pressure at the radius of influence (static piezometric)
h = piezometric pressure at the well
r_i = radius of influence
r_w = radius of the well

When these equations are adjusted to solve for K at any two radii, r_1 and r_2, using drawdown at those two radii, s_1 and s_2, then the equations become
for an unconfined aquifer

$$K = \frac{Q\ln\left(\frac{r_2}{r_1}\right)}{\pi(s_1 - s_2)} \tag{3}$$

and for a confined aquifer

$$K = \frac{Q\ln\left(\frac{r_2}{r_1}\right)}{2\pi M({h_2}^2 - {h_1}^2)} \tag{4}$$

These equations can be used as part of a pump test to determine the permeability of an aquifer. The distances to the various confining layers and the thickness of the aquifers (as well as the static levels) should have been determined by soil borings. So, H and M are known. A pumping well is drilled along with one or more observation wells set at known radii from the pumping well. The well is then pumped at a known rate, Q, and time–drawdown data are recorded for each of the wells. From this information, the coefficient of permeability for the aquifer can be developed. This coefficient can then be applied to design other wells in this aquifer or for modeling the aquifer.

READING LIST

Cedergran, H. (1989). *Seepage, Drainage and Flow Nets*, 3rd Edn. John Wiley & Sons, New York.

Corbitt, R.A. (1999). *Standard Handbook of Environmental Engineering*, 2nd Edn. McGraw-Hill, New York, pp. 5.32–5.56.

Driscoll, F.G. (1987). *Groundwater and Wells*, 2nd Edn. Johnson Division, St. Paul, MN.

Ground Water Manual, A Water Resources Technical Publication. (1985). U.S. Department of the Interior, Bureau of Reclamation.

Parmley, R.O. (1992). *Hydraulics Field Manual*. McGraw-Hill, New York.

Powers, J.P. (1992). *Construction Dewatering*, 2nd Edn. John Wiley & Sons, New York.

WATER WELL DRILLING TECHNIQUES

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Water well installation, for groundwater monitoring projects or for water supply wells for irrigation or human consumption involves a variety of drilling techniques. Rig selection is related to accessibility, time and cost of project, sediment type (consolidated rock or unconsolidated soils), sample type (undisturbed vs. disturbed), and sample integrity. For environmental projects, designing wells and evaluating groundwater also involves assessing the soil, sediments, or rocks above and below the water table.

The vadose zone includes the zone immediately above the water table to the surface. The lower vadose zone includes the capillary fringe, the zone where water is drawn upward by capillary force. The water table is the top of the saturated or phreatic zone within the aquifer.

More detail regarding water wells, aquifers, and drilling techniques is provided in Driscoll (1), Testa (2), Sisk (3), and DWR (4,5). There are numerous differences in drilling techniques, methods and equipment, many regional variations, and specific local requirements. A generalized summary of selected water well drilling techniques follows.

ROTARY DRILLING

Rotary drilling techniques include direct mud rotary, air rotary, air rotary with a casing driver, and dual-wall reverse circulation. Rotary drilling techniques are commonly used for deep water supply wells. Direct mud rotary drilling uses fluid, which is pumped down through the bit at the end of the drill rods and is circulated up the annular space back to the surface. The fluid at the surface is routed via a pipe or ditch to a sedimentation tank or pit, then to a suction pit where the fluid is recirculated back through the drill rods. Air rotary drilling uses air as a circulation medium instead of water. In unconsolidated deposits, direct mud or air rotary can be used, providing that a casing is driven as the drill bit is advanced. In dual-wall reverse circulation, the circulating medium (mud or air) is pumped downward between the outer casing and inner drill pipe, out through the drill bit, then up the inside of the drill pipe.

Rotary drilling techniques are commonly limited to consolidated deposits of rocks (Fig. 1). In mud rotary, a mud filter cake develops along the borehole wall, potentially reducing aquifer permeability. Where a resistant



Figure 1. Rotary drilling rig used to assess shallow spillage from train derailment area at mile 262 (Photo P045; EPA).

layer such as overlying basalt flows or conglomerate strata exists at shallow levels within the vadose zone and above the target depth, an air rotary rig can be used to drill to a predetermined depth followed by another more suitable drilling method (2).

CABLE-TOOL DRILLING

Cable-tool drilling is the oldest drilling technique available and is for installing water supply wells in selected locations. It is not used often in the environmental field, as the technique is slow, noisy, and dusty. The exception is the use of cable-tool drilling in glacial environments containing large cobbles in the Pacific Northwest portion of the United States or in young volcanics such as in Hawaii. Cable-tool rigs, called percussion or spudder rigs, operate by repeatedly lifting and dropping the heavy string of drilling tools in the borehole, crushing larger cobbles and rocks into smaller fragments. During cable-tool drilling, the hole is continuously cased by an unperforated steel casing with a drive shoe. The casing is attached on top by a rope socket to a cable that is suspended through a pulley from the mast of the drill rig. The process of driving the casing downward a few feet is followed by periodically bailing the borehole of the broken rocks and accumulated soils from the bottom of the borehole. Formation water or added water is used to create a slurry at the bottom of the borehole.

WIRE LINE CORING

Coring is the drilling method that produces cylindrically shaped cores. A rotary rig is used in conjunction with water, drilling mud, or air. Cutting is accomplished by drill bits located at the end of the rotating barrel or tube. The barrel gradually slides down into the annular opening. The core is then separated from the rest of the formation mass, and the barrel containing the core is retrieved.

HOLLOW-STEM AUGER DRILLING

Hollow-stem continuous flight auger drilling techniques are commonly used for subsurface environmental projects (Fig. 2). Hollow stems consist of a series of continuous, interconnected hollow auger flights. The hollow-stem flight augers are hydraulically pressed downward and rotated to start drilling. Soil cuttings are rotated up the outside of the continuous flighting in the borehole annulus. A center rod with plug and pilot bit are mounted at the bottom. The plug is designed to keep soil from entering the mouth of the lead auger while drilling. Upon reaching the sampling depth, the center rod string with plug and pilot bit attached is removed from the mouth of the auger and replaced by a soil sampler.

The soil sampler is lowered into the borehole through the hollow stem of the auger (the center tube), and sampling is started. Samples can be continuously retrieved but are typically collected at 5-foot intervals, at hydrologic or lithologic changes, or at intervals of obvious contamination.

HORIZONTAL DRILLING

Horizontal or lateral radial wells are used more in subsurface environmental remediation although they have been used by the oil industry for decades. Based on the configuration in map view, horizontal water wells emanate from a center hub well. The most obvious application is where the area of concern, such as a contaminant plume, is inaccessible due to aboveground structures, tankage, roads, or subsurface structures such as landfills, lagoons, pits, pipelines, or wells.



Figure 2. Close-up of a hollow-stem auger rig (Courtesy of Joe Ryan, University of Colorado).



Figure 3. Direct push technology rig (Courtesy FAST-TEK).

DIRECT PUSH DRILLING

Direct push technology (DPT) rigs are used almost exclusively in the environmental field (Fig. 3). DPT rigs rely on the static weight of the vehicle, typically a pick-up truck or van, combined with the percussion of the onboard industrial jackhammer as the energy for advancing the soil and groundwater samplers. DPT rigs are designed for easier accessibility than larger more conventional drilling rigs. DPT rigs can install small-diameter driven well points or piezometers. Unlike rotary auger rigs, DPT rigs do not generate large amounts of drilling derived wastes. DPT rigs, including cone penetrometer technology (CPT) rigs, can also drive various sensors tools to obtain data about subsurface conditions (6).

WELL INSTALLATION

Well materials for water supply wells and monitoring wells must be chemically compatible with potential contaminants as well as water geochemistry, such as pH, iron content, turbidity, alkalinity, and other parameters (Fig. 4). Casing, both blank and screen sections, can be constructed of fiberglass-reinforced plastic, stainless steel, concrete, or thermoplastic which include polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), and styrene rubber (SR). Based on cost, availability, and chemical compatibility, the most common casings and screens used for shallow drilling projects in the environmental field are made of PVC. Deeper wells are typically constructed of either thicker gauge PVC or steel. Well screen openings are commonly slotted, lowered, or created through a wire wrapping process. Slot sizes can be determined by previous well installations in the area or by a grain size sieve analysis. Centering devices may be fastened to the casing to assure even distribution of filter material and grout within the borehole annulus.

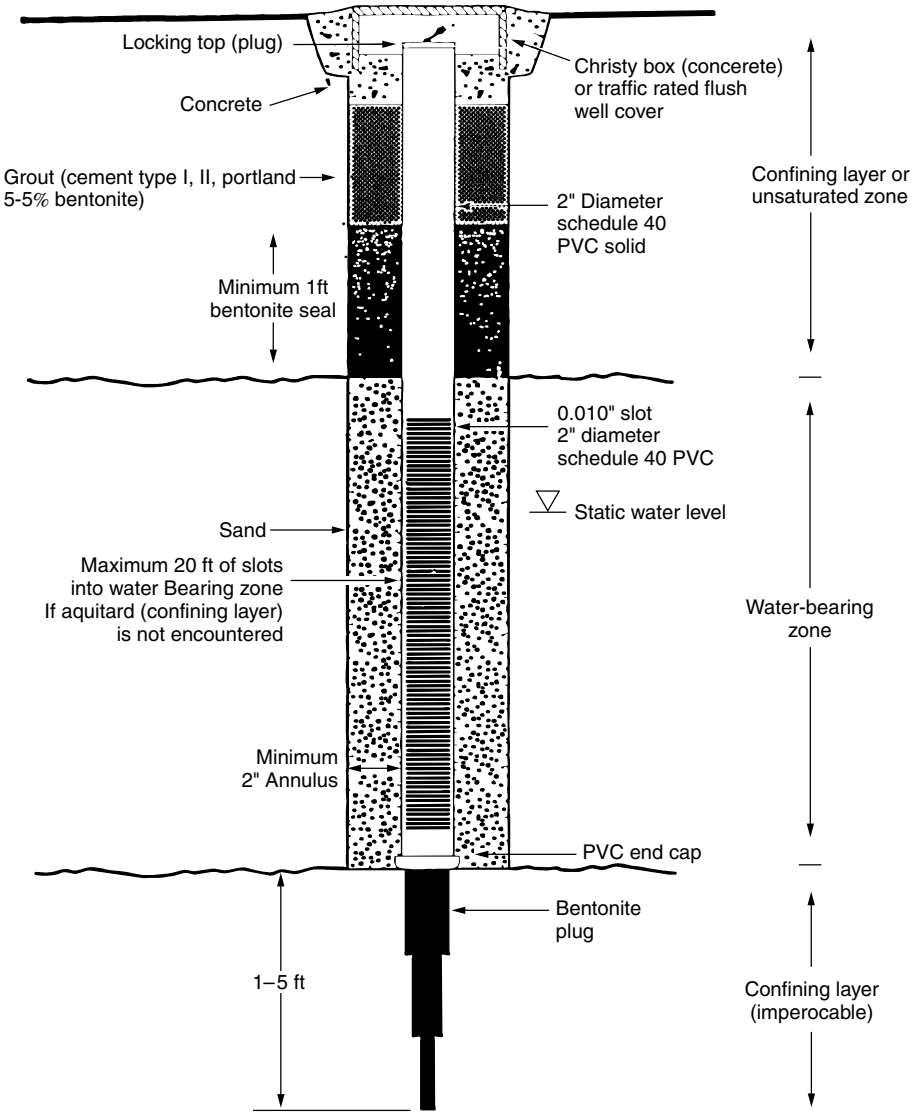


Figure 4. Groundwater monitoring well construction diagram.

BIBLIOGRAPHY

1. Driscoll, F.G. (1986). *Groundwater and Wells*, 2nd Edn. Johnson Filtration Systems, St. Paul, MN, pp. 268–339.
2. Testa, S.M. (1994). *Geologic Aspects of Hazardous Waste Management*. CRC, Boca Raton, FL, pp. 145–187.
3. Sisk, S.J. (1981). *NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites*. EPA-330/9-81-002, U.S. Environmental Protection Agency, Denver, CO.
4. California Department of Water Resources. (1981). California Well Standards, Bulletin 74–81, Sacramento, CA.
5. California Department of Water Resources. (1990). California Well Standards, Bulletin 74–90, Sacramento, CA.
6. Jacobs, J. (2000). Monitoring well construction and sampling techniques. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 11.46–11.68.

READING LIST

American Society for Testing Materials. (1984). *Standard Practice for Description and Identification of Soils (Visual-Manual Procedure), Method D 2488-84*. Philadelphia, PA.

California Regional Water Quality Control Board. (1989). *Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure*. Sacramento, CA.

California Regional Water Quality Control Board. (1990). *Tri-Regional Board Staff Recommendations for Preliminary Investigation and Evaluation of Underground Tank Sites*. Sacramento, CA.

Munsell Color. (1988). *Munsell Soil Color Charts*. Munsell Color, Baltimore, MD.

GROUNDWATER DYE TRACING IN KARST

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Groundwater dye tracing has proven to be an effective tool for aquifer characterization, protection, and to provide remediation strategies in karst areas. Tracing

groundwater flow routes with fluorescent dyes is highly successful because they are water soluble and inexpensive. Fluorescent dyes are usually the best tracers to use in karst because they are easily detected in concentrations that are one to three orders of magnitude less than those at which nonfluorescent dyes can be measured spectrometrically (1). Additionally, they are safe to use, work effectively in different hydrogeologic settings, and can be used effectively to trace water from subsurface to surface water bodies. Dye tracing in karst has been used successfully to (1) delineate spring recharge areas and subsurface basins, (2) determine site-specific hydrology, (3) estimate groundwater flow velocities, (4) trace groundwater flow from areas of recharge to discharge, (5) delineate wellhead protection areas, (6) map and characterize conduit flow routes, (7) detect leakage from residential sewage disposal systems, (8) identify sources of potential pollution from hazardous waste sites, (9) detect leakage from dam sites, and (10) characterize groundwater flow routes to important springs and cave streams along highway corridors.

WHAT IS KARST?

To understand why groundwater dye tracing is an effective tool for characterizing karst groundwater resources, one must have a basic understanding of karst and the unique hydrologic characteristics of its landscape. Karst refers to lands primarily underlain by limestone and dolomite where surface water is integrally connected to the groundwater system through preferential flow routes, which results in the formation of distinctive surface landforms and hydrologic features as well as subsurface features. Lack of these landforms and features does not mean that karst is not present.

A characteristic feature of karst areas is the sometimes rapid interconnection of surface water with the groundwater flow system. Even in the absence of surface streams, a karst region is a zone of drainage into the aquifer; the entire area can be a recharge zone (21). In most karst areas, two general types of recharge have been recognized: discrete and diffuse recharge. Discrete recharge, also known as concentrated recharge, is characterized by relatively rapid movement of water through localized areas (such as through sinkholes, losing streams, or other areas) toward the groundwater flow system. Areas of discrete recharge transport much of the water through preferential flow routes that commonly transport water at rates several orders of magnitude greater than those encountered on nonkarst groundwater systems, support turbulent flow, are too large to provide effective filtration for most pathogens, and provide minimal adsorption or other natural cleansing processes (4). Substantially greater quantities of water per unit area enter the groundwater system through discrete recharge areas than through diffuse recharge (5). For this reason, the groundwater system is highly vulnerable to contamination from accidental spills and poor land use practices. Groundwater flow velocities in many karst areas vary as much as 10 to 1500 ft per hour between the same two points—the latter, in response to storms—and are tens of thousands to several million times faster than those characteristic of many granular aquifers (1).

Diffuse recharge refers to the general and relatively slow seepage and percolation of recharge toward the groundwater system.

THE EPIKARST

The epikarst is the uppermost portion of the bedrock that consists of fissures and cavities formed by dissolution. The dissolution features in the epikarstic zone are organized to move infiltrating water laterally to downgradient seeps and springs or to collector structures such as shafts that conduct the water farther into the subsurface (6). The epikarst can vary from essentially zero to 30 meters or more (4) and is controlled by such factors as climate, depth of groundwater circulation, and bedrock structure.

Aley (7) summarized general dye recovery results for karst aquifers where dye was introduced directly into locations of discrete recharge that ultimately discharged to springs that passed through the epikarst. Aley recognized three hydrologically distinctive epikarstic zones in karst areas; rapid draining epikarsts, seasonally saturated epikarsts, and perennially saturated epikarsts. Rapid draining epikarsts commonly occur in areas of high topographic relief in bedrock of high solubility and negligible sediment infiltration. Rapidly draining epikarsts are saturated with water for short periods of time, especially after storms, and have little water storage or detainment. Seasonally saturated epikarsts occur in areas of moderate relief where the solubility of the bedrock has resulted in the development of soil and residuum thickness and at elevations greater than local perennial streams. Water is typically stored seasonally and after major storms lasting periods of weeks to months. Perennially saturated epikarsts occur in areas of low to moderate relief along perennial streams and are mostly saturated with water.

Groundwater dye tracing in the epikarst is more complex than that reported in most karst groundwater tracing reports. Aley (7) stressed that dye tracing in the epikarst requires extensive sampling and quantitative analysis, more detailed and quantitative analysis of background fluorescence characteristics, and simultaneous use of multiple dyes with dye quantities and analytical approaches selected to minimize the chance that small dye recoveries are obscured by another dye.

Fluorescent Dyes

Many fluorescent dyes have been used in groundwater dye tracing to characterize flow routes in karst areas. For general problem solving in karst areas, eosine, fluorescein, pyranine, rhodamine WT, and sulforhodamine B are the most useful fluorescent dyes (8). The characteristics of these dyes are well documented in Aley (9), Smart and Laidlaw (10), and Kass (11). The selection of dyes to be used, the location of dye introduction points, the manner in which the dyes are introduced, the sampling strategy employed, and the analytical approach used must be tailored to the hydrogeologic setting, the issues of concern, and the quality and credibility of the data needed for the study (12).

Sampling Locations

In karst landscapes, water that goes down into the subsurface eventually comes up at a spring or a series of springs. Springs represent the final terminus or discharge points of groundwater flow in karst areas and serve as excellent sampling locations to monitor for dye introduced into the groundwater system (surface streams, pumping wells, and monitoring wells can also be used).

It is equally important to know where the dye does not go as where the dye does go. All possible discharge points should be sampled. All springs within a radius of perhaps 5 to 15 miles from a facility, especially those within $\pm 90^{\circ}$ of the vector of the hydraulic gradient from it, should be monitored during dye traces (13). For maximum results, dye tracing should be conducted during low and high flow conditions. Groundwater movement during periods of high flow may be diverted to higher preferential flow routes that may discharge at springs in adjacent groundwater basins. For this reason, it may be necessary to monitor 10 to 40 sites during a single trace to ensure that dye is detected. However, due to time and budget constraints, dye trace tests are often designed to maximize current hydrologic conditions.

GROUNDWATER TRACING METHODS

Activated carbon samplers are often used to recover dyes. Activated carbon samplers (also called charcoal samplers or passive detectors) consist of a few grains of activated coconut charcoal placed in heat-sealed packets of fiberglass screening. They are placed at sampling locations to adsorb continuously and thus accumulate specific fluorescent dyes (Figs. 1 and 2). As an illustration, a charcoal sampler in place in flowing water containing fluorescein or rhodamine WT for a week will typically contain about 400 times more dye upon analysis than the mean dye concentration in the water being sampled (14).

The sampling interval is based on site-specific conditions and the questions that need to be answered by the study. Weekly sampling intervals are appropriate for most studies. Once dye introduction points and sampling locations have been identified, Aley (7) recommends one or more rounds of sampling at most (and preferably all) of the sampling locations to characterize background fluorescence before the final selection of dye types and quantities are determined. The amount of dye used for tracing studies is typically based on professional experience, as there is no credible standard equation for estimating dye quantities needed for groundwater tracing work (8).



Figure 1. Activated charcoal packet placed at Big Spring, Hardy County, West Virginia. Spring discharges near red house located in the upper left corner of photo.



Figure 2. Activated charcoal packet attached to rock prior to placement in Waites Run, Hardy County, West Virginia.

SELECTION OF DYE INTRODUCTION POINTS

In karst areas, sinking streams (Fig. 3) and sinkholes (Fig. 4) are commonly used as dye introduction points. However, the selection of appropriate dye introduction points depends on the type of study being performed. On some occasions, it is often difficult to encounter overland flow at ideal introduction points. This problem can be resolved by using "dry sets." A dry set involves the placement of a dye so that it will be flushed into a surface drainageway, sinkhole, culvert, or roadside ditch by the first storm flow (8).

Additional successful techniques used for introducing dye, especially at hazardous waste sites, include epikarstic dye introduction points (EDIPs) and dye introduction trenches (DITs). EDIPs are vertical boreholes that enter the top of the bedrock. DITs are constructed with a backhoe, typically 17 to 33 feet long, and extend into the epikarst. The construction and use of EDIPs and DITs, in addition to determining water quantities used to flush dye into the subsurface, are described in Aley (7,8).

Groundwater monitoring wells are typically poorly suited for use as dye introduction points primarily because they often fail to intersect the preferential flow openings that transmit water flow.

ANALYTICAL STRATEGIES

Quinlan (13) identified three analytical strategies used during dye trace studies. Qualitative tracing involves introducing dye at some discrete recharge point or zone and either visually observing the dye plume or



Figure 3. Fluorescein dye introduced into a sinking stream that flows across recharge units of the Capon Warm Springs Complex in Hampshire County, West Virginia.

visually observing dye removed from passive detectors. This method can be somewhat problematic especially when the dye arrives at a monitoring station at night. Qualitative dye tracing can be used to delineate boundaries of groundwater basins and identify point-to-point connections between input and recovery points, allowing special attention to be given to those points that have the highest potential for contaminating the groundwater system (15). Time of travel and flow velocity may generally be determined through qualitative dye tracing. Semiquantitative tracing uses passive detectors at sampling points followed by analysis with an instrument such as a scanning spectrofluorometer. Quantitative tracing includes instrumental analysis of water samples collected at sampling stations. Passive detectors are often used in concert with collection of water samples. The result of quantitative dye tracing is a set of measured dye concentrations, each sampled at a specific place and time. This method makes it possible to determine, with greater precision, groundwater flow velocities within preferential flow routes from points of recharge to discharge. Quantitative tracing provides a measure for determining the effectiveness of the monitoring system by estimating the tracer loss involved. Inadequate tracer recoveries are an indication that losses other than sorption or decay may be significant (16).

DYE TRACING AT WASTE DISPOSAL SITES

Groundwater dye tracing in karst is used for a wide variety of purposes, however, one of the most important



Figure 4. Fluorescein dye introduced into a perennial stream that flows into a sinkhole near Greenland Gap, Grant County, West Virginia.

uses of dye tracing is for investigations at waste disposal sites. Investigations at waste sites in mature karst should include, locating all springs, streams in sinkhole bottoms, and major streams in caves; dye tracing to establish connections between the disposal site, springs, and underground streams; monitoring connected points; monitoring at least one spring shown by dye tracing not connected to the site, as a control; and, dye tracing to delineate boundaries of groundwater basins (17).

Groundwater monitoring at facilities regulated under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Conservation, and Liability Act (CERCLA, more commonly known as Superfund sites) require the installation of groundwater wells to monitor the potential leakage of contaminants from the site. The problem with using groundwater monitoring wells in karst areas is that they often fail to intercept the conduits through which pollutants move. In many karst settings, most groundwater flow occurs in discrete conduits that are dendritic or trellised and terminates at springs whose water quality is representative of the mean of the ground water basin (17). Monitoring wells located on the basis of fracture trace and lineament analysis often fail to intercept major conduits in karst areas (18).

BIBLIOGRAPHY

1. Quinlan, J.F. et al. (1992). Rationale for the Design of Cost-Effective Groundwater Monitoring Systems in Limestone and Dolomite Terranes: Cost-Effective as Conceived is Not Cost-Effective as Built if the System Design and Sampling Frequency Inadequately Considers Site Hydrogeology. In: *Proceedings of the 8th Waste Testing and Quality Assurance Symposium*. U.S. Environmental Protection Agency, pp. 552–570.
2. Veni, G. et al. (2001). *Living With Karst: A Fragile Foundation*. American Geological Institute.
3. Aley, T. (1978). Ozark hydrology: A predictive model. *Journal of the Missouri Speleological Survey* **18**: 185.
4. Aley, T. (2000). Karst systems. In: *The Standard Handbook of Environmental Science, Health, and Technology*. H. Jay and J.K. Lehr (Eds.). McGraw-Hill, New York, pp. 19.1–19.10.
5. Aley, T. and Halterman, D. (1982). A Conceptual Characterization of the Subsurface Movement of Toxic Chemicals in Soluble Rock Lands. In: *Proceedings of the Fifth National Cave Management Symposium*, pp. 77–80.
6. Huntoon, P.W. (1995). Is it appropriate to apply porous media ground water circulation models to karstic aquifers?. In: *Groundwater Models for Resources Analysis and Management*. Lewis Publishers, Boca Raton, FL, pp. 339–358.
7. Aley, T. (1997). Groundwater tracing in the epikarst. In: *The Engineering Geology and Hydrogeology of Karst Terranes*. Beck and Stephenson (Eds.). Balkema, Rotterdam, pp. 207–211.
8. Aley, T. (1999). *The Ozark Underground Laboratory's Groundwater Tracing Handbook*. The Ozark Underground Laboratory, p. 35.
9. Aley, T. (1995). *Recharge Area Delineation for Bear Creek Springs and Smokehouse Spring*. Contract Report to the Arkansas Highway and Transportation Department.
10. Smart, P.L. and Laidlaw, I.M.S. (1977). An evaluation of some fluorescent dyes for water tracing. *Water Resources Research*, **13**(1): 15–33.
11. Kass, W. (1998). *Tracing Technique in Geohydrology*. A.A. Balkema, Rotterdam.
12. Bednar, D., Jr. and Aley, T. (2001). Groundwater dye tracing: An effective tool to use during the highway development process to avoid or minimize impacts to karst groundwater resources. In: *Geotechnical and Environmental Applications of Karst Geology and Hydrology—Proceedings of the 8th Multidisciplinary Conference on Sinkholes and The Engineering and Environmental Impacts of Karst*. B.F. Beck and J.G. Herring (Eds.). A.A. Balkema Publishers, Louisville, KY, April 1–4, pp. 201–207.
13. Quinlan, J.F. (1989). *Ground-Water Monitoring in Karst Terranes: Recommended Protocols and Implicit Assumptions*. U.S. Environmental Protection Agency.
14. Aley, T. (1994). *Final Report: Tracing Study to Assess Groundwater Flow Routes for Selected Springs Near Appalachian Corridor H*. Contract report prepared for Michael Baker Jr. Inc. for the benefit of the West Virginia Department of Transportation.
15. Mull, D.S., Liebermann, T.D., Smoot, J.L., and Woosley, Jr., L.H. (1988). *Application of Dye Tracing Techniques for Determining Solute-Transport Characteristics of Ground Water in Karst Terranes*. EPA 904/6-88-001, United States Environmental Protection Agency.
16. Field, M.S. (1999). *The QTRACER Program for Tracer-Breakthrough Curve Analysis for Karst and Fractured-Rock Aquifers*. U.S. Environmental Protection Agency.
17. Quinlan, J.F. and Ewers, R.O. (1985). Ground Water Flow in Limestone Terranes: Strategy Rationale and Procedure for Reliable, Efficient Monitoring of Ground Water Quality in Karst Areas. In: *Proceedings of the National Symposium and Exposition on Aquifer Restoration and Groundwater Monitoring*. National Groundwater Association, pp. 197–234.
18. American Society For Testing and Materials (ASTM). (1995). *Standard Guide for Design of Ground-water Monitoring Systems in Karst and Fractured-Rock Aquifers*. American Society For Testing and Materials.

EARTHQUAKES—RATTLING THE EARTH'S PLUMBING SYSTEM

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Hydrogeologic responses to earthquakes have been known for decades, and have occurred both close to, and thousands of miles from earthquake epicenters. Water wells have become turbid, dry or begun flowing, discharge of springs and ground water to streams has increased and new springs have formed, and well and surface-water quality have become degraded as a result of earthquakes. Earthquakes affect our Earth's intricate plumbing system—whether you live near the notoriously active San Andreas Fault in California, or far from active faults in Florida, an earthquake near or far can affect you and the water resources you depend on.

RESPONSES IN WATER WELLS

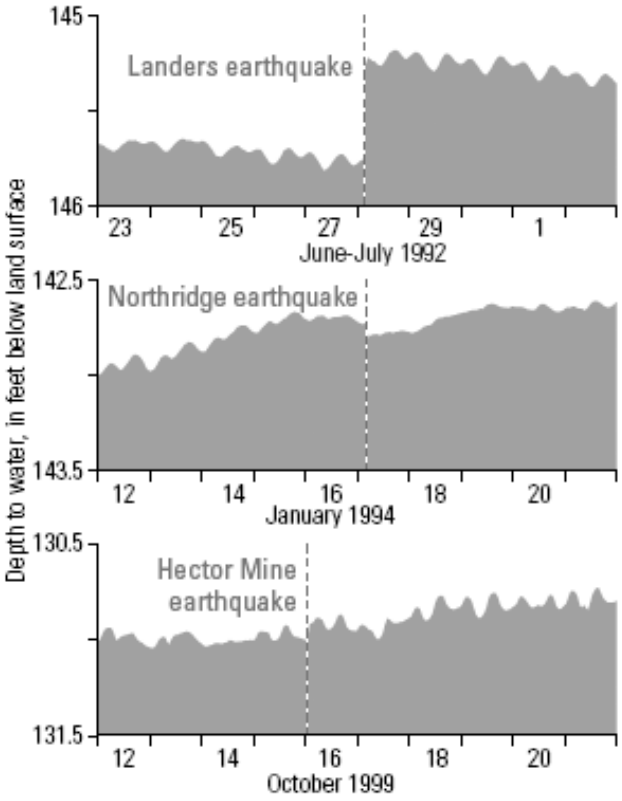
Water-level fluctuations caused by the 1964 magnitude(M) 8.5 Alaska earthquake were recorded in 716 wells in the United States (1); the earthquake also was registered on water-level recorders in many other countries. Responses of water levels in wells to earthquakes are influenced by such factors as the magnitude and depth of the earthquake, distance from the epicenter, and the hydrogeologic environment, which may be consolidated rock, unconsolidated sediment, karst, or hydrothermally altered. The depth of the well, whether the aquifer is confined or unconfined, and well construction also influence the degree of water-level fluctuations in wells in response to seismic waves. Some aquifers may act as resonators, which may amplify the response.

The most common type of observed ground-water response is an instantaneous water-level offset, or step, which may be either an increase or a decrease and may occur near or far from the epicenter. Recovery to the pre-earthquake water level can be so rapid that no change will be detected if the water level is measured

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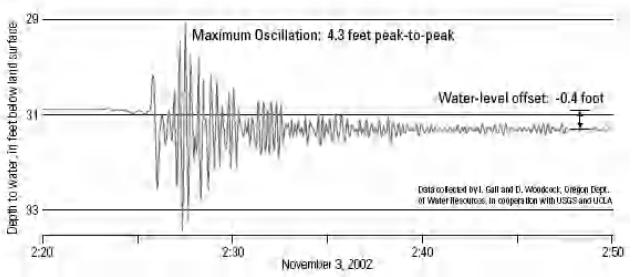
This petroleum seep in the Ojai Valley, California developed as a direct result of the 1994 Northridge earthquake in southern California. Notice the oil has not yet spread far and grass blades can be seen standing through the crude oil. The photo was taken a few days after the earthquake.



Well MO-18/02W/29-0017 in Wisconsin responded to the distant Denali Fault earthquake in Alaska.

infrequently, or it may take as long as days or months. Steps can be large enough to make a well flow at land surface, or render it dry. The 1998 M5.2 Pymatuning earthquake in northwestern Pennsylvania caused about 120 local household-supply wells to go dry within 3 months after the earthquake (2). The 2002 M7.9 Denali Fault earthquake in Alaska caused a 2-foot water-level rise in a well in Wisconsin, more than a thousand miles from the epicenter.

The other type of ground-water response is a water-level oscillation, which occurs more often, but is less commonly recorded. In the few cases where oscillations have been recorded, they resemble long-period seismograms, known as hydroseismograms. A well in Grants Pass, Oregon, is instrumented to record water levels at 1-second intervals, and the record from the Denali Fault earthquake shows peak-to-peak seismic oscillations of more than 4 feet and a permanent offset of 0.4 feet.



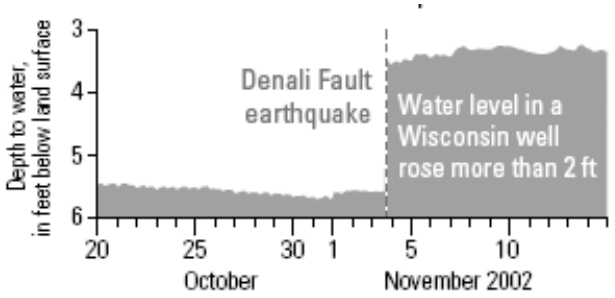
Hydroseismogram recorded in a well near Grants Pass, Oregon, shows water-level oscillations and a small offset relative to pre-earthquake water level in response to the Denali Fault earthquake.

RESPONSES IN STREAMS, SPRINGS, SEEPS, AND LAKES

Well 8N/10W-1Q1 in the western Mojave Desert, California responded to several southern California earthquakes.

Surface-water responses to earthquakes include changes in chemistry, seiches (wave oscillations) in lakes and other open water bodies, increases in stream, spring, and seep discharge, some instances of springs going dry or the appearance of new springs, and a very few examples of decreases in stream discharge. After the Denali Fault earthquake, many eyewitnesses throughout the contiguous United States reported water "sloshing" back and forth in lakes, bayous, ponds, and pools. Seiches lasted as long as half an hour, resulting in broken moorings in Lake Pontchartrain, Louisiana (Seth Moran, U.S. Geological Survey, written commun., 2002).

Streamflow may continue to increase for a few days and then gradually decline toward the pre-earthquake baseline condition for several months. Water flowing in a stream can come from overland flow or from ground water discharging into the streambed (baseflow). An abrupt increase in streamflow without precipitation or upstream reservoir release indicates increased contributions from the ground-water system. A coseismic (at the time



the seismic wave train arrives) discharge increase of approximately 40 percent was recorded in Santa Paula Creek, California, 35 miles WNW., of the 1994 M6.7 Northridge, California earthquake epicenter (3), and increased discharges were measured at numerous sites in the California Coast Range in response to the 1989 M7.1 Loma Prieta, California earthquake (4). The appearance of new seeps and springs and turbidity in streams also are common. Following the Northridge earthquake, a new oil seep began flowing in the Northern Ojai Valley (Stephen P. Mulqueen, Department of Conservation, Division of Oil, Gas, and Geothermal Resources, oral commun., 2003).

PRECURSORY RESPONSES

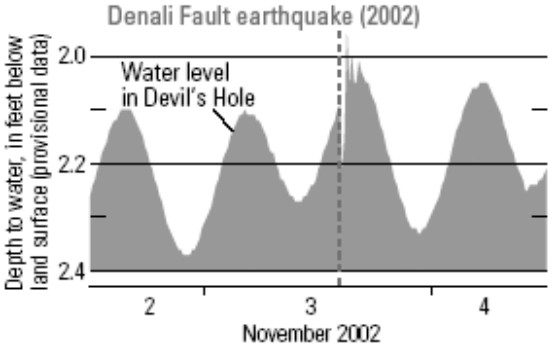
Many preseismic or precursory hydrogeologic responses have been reported, but in most cases, documentation has not been sufficient to convince the scientific community of their predictive value or to rule out explanations unrelated to earthquakes. Some investigators believe earthquakes cannot be predicted (5), whereas others believe that while earthquake prediction is difficult because of the youthfulness of seismic research and the limited number of case studies to investigate, prediction will not forever be impossible (6). Roeloffs (7) states "The documentation of a few of these reports [of precursory hydrogeologic changes] is now approaching levels that require them to be given scientific credibility." Water levels and chemical data seem to be the best documented precursory signals to date, and are monitored in several countries as potential indicators of an impending earthquake.

Japan has some of the best documented occurrences of precursory hydrogeological changes, preceding both the 1978 M6.8 Izu-Oshima earthquake (8,9), and the more recent, disastrous 1995 M7.2 Kobe earthquake (10). Before either or both of these events, water-level changes occurred in many wells, and there appeared to have been precursory changes in ground-water temperature, radon, chloride, and sulfate concentrations, as well as dissolved gas ratios in mineral springs (11,12). The preseismic changes in chloride and sulfate content of the Kobe event were reconstructed by analyzing dated, bottled ground water that is distributed in the domestic market.

The well-documented and similar hydrogeologic precursors at Izu-Oshima and Kobe have motivated the Japanese government to continue water-level monitoring at more than 30 wells in seismically active areas (13). The suggestion of precursory hydrogeologic changes is tantalizing, because the ultimate goal of most earthquake research is to reduce the hazard posed by major events, and providing some warning of impending activity would be very useful in that regard.

HAZARDS RELATED TO HYDROGEOLOGIC RESPONSES

Hydrogeologic responses to earthquakes can create a variety of hazards. Water supply may be disrupted if wells go dry or become too turbid to pump, and infrastructure damage may result from ground motion. After the 1992 M7.3 Landers, California earthquake, bubbles of gas (carbon dioxide-enriched air) appeared in water from several San Bernardino, California, supply wells, clogging and disabling the filtration system (14). Hydrogeologic responses that cause wells to flow or streamflow to increase may cause flooding, landslides, erosion, and other related problems. Water quality also may be adversely affected





This pristine spring in the unique environment of Ash Meadows in Nevada is hydrologically connected to Devil's Hole, which is a nearly vertical cavern below the water table in southern Nevada. An endangered species, Devil's Hole pupfish, has lived in Devil's Hole pool for thousands of years. The water level in Devil's Hole oscillated in response to the Denali Fault earthquake, which disrupted the spawning areas of the pupfish near the surface of the pool.

by increased discharge, turbidity, or hydrogeochemical changes. Following the Landers earthquake, a pre-existing oil and natural gas seep in Tapo Canyon became more active, eventually flowing into and polluting the Santa Clara River (14).

Water-quantity and quality changes following an earthquake can adversely affect sensitive ecosystems, harming the plants and animals that live there. The endangered Devil's Hole pupfish (Cyprinodon diabolis) has lived for thousands of years in only one pool in Ash Meadows, Nevada, spawning on a single 6×13 foot shelf just below the water surface. In 1978, an earthquake in Mexico caused such violent water-level oscillations in Devil's Hole that algae was scoured from the shallow shelf (15), and the 2002 Denali Fault earthquake also apparently caused oscillations of 5–6 feet (Jim Roche, National Park Service, written commun., 2002). A persistent drop of water level below the shelf could extinguish the pupfish, whose life span is only a few years. Although court orders and careful management have led to population stability, the existence of the Devil's Hole pupfish remains precarious.

Ground-water systems are mechanically coupled to the rocks and sediments in which they exist. In addition to hydrogeologic responses to earthquakes, hydrogeologic changes may cause earthquakes or volcanic events. Earthquakes can be induced by the filling of surface reservoirs, or by annual or shorter-term fluctuations in reservoir levels, as is the case in most shallow earthquakes in the Aswan, Egypt area (16). Earthquakes also can be induced by the injection or withdrawal of fluids through wells, as was illustrated by the earthquakes caused by injection of waste fluid from munitions production at the Rocky Mountain Arsenal in the 1960s (17). More speculatively, the observation that large earthquakes can cause distant hydrogeologic changes may help explain how the 1992 M7.3 Landers, California earthquake triggered microearthquakes at a number of locations many hundreds of miles from the epicenter (18).

MECHANISMS FOR HYDROGEOLOGIC RESPONSES TO EARTHQUAKES

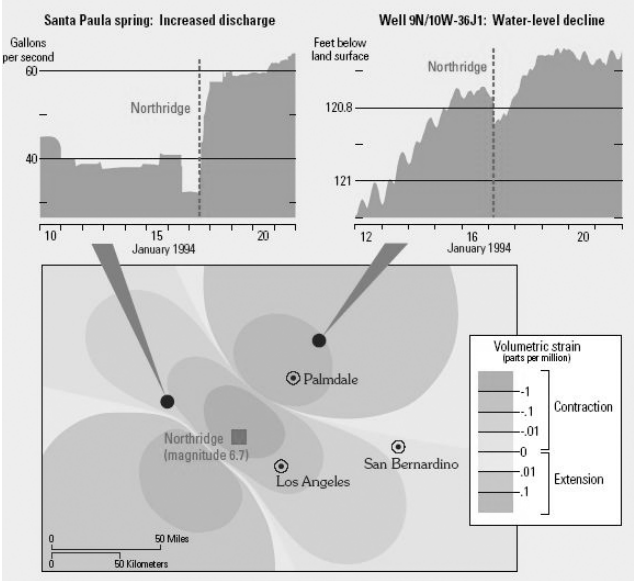
Known hydrogeologic responses most often occur as the seismic wave train arrives (coseismic) or sometime thereafter (postseismic); evidence of precursory (preseismic) hydrogeologic changes is becoming more compelling, but additional scientific investigation is needed to explain these phenomena.

Water levels in wells respond to the seismic-wave induced expansion and contraction of the aquifer tapped by the well, in turn causing step or oscillatory fluid-pressure changes. If flow in the well-aquifer system is fast enough, then these pressure changes cause flow into and out of the well, which sets up resonant motion of the water column, and the result is the seldom-recorded water-level oscillation. The more commonly recorded water-level offsets have been measured both near and far from earthquake epicenters. Offsets are expected in the 'near field', or static strain field, of an earthquake because the earthquake subjects the earth's crust, including its aquifer systems, to stress and permanent strain (deformation). This deformation process results in altered fluid pressure within the aquifer systems, and consequently, a steplike change in water level would be expected (3,14). The earthquake-induced water-level decline in well 9N/10 W-36J1 is the expected response for an extensionally strained region (14). Providing that the water-level response to strain is known, this relation allows scientists to use the earthquake response of water levels in favorably located and designed wells to measure strain, and also to calculate otherwise difficult-to-measure hydrologic properties of the aquifer. At distances of hundreds or thousands of miles, the offset can often be directly related to the amount of deformation produced by movement on the earthquake fault (19).

Possible mechanisms for responses are variable. For upward steps in shallow wells, compaction of overlying alluvium such as occurs during liquefaction may be the mechanism producing the offset (19). Fluid-pressure declines also can be caused by the escape of small amounts of exsolved gas from pore spaces in response to seismic waves. In a fractured rock environment such as northwestern Pennsylvania where the Pymatuning earthquake occurred, permeability may be altered due to the unclogging, widening, or narrowing of a fracture, or the creation of new fractures (2). Similarly, an increase in co- and postseismic ground-water discharge at the surface through a spring, seep, or stream, can be caused by an increase in vent or fracture conductance (20), or an increase in the subsurface fluid pressure or permeability in the formation (4,14). The earthquake-induced increased discharge in Santa Paula spring is the expected response for a contractionally strained region (14). For a brief review of streamflow and water well responses to earthquakes and discussion of potential mechanisms see Montgomery and Manga (21).

RECORDING ACCURATE HYDROGEOLOGIC RESPONSES

Measurement techniques often do not adequately reflect hydrogeologic responses to earthquakes. In the recent past, water levels and discharge were recorded continuously using a drum recorder, similar to the method in which earthquakes are recorded on a seismograph. More recently, scientists have migrated to more cost-effective digital measurements that are recorded on an electronic datalogger. Ground-water levels typically change slowly, and dataloggers have limited storage capacity, such that data are recorded at 15-minute intervals, or more often, at 30- or 60-minute intervals. With a recording interval on this order, a water-level response from an earthquake may not be adequately defined by the periodic data; the recovery to the pre-earthquake water level can occur so



quickly that no change will be detected. In some cases, the water-level response is not in the expected direction because the initial response was not recorded, or because the response is affected by the particular well construction (the well-bore storage effect). Although stream or spring discharge may change as a result of a change in the ground-water contribution to the baseflow of the stream, surface-water discharge measurements often are not accurate enough to reliably detect small changes in flow. Additionally, flow is often controlled artificially, either partially or completely, preventing the detection of earthquake-induced changes.

CONCLUSIONS

Hydrogeologic responses to large distant earthquakes have important scientific implications with regard to our earth's intricate plumbing system. The exact mechanism linking hydrogeologic changes and earthquakes is not fully understood, but monitoring these changes improves our insights into the responsible mechanisms, and may improve our frustratingly imprecise ability to forecast the timing, magnitude, and impact of earthquakes.

BIBLIOGRAPHY

1. Vorhis, Robert C., 1966, Hydrologic effects of the earthquake of March 27, 1964 outside Alaska: U.S. Geological Survey Professional Paper 544-C, 54 p.
2. Fleeger, Gary M., Goode, D. J., Buckwalter, T.F., and Risser, D.W., 1999, Hydrologic effects of the Pymatuning Earthquake of September 25, 1998, in Northwestern Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 99–4170, 8 p.
3. Quilty, E.G., Farrar, C.D., Galloway, D.L., Hamlin, S.N., Laczniak, R.J., Roeloffs, E.A., Sorey, M.L., and Woodcock, D.E., 1995, Hydrologic effects associated with the January 17, 1994 Northridge, California, earthquake: U.S. Geological Survey Open-File Report 95–813, 47 p.
4. Rojstaczer, S., and Wolf, S., 1992, Permeability changes associated with large earthquakes: An example from Loma Prieta, California, 10/17/89: Geology, 20, p. 211–214.
5. Geller, R.J., Jackson, D.D., Kagan, Y.Y., and Mulargia, F., 1997, Earthquakes cannot be predicted: Science, 275, p. 1616–1617.
6. Wyss, Max, 2001, Why is earthquake prediction research not progressing faster?: Tectonophysics, 338, p. 217–223.
7. Roeloffs, E., 1996, Poroelastic techniques in the study of earthquake-related hydrologic phenomena: Advances in Geophysics, 37, p. 135–195.
8. Oki, Y., and Hiraga, S., 1979, Water level anomalies prior to the Izu-Oshima earthquake, January 14, 1978, Translated from the Japanese by E. Silberman, in Technical Report 79–2, Lamar-Merifield Geologists, Special Technical Report for the U.S. Geological Survey.
9. Groundwater-level monitoring for prediction of earthquakes: Pure and Applied Geophysics 126, 1987.
10. Tsunogai, U., and Wakita, H., 1995, Precursory chemical changes in ground water: Kobe earthquake, Japan: Science, 269, p. 61–63.
11. Igarashi, G., Saeki, S., Takahata, N., Sumikawa, K., Tasaka, S., Sasaki, Y., Takahashi, M., and Sano, Y., 1995, Groundwater radon anomaly before the Kobe earthquake in Japan: Science, 269, p. 60–61.
12. Sugisaki, R., Ito, T., Nagamine, K., and Kawabe, I., 1996, Gas geochemical changes at mineral springs associated with the 1995 southern Hyogo earthquake (M=7.2), Japan: Earth and Planetary Science Letters, 139, p. 239–249.
13. Tsukuda, E., Koizumi, N., and Yasuto, K., 2000, Integrated groundwater monitoring studies in the intensified observation area and near major active faults, Bulletin of the Geological Survey of Japan, v. 51, no. 9, p. 435–445.
14. Roeloffs, E., Danskin, W.R., Farrar, C.D., Galloway, D.L., Hamlin, S.N., Quilty, E.G., Quinn, H.M., Schaefer, D.H., Sorey, M.L., and Woodcock, D.E., 1995, Hydrologic effects associated with the June 28, 1992 Landers, California, earthquake sequence: U.S. Geological Survey Open-File Report 95–42, 68 p.
15. Death-Valley.us, Devil's hole pupfish—*Cyprinodon diabolis*: Death-Valley.us Forums, article 107, posted July 18, 2002, accessed January 29, 2003, at http://www.death-valley.us/article107.html
16. Awad, M., and Mizoue, M., 1995, Earthquake activity in the Aswan region: Pure and Applied Geophysics, 145, p. 69–86.
17. Healy, J.H., Rubey, W.W., Griggs, D.T., and Raleigh, C.B., 1968, The Denver earthquakes: Science 161, p. 1,301–1,310.
18. Hill, D.P., and others, 1993, Seismicity remotely triggered by the magnitude 7.3 Landers, California, earthquake: Science, v. 260, no. 5114, p. 1617–1623.
19. Roeloffs, E., 1998, Persistent water level changes in a well near Parkfield, California, due to local and distant earthquakes: Journal of Geophysical Research, v. 103 (B1), p. 869–889.
20. Muir-Wood, R., and King, G.C.P., 1993, Hydrological signatures of earthquake strain: Journal of Geophysical Research, 98, p. 22,035–22,068.
21. Montgomery, D.R., and Manga, M., 2003, Streamflow and water well responses to earthquakes: Science, v. 300, p. 2047–2049.
22. Roeloffs, E., 1988, Hydrologic precursors to earthquakes: A review: Pure and Applied Geophysics 126, p. 177–209.

IN SITU ELECTROKINETIC TREATMENT OF MtBE, BENZENE, AND CHLORINATED SOLVENTS

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INTRODUCTION

The practice of soil and groundwater cleanup should follow the intent of the U.S. EPA laws and regulations such as the Safe Drinking Water Act (SDWA), the Resources Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Any environmental treatment process must be able to, or must be engineered to protect and conserve our resources (air, water, soil, and human) and not create undesirable side effects. Many of the conventional waste treatment technologies cannot meet these objectives and simply involve transferring the waste from one location or phase to another. This is true for waste excavation, landfill disposal, incineration, pump and treat, thermal desorption, and soil vapor extraction. Sound waste treatment technologies must be able to transform toxic and hazardous chemicals into harmless chemicals or render them harmless with the least energy consumption to achieve a good economic balance. To the extent possible, all treated soil and groundwater should be recycled for beneficial use. Most organic chemicals can be oxidized to harmless carbon dioxide, water, and inorganic chloride with existing and available innovative waste treatment technologies. The most difficult media for most waste treatment processes are relatively impermeable clayey media and fracture media. These media often absorb/adsorb the toxic and hazardous wastes spilled below the ground surface. Often, more than 90% of the waste spilled is attracted to these media. It is most fortunate that electrokinetic treatment processes can overcome the difficulties of relatively impermeable media and achieve or enhance the oxidation of many toxic and hazardous wastes at relatively low energy consumption.

The following sections discuss the *in situ* treatment processes, tests and design parameters, achievable cleanup levels, and case histories of successful treatment.

ENGINEERED ELECTROBIOCHEMICAL PROCESSES

Most petroleum hydrocarbons, including gasoline, diesel, jet fuel, kerosene, aviation fuel, motor oil, benzene, toluene, ethylbenzene, and xylenes are biodegradable. There has been some concern over the bioremediation of MtBE. However, electrokinetically enhanced cometabolic biotreatment of MtBE has been demonstrated in the field with repeated success (1).

Most chlorinated solvents are biodegradable through the application of the cometabolic biotreatment processes. However, because of the earlier publication of laboratory successes by the U.S. EPA in the 1980s, many scientists and engineers began to apply flammable methane and butane blindly into the vadose zone without questioning the side effects for health and safety (2–4). The same applies to the addition of toxic phenol, dichlorobenzene, and toluene into the groundwater as cosubstrates for bioremediation, which violates the underground injection control regulation established by the U.S. EPA. However, electrokinetically enhanced cometabolic biotreatment of chlorinated solvents using glucose sugar has been demonstrated in the field with repeated success (1).

Biochemical Processes

Bioremediation can be defined as the use of naturally occurring microorganisms to detoxify hazardous wastes (1), which is particularly true for hazardous organic wastes. The basic mechanism of bioremediation is promotion of the growth of microorganisms that are adapted to the organic wastes spilled in soil and groundwater. Stimulation of the growth of the microorganisms is controlled by proper temperature, oxygen, moisture, nutrients, and distribution of such in the impacted media. During growth, the microorganism will secrete enzymes and biosurfactants to break down the hazardous organic molecules (detoxification) and make them available for cellar absorption. Subsequently, the microorganism will grow and multiply, and the process will repeat itself. The end result is mineralization of the carbon source (from spilled hazardous organic wastes) aerobically into carbon dioxide, water, and biomass without undesirable side effects.

The application of bioremediation in hazardous waste management began in the early 1980s. The basic principles of biotreatment in the environment are described by Gaudy and Gaudy (5), who emphasized the enhancement factors, or engineering, in applying the bioremediation technology in the field. The biotreatment of excavated soil in engineered biopiles began to gain recognition in the late 1980s. In the 1990s, engineered bioremediation took such forms as soil bioventing, *in situ* aqueous phase biotreatment of soil and groundwater, and bioreactors to treat water, sludge, and organic vapor. In the mid-1990s, the evaluation of intrinsic or natural attenuative bioremediation prior to an engineering feasibility study became popular. The application of cometabolic bioremediaion treatment processes also flourished for chlorinated solvents to petroleum hydrocarbons.

The bioremediation professional must follow the basic fundamental science and engineering to complete a bioremediation project successfully. The following sections cover the science and engineering of bioremediation processes, microbial ecology, bioenhancement, soil microbes and pathogens, the aerobic process, the anaerobic processes, and the cometabolic process.

To carry out a bioremediation process properly, the living environment favorable for the microorganism must be understood. Microorganisms used in bioremediation are generally classified as mesophiles or the warm temperature type. The optimum range of temperature in which they thrive is from 80–100 °F. When the temperature of the bioremediation system drops below 40 °F,

the microorganism goes into hibernation. Microorganisms must also have optimal moisture to grow and to survive. Dry conditions are not favorable for bacterial growth. All microorganisms require an available carbon source and nutrients for growth. An adapted indigenous microorganism in a hazardous waste environment relies on the carbons in organic chemicals as a food source (substrate). The nutrient requirements include sources of phosphorus, nitrogen, and iron. The microorganism also relies on the availability of oxygen in the environment to mineralize the hazardous chemicals into carbon dioxide and water under aerobic conditions.

Bioenhancement Methods. It is evident that when hazardous wastes spill into soil and groundwater, it is not an optimized microbial ecology for bioremediation. Therefore, we must engineer a favorable microbial ecology for optimal bioremediation to take place. The following sections cover an optimal microbial ecology that can be engineered or enhanced for all situations.

Oxygen Enhancement. If oxygen is not available in soil (vadose soil) or in groundwater (aquifer), this anaerobic condition is prone to create hydrogen sulfide (toxic gas) and methane gases (flammable gas). The quantity of oxygen required must satisfy the chemical oxygen demand (COD) of the soil and groundwater media. It is important to point out that in fully saturated media, both the COD of the soil and the groundwater must be satisfied. The objective is to supply enough oxygen to satisfy the COD of the impacted media. Oxygen can be enhanced by injecting air or oxygen into the pore space of the vadose soil. Dissolved oxygen in groundwater can be enhanced by adding oxidants, by *in situ* electrolytic (electric current) generation of water in the impacted media, or by creating of hydroxyl radicals (a strong oxidant) at the initial stage of the electrolysis of water. Another source of oxygen is through introducing carbohydrates, which will biodegrade and provide enough oxygen to mineralize the hazardous organic compound into carbon dioxide, water, and biomass.

Heat Enhancement. To achieve an optimal growth temperature (80–100 °F) for mesophilic microorganisms, the vadose zone soil can be heated by circulating warm air into the pore space in the soil. It may not be necessary to heat up the entire solid matrix of the mass because most of the hazardous waste tends to adhere to the surface of the solid matrix. Passive solar panel air heating can provide an economical means of heat delivery. Recirculation of heated air in the subsurface will also save energy cost because the soil mass itself acts like a heat sink that has very good insulating value. The same applies to heating groundwater by a passive solar water heater. The heating requirements (in BTUs) must be estimated based on the weight of the impacted media. The weight of the impacted media can be calculated as the volume of the soil or groundwater plumes. A swimming pool passive solar heating panel can supply more than adequate heating value in less than 30 days for most bioremediation projects.

Nutrient Enhancement. Sometimes, there are insufficient nutrients in the form of nitrogen, phosphorus, and iron in the soil and groundwater plumes. Nutrient enhancement applies only when there is a deficiency. For proper bioremediation, a carbon (C) to nitrogen (N) to phosphorus (P) weight ratio of 100:10:1 should be followed. The weight of carbon in the plume is determined by the total organic carbon (TOC) concentration times the weight of the plume that requires cleanup.

Moisture Enhancement. If warm air (80° to 100 °F) is being recirculated within the soil plume for soil remediation, the moisture in the warm air (humidity) should be adequate enhancement. No need exists for moisture enhancement in saturated media.

Nutrient Distribution. The most difficult media for hazardous waste treatment processes to work in are a relatively low-permeability clayey medium and a fracture medium. These media often absorb/adsorb the toxic and hazardous waste spilled below the ground surface. Often, more than 90% of the waste spilled is attracted to these media. It is most fortunate that the electrokinetic treatment process (electro-osmosis and electromigration of water) can overcome the difficulties of relatively low-permeability media, achieve or enhance the aerobic biochemical oxidation of the human toxic and hazardous wastes, and consume relatively little energy (see ELECTROKINETIC PROCESSES).

CoMetabolic Processes With Glucose and Sugar. The basic mechanism of bioremediation is triggering the growth of microorganisms that are adapted to organic wastes spilled in the soil and groundwater. Stimulation of the growth of the microorganism is controlled by proper temperature, oxygen, moisture, nutrients, and cosubstrates, and distribution of such in the impacted media. During growth, the microorganism will secrete enzymes and biosurfactants to break down the hazardous organic molecules (detoxification) and to make them available through cellular absorption. Subsequently, the microorganism will grow and multiply, and the process repeats until the food source is depleted. The end result is mineralization of the carbon source (from spilled hazardous organic wastes) aerobically into carbon dioxide, water, and biomass without undesirable side effects. The cometabolic processes for bioremediation of chlorinated solvents and petroleum hydrocarbons are the most promising trouble-free biotreatment processes and are very efficient. The cometabolic process can be defined as the introduction of an easily biodegradable substrate into the environment, which triggers the secretion of enzymes from microorganisms that are adapted to the spilled hazardous organic waste.

The biotreatment of chlorinated solvents is a highly sought after solution to widespread soil and groundwater contamination problems. However, most of the knowledge of biotreatment of chlorinated solvents is found only in research laboratories. A successful laboratory demonstration of the cometabolic biotreatment of trichloroethene (TCE) by methanotrophic bacteria columns was achieved by the EPA Ada Laboratory in 1985 (6). In 1987, the EPA Gulf Breeze Laboratory successfully demonstrated

the cometabolic biotreatment of TCE by *Pseudomonas putida* through an aromatic pathway (7). In 1989, Loo, (8) successfully demonstrated the first field closure of the cometabolic biotreatment of TCE and trichloroethane (TCA) together with toluene in soil through heat and nutrient enhancement by the growth of indigenous bacteria *Bacilli* and *Pseudomonas fluorescens*. In 1991, Stanford University demonstrated partial success of the cometabolic biotreatment of chlorinated solvents in groundwater by methanotrophic bacteria at Moffet Field, California. Loo et al. (9) demonstrated the bio-treatment of TCE in the laboratory, field pilot, and in field application using glucose, which is nontoxic and nonhazardous, as a co-substrate. Loo et al. (9) developed and successfully applied the cometabolic biotreatment of petroleum hydrocarbons using glucose and sucrose as a co-substrate in both soil and groundwater Subsequently, many other site closures were achieved through the application of the cometabolic bioremediation of petroleum hydrocarbons.

Electrokinetic Processes

Direct current (DC) electricity is a widely used technology in industrial, commercial, and military applications. Direct current from solar panels is also used in space age technology for the electrolysis of water to produce hydrogen as fuel and oxygen for breathing. For environmental protection, direct current is used in the cathodic protection of steel underground storage tanks and pipelines from corrosion and leaks. Electrokinetic (EK) processes involve the application of DC electricity to soil and groundwater in the subsurface (1). EK processes originated or based their work on the geotechnical dewatering of clayey material by Casagrande (10–12). Other significant pioneering EK applications in oil and gas recovery were developed by Chilingar et al. (13–16).

The application of EK technology in the environmental field was first reported in the literature in the 1980s (17), most of the applications were for the isolation or recovery of metals. Van Doren and Bruell (18) first reported that the EK process destroyed benzene in wet clay in a laboratory bench scale test. Loo (8) and Loo and Wang (33) first reported the successful commercial application of the EK process as the primary enhancement process for removing or desorbing chlorinated solvents from a thick clayey soil layer at a defense contractor site closure located in Anaheim, California. The U.S. Army Corp of Engineers (19) listed EK treatment as a viable remedial process for treating hazardous wastes. In 1995 at the HAZMACON Conference, Santa Clara, California, the best paper award was given to the paper entitled "Elecrokinetic Treatment of Hazardous Wastes in Soil and Groundwater" (20). In 1995, the U.S. EPA (21) summarized the application and development of electrokinetic (EK) treatment processes by various private companies, the U.S. Department of Defense, the U.S. Department of Energy, and various universities as a potential cost-effective treatment for hazardous wastes. In 1997, the U.S. EPA (17) summarized and updated various EK applications in research, development, and commercial treatment of hazardous and radioactive wastes.

The EK processes works effectively for both permeable and relatively impermeable media. For relatively impermeable porous media like clay and silt, direct current conducts well in the media. The electrical conductivity of clay is often 1000 times greater than that of sand, sandstone, limestone, and igneous and metamorphic rocks. The same applies to fractured media where the fractures are often filled with highly conductive clayey and fine grain minerals. For porous media like sand, the flow of electricity is most likely through water that has naturally occurring electrolytic ions such as chloride, bicarbonate, nitrate, potassium, and sodium. The water molecules and positively charged ions (cations) will also be "dragged" by the electron flow from the anode toward the cathode and create a hydraulic mound (high) around the cathode by the induced electrokinetic gradient (Fig. 1). The EK processes works for both the vadose zone and the saturated zone in the subsurface, as long as there is adequate moisture in the medium. A dry medium does not conduct electricity very well.

As mentioned in the previous section, electrolysis of the water molecule will produce dissolved hydrogen around the anode and dissolved oxygen around the cathode. Therefore, higher dissolved oxygen around the cathode will help and encourage aerobic biotreatment of organic compounds. Electromigration will also help to bring the desorbed organic compounds to places enriched with oxygen and nutrients.

Regulatory And Permitting Requirements. No regulation or permitting requirement apply directly to the use of direct current in the subsurface. When the EK process is applied as an enhancement process for bioventing in the vadose zone, the extracted volatile organic vapor can be recirculated back into the center of the soil plume to avoid an air emission permit.

The EK process can make the groundwater migrate back and forth within the groundwater (thorough *in situ* mixing), so there is no need to pump and treat and thus no discharge permit. Also, when electrolytes and nutrients are added into the subsurface for EK processes, no underground injection control permit is required as long as all electrolytes and nutrients added are nontoxic and nonhazardous.

EK application in the subsurface is similar to cathodic protection with an impressed current and to the function of electrical grounding devices, which require no permit to construct and operate.

IN SITU FIELD FEASIBILITY CHARACTERIZATION

Before implementing a full-scale bioremediation project, one should conduct a field pilot confirmation test for mineralization products. The purpose of the field pilot test is to determine if the indigenous microorganism responds to the various enhancement elements. A simple oxygen slug injection into a vadose zone well while monitoring the respiration of the metabolic function of the indigenous microorganism will suffice. The simple oxygen enhancement field test should show a favorable increase in carbon dioxide and a reduction in oxygen in the well.

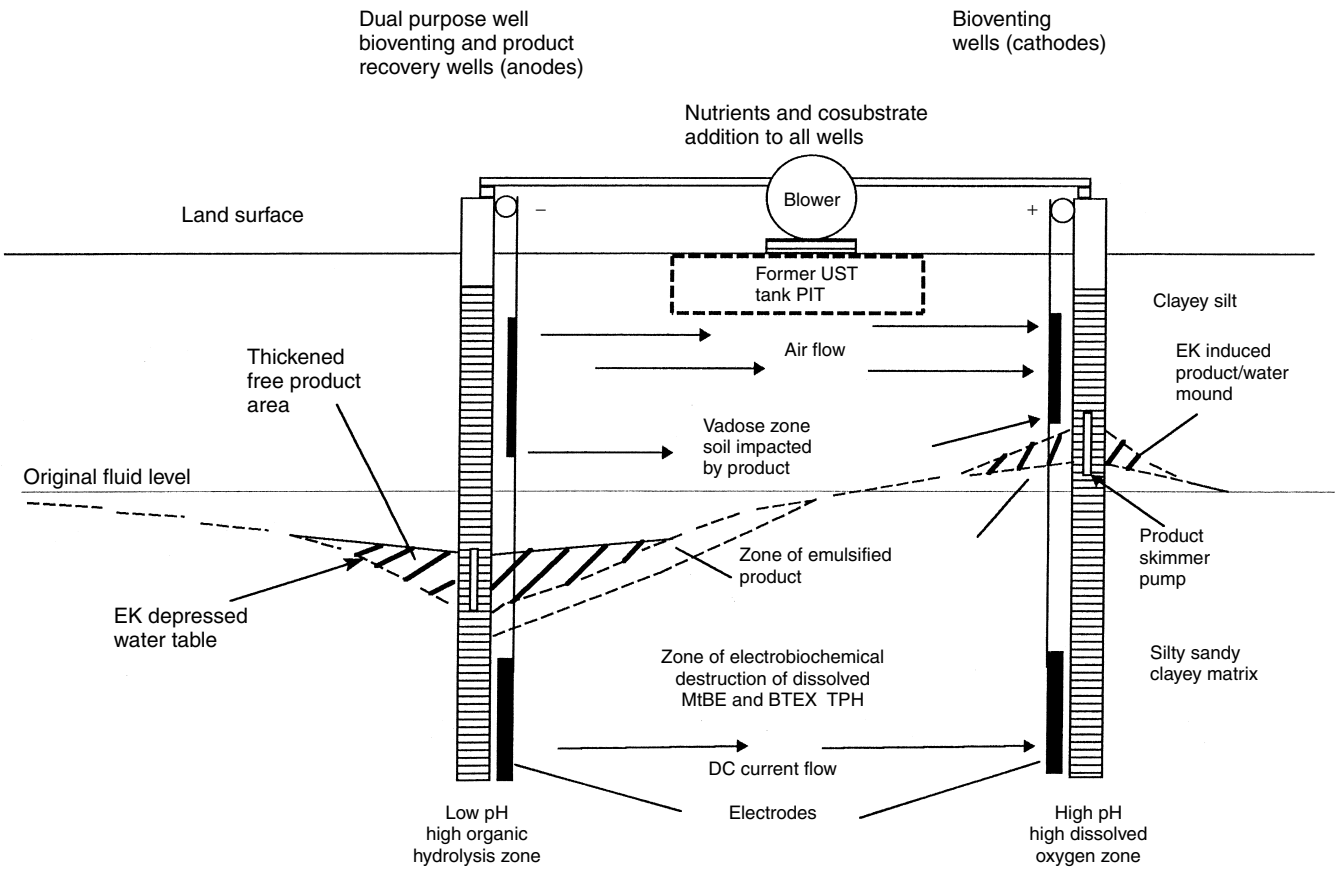


Figure 1. Generalized *in situ* electrobiochemical remedial cross section.

This whole field test involves only one vadose well in the middle of the impacted soil plume, one compressed oxygen bottle, and an oxygen/carbon dioxide field.

Biochemical Field Survey

The initial distribution of the organic hazardous waste in the soil and groundwater is the starting point for the design of a bioremediation project. For the baseline condition of a soil plume, a statistically significant soil sampling plan will be required because of the heterogeneous nature of the distribution of organic hazardous wastes in the soil. The plan should follow the requirements of the EPA SW-846 sampling procedure for the lateral extent of a soil plume to ensure statistical significance. For the vertical extent, one should add randomness by staggering depths instead of using a regular depth interval to ensure even distribution and to eliminate any significant lithologic layering effects. It is fairly easy to establish a baseline for dissolved constituents in the groundwater because of the slow dilution resulting from the influx of clean groundwater from upgradient. The only requirement is an adequate number of monitoring wells. The key sample analysis parameters required for bioremediation design and engineering are as follows:

- weight of the soil and groundwater plumes
- concentration of wastes in soil and water
- total heterotroph plate count
- chemical oxygen demand (COD)
- total organic carbons (TOC)
- total Kjeldahl nitrogen (TKN)
- nitrate
- total phosphorus
- iron
- temperature within the soil and groundwater plume
- dissolved oxygen and pH in groundwater
- moisture content in soil
- concentration of oxygen and carbon dioxide in soil pores

When the soil and groundwater plumes are fully characterized in weight, chemical requirement, engineering, installation, equipment, delivering lines, monitoring, and analysis, operating and maintenance costs can then be estimated for economic feasibility. The ultimate cost should be presented in dollars per ton of soil or groundwater plume that requires biotreatment.

Electrokinetic Field Surveys

The main purpose of the *in situ* direct current survey is to detect any anisotropic (uneven and bias) flow directions. The survey also may provide clues to unidentified buried metallic lines and structures that may require cathodic

protection. Field DC flow should be conducted with combinations in pairs of all available wells located inside and outside of the plume. For example, for four wells there should be six survey measurements. For six wells, there should be 15 survey measurements. The survey should be conducted at fixed voltage (electrical potential) and measure the direct current flow in amperes. The DC flow survey requires 110 volt AC power with a DC converter rated for 50 to 100 DC volts (range) and a maximum of 10 DC amperes. Wires must be insulated to prevent short circuits.

IN SITU ELECTROBIOCHEMICAL TREATMENT DESIGN

The economical alternative to digging, hauling, and disposing or *ex situ* treatment of contaminated soil is bioventing in the subsurface. The economical alternative to pumping, treating, and discharging of contaminated water is *in situ* groundwater biotreatment.

Soil Bioventing

Bioventing is a method of treating petroleum hydrocarbon contaminated soil in the vadose zone by circulating air through the pores of the soil matrix. It is particularly effective when the moisture content and nutrient level in the soil can be amended to prime enhancement conditions for bio treatment. Bioventing can treat both volatile and nonvolatile organic hydrocarbons. Hinchee et al. (22,23) and Miller et al. (24) developed the bioventing concept for bioremediating petroleum hydrocarbons at many U.S. Air Force sites. However, only oxygen enhancement was adopted for soil cleanup at many of these sites. The process involved injecting air at one well into the contaminated soil plume, with little evaluation of the engineering feasibility. Little engineering consideration was given to the migration of organic vapor that was pushed out of the soil plume and formed condensates, which further spreads the groundwater contamination. This may be the most economic means of treating petroleum hydrocarbons in soil for the U.S. Air Force, but it may face the side effects of uncontrolled spreading of the dissolved groundwater plume.

The first fully enhanced bioventing system for treating gasoline was applied in the clayey marine conglomerate at the PepBoys site, San Diego, California (25). The electro-osmosis process desorbed or squeezed out the gasoline in the clayey soil and made the gasoline available for bioventing. The extracted air was heated and reinjected into the vadose zone soil for heat enhanced biotreatment. The heated air also carried the water squeezed from the clay layer as humidity for moisture enhancement. Pure oxygen gas was injected into the middle of the soil plume to replenish the oxygen used during aerobic bioventing. Nitrogen-based nutrient gas was also injected into the middle of the soil plume for nutrient enhancement. Nitrogen-based nutrient gas injection into soil is widely used in large-scale agricultural farming practices.

Groundwater Biotreatment

The aqueous phase biotreatment discussed in this section does not involve pumping out any water from the ground. The most challenging aspect of *in situ* aqueous biotreatment is the distribution or penetration of nutrient, oxygen, and heat into the clayey or less permeable areas within the saturated media. Electrokinetic processes can overcome these conditions.

Passive Biotreatment. Passive biotreatment involves oxygen, nutrient, heat, and electrokinetic enhancement to biodegrade toxic organic chemicals into harmless carbon dioxide, water, and biomass. Oxygen can be enhanced by creating dissolved oxygen through electrolysis of groundwater or by using the oxygen in food additive cosubstrates dissolved in the groundwater. Nutrients can be enhanced by adding ammonium-based food additive chemicals into the groundwater. Heat can be enhanced economically by infiltrating solar heated water into the groundwater through an infiltration gallery or through injection into a remedial well. Electrokinetic enhancement or mixing can be achieved by electromigration of nutrient/electrolyte through permeable and impermeable water saturated media.

Loo (26) demonstrated that benzene can be biotreated to a nondetectable level in groundwater. Loo (27) also demonstrated that MtBE can be electrobiochemically treated to a nondetectable level in groundwater. Finally, Loo et al. (28) and ETS showed that chlorinated solvents can be biotreated to nondetectable levels in groundwater.

The following sections provide the requirements for EK design and implementation. The basic electrokinetic feasibility test parameters are as follows:

- field pH, conductivity, and dissolved oxygen of water
- laboratory pH and conductivity of soil
- chemical oxygen demand (COD)
- contaminant concentration in soil above and below the water table
- contaminant concentration in groundwater
- selective anion and cation analysis

Representative samples must be obtained at the center of the plume where the concentration of the contamination is the highest. Representative samples must also be obtained at the peripheral monitoring wells upgradient, downgradient and cross gradient.

Electrokinetic System Components

Electrokinetic system components may include but are not limited to electrodes, electrolytes, wiring, and power supply. The description and selection of these components are described in the following sections.

An electrode can be made of any good conductor. All electrodes for environmental cleanup must be relatively inert and should not contain hazardous or toxic chemicals. Typically, copper and stainless steel electrodes should be avoided. The most common electrodes are made of iron, black steel, carbon, and graphite. More exotic electrodes used are made of gold, platinum, and titanium. The electrodes can be ordered in any shape and form to fit the particular application. The most common form is a round solid rod or a tube from 1 to 10 feet long.

The use of food additive chemicals as an electrolyte is preferred to increase the flow of direct current in the ground. Note that the electrolyte should be applied on an as needed basis. Soil and groundwater may contain enough electrolyte minerals to provide adequate direct current flow. The application of electrolyte sometimes is necessary for maintenance of electrodes to prevent corrosion at the anode and mineral scaling at the cathode. Potassium and sodium chlorides are not considered environmentally friendly electrolytes electrolysis of potassium and sodium chlorides will yield toxic chlorine gas, which may create unsafe and unhealthy conditions.

All electrical wiring must be insulated and rated for at least 30 amperes. The length of wires to cathodes and anodes need not be equal, but multiple wires to either cathode or anode must be equal in length and size to prevent short circuits. It is often very common for each circuit wire to carry less than 2 amperes of DC current.

Direct current power supplies often draw from 110 Volt AC or 220 Volt AC power sources. Same of the common names for the DC power converter are DC testing power supply, DC welding units, an automobile battery with a proper recharging source, and electrical solar panels. It is advised that no more than 10 DC amperes be drawn from any converters to prevent overheating.

ACHIEVABLE CLEANUP LEVELS

EK processes can achieve the very low levels of concentrations of various hazardous wastes in soil and groundwater listed here as examples:

	In Soil	In groundwater
Petroleum hydrocarbon (gasoline)	Less than 50 ppm	Nondetectable (less than 1 ppm)
Petroleum hydrocarbon (diesel kerosene, jet fuel, motor oil, etc.)	Less than 100 ppm	Nondetectable (less than 1 ppm)
Benzene	Less than 100 ppb	Nondetectable (less than 1 ppb)
Methyl tertiary-butyl ether (MtBE)	Less than 1 ppm	Nondetectable (less than 5 ppb)
Chlorinated solvents (PCE, TCE)	Less than 100 ppb	Nondetectable (less than 5 ppb)

ECONOMICS OF *INSITU* ELECTROBIOCHEMICAL TREATMENT

For a typical small-scale project, assuming less than 3,500 tons of contaminated soil and groundwater, the following is a breakdown of the in-situ electrobiochemical treatment project cost estimate in 2002 US dollars:

Planning and preliminary design	$3,000
Field feasibility testing	$20,000
Detailed engineering design	$5,000
Remedial system installation (six remedial wells)	$40,000
Startup remedial testing	$13,000
Operation and maintenance (6 months)	$18,000
Remedial monitoring	$6,000
Closure confirmation sampling	$5,000

The unit price remedial cost estimate is about $30 per ton. For medium size remedial projects of more than 10,000 tons, it is not unusual to complete the project at less than $20 per ton. For larger size remedial projects of 50,000 tons or more, it is not unusual to complete the project at less than $15 per ton.

The economics of power consumption can be measured in kilowatt hours (kwh) and each kwh costs US $0.10 to $0.20 or less than $2 per ton depending on the cost of power at the location. Each watt of energy is equal to the product of voltage (1 volt) and amperage (1 ampere). Normally, the cost of electricity is insignificant compared to the overall remedial project cost.

CASE HISTORIES

There are many documented examples of field pilot-scale EK remediation of toxic/radioactive metals and hazardous organic chemicals. The individual project descriptions are included in the publicly available reference documents listed below:

U.S. ARMY CORP OF ENGINEERS 1992
Installation Restoration and Hazardous Control Technologies

U.S. EPA 1995 PUBLICATION 542-K-94-007
In-Situ Remediation Technology: Electrokinetics

U.S. EPA 1997 PUBLICATION 402-R-97-006
Electrokinetic Laboratory and Field Processes Applicable to Radioactive and Hazardous Mixed Waste in Soil and Groundwater

Electrokinetic Enhanced Soil Bioventing

The conventional application of soil vapor extraction of volatile organic chemicals (VOCs) cannot overcome low permeability soil media to render the successful completion of a project. The electrokinetic process can enhance the desorption of water and contaminants from clay by breaking down the clay layer's electrically charged bonds. This will make the VOCs available for contact and treatment. The major drawback of soil vapor extraction is air emission which is a physical phase transfer process instead of destruction. The EK enhanced closed loop bioventing process was applied to destroy the VOCs without air emission at sites with clayey soil. The following

is a list of sites where EK enhanced bioventing processes were successfully implemented:

PepBoys Site, San Diego, California (25)
Bioventing of gasoline in clayey soil

Bat Rentals Site, Las Vegas, Nevada (29)
Bioventing of gasoline, diesel and kerosene in clayey caliche soil

Evergreen Site, Los Angeles, California (30)
Bioventing of gasoline in clayey soil

DBM Oil Site, Long Beach, California (30)
Bioventing of diesel and waste oil in clayey soil

Cadillac Site, Northridge, California (27)
Bioventing of gasoline in clayey soil

Former Texaco Site, Long Beach, California (27)
Bioventing of gasoline in silty/clayey soil

Former ARCO Site, Monterey Park, California (27)
Bioventing of gasoline in clayey soil

Electrochemical Oxidation

It is difficult to distinguish which electrokinetic process is responsible for destroying petroleum hydrocarbons. The bench test on a soil sample from the PepBoys Site indicated that electrochemical oxidation is responsible for destroying petroleum hydrocarbons.

For all the bioventing projects described in the previous section, the electrochemical oxidation process is responsible for a portion of the destruction of the petroleum hydrocarbons rather than bioventing alone.

Electrobiochemical Oxidation

Electrobiochemical oxidation applies to the aqueous phase biotreatment of petroleum hydrocarbons in soil and groundwater. Electrokinetic processes are responsible for distributing nutrients and oxidants in impacted soil and groundwater. It can be used together with bioventing in the vadose zone. The following is a list of sites where EK enhanced aqueous phase biotreatment processes were successfully implemented:

Westland Site, Hayward, California (26)
Electrobiochemical of gasoline and diesel in Bay Mud clay and water

Bat Rentals Site, Las Vegas, Nevada (29)
Bioventing(wet) of gasoline, diesel and kerosene in clayey caliche soil and shallow groundwater

Cadillac Site, Northridge, California (27)
Bioventing(wet) of gasoline in clayey soil and groundwater

Former Texaco Site, Long Beach, California (27)
Bioventing(wet) of gasoline in silty/clayey soil and groundwater

Former ARCO Site, Monterey Park, California (27)
Bioventing(wet) of gasoline in clayey soil

At all these sites, food additive nutrients and oxidants were introduced as electrolytes by electrokinetically induced migration through wells (horizontal migration) and infiltration galleries (vertical migration) to penetrate into the clayey matrix of soil and groundwater. Additions of nontoxic and nonhazardous food additives, nutrients, and oxidants into the subsurface are not regulated by underground injection control regulations. Petroleum hydrocarbons like BTEX in soil and groundwater were treated to nondetectable levels at most sites.

Electrolysis of MtBE and Benzene

The two most resistant dissolved petroleum hydrocarbons in the environment are MtBE and benzene due to their higher solubility in water and low cleanup levels which most often cannot be achieved by conventional remedial treatment technologies.

The gasoline additive MtBE is highly soluble in water and usually migrates furthest away downgradient from the spill location. Air stripping of MtBE is not an effective treatment option. There are reports that MtBE in the air were solublized into air-stripper blowdown water. Plus, MtBE is not readily biodegradable in the subsurface. The following is a list of sites where EK induced electrolysis processes were successfully implemented:

Cadillac Site, Northridge, California (27)
Bioventing(wet) of gasoline in clayey soil and groundwater

Former Texaco Site, Long Beach, California (27)
Bioventing(wet) of gasoline in silty/clayey soil and groundwater

MtBE was first treated in groundwater, accidentally (not by design), in 1997 at the Cadillac Site, Northridge, California, while treating dissolved BTEX using the electrobiochemical aqueous phase treatment. It was discovered that MtBE soon "disappeared" after the start-up of the electrokinetic enhanced biotreatment. The MtBE in groundwater was treated to nondetectable levels in less than 3 months of treatment. It also appeared that benzene concentration was decreasing at a slower rate at various monitoring wells. The electrolysis of MtBE and benzene cannot actually be confirmed. It was a surprise to document the MtBE disappearance at the Cadillac Site while at the time the oil company sponsored numerous seminars that pointed to no effective remedy for MtBE in the environment.

The same electrobiochemical treatment technique was applied to MtBE and BTEX at the former Texaco Site in Long Beach, California, in 1997. The dissolved benzene

and MtBE in groundwater were treated to nondetectable levels in two monitoring wells outside of the zone of influence of the electrobiochemical treatment area which was focused on the former underground storage tank pit area. This indicated that the only thing that can influence these peripheral monitoring wells is the DC flow field. This is the first confirmation of the electrolytic breakdown of dissolved MtBE and benzene in groundwater. The nondetectable MtBE and benzene performance in the vadose zone soil in the tank pit area is also a first.

Chlorinated Solvents

The conventional remedial treatment technology of chlorinated solvent in soil is soil vapor extraction. The newer and innovative remedial treatment of chlorinated solvents in groundwater is cometabolic biotreatment. None of the above will be effective when treating clayey material. Electrokinetic processes excel in desorbing the contaminants from clay and distributing nutrient, oxidants and cosubstrates in the soil and groundwater.

The following is a list of sites where the EK enhanced chlorinated solvent treatment processes were successfully implemented:

Northrop ESD Site, Anaheim, California (31)
EK enhanced soil vapor extraction of chlorinated solvents in clayey soil

The Good Guys Site, Emeryville, California (8,20,28, 30,32) EK enhanced cometabolic biotreatment of chlorinated solvents in clayey soil and groundwater

BIBLIOGRAPHY

1. Loo, W.W. (2001). Bioremediation & electrokinetic treatment of hazardous wastes. *Standard Handbook of Environmental Health, Science and Technology*. J.H. Lehr (Ed.). McGraw-Hill, New York, Chapters 14.4 & 14.6.
2. Roberts, P. et al. (1990). Biostimulation of Methanotrophic Bacteria to Transform Halogenated Alkene for Aquifer Restoration. *Conference Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, Houston, TX, pp. 203–217.
3. Garnier, P., Auria, R., Magana, M., and Revah, S. (1999). Cometabolic Bio-treatment of MTBE by a Soil Consortium. *Proceedings of The Fifth International In situ and On-Site Bio-remediation Symposium*, Battelle Press, San Diego, CA, Vol. 5(3), pp. 31–35.
4. Battelle Press. (1999). Engineered Approaches for *In situ* Bio-remediation of Chlorinated Solvents. *Proceedings of The Fifth International In Situ and On-Site Bio-remediation Symposium*, San Diego, CA, Vol. 5(2).
5. Gaudy, A.F. and Gaudy, E.T. (1980). *Microbiology for Environmental Scientists and Engineers*. McGraw-Hill, New York.
6. Wilson, J.T. and Wilson, B.H. (1985). Biotransformation of trichloroethylene in soil. *Applied and Environmental Microbiology* **49**(1): 242–243.
7. Nelson, M.J.K. et al. (1987). Bio-treatment of trichloroethylene and involvement of an Aromatic Biodegradative pathway. *Applied and Environmental Microbiology* **53**(5): 949–954.
8. Loo, W. W. (1991). Heat Enhanced Bio-remediation of Chlorinated Solvents and Toluene in Soil. *Conference Proceedings of R&D 1991*, Anaheim, CA, pp. 133–136.
9. Loo, W.W. et al. (1993). Field Bio-treatment of Chlorinated Solvents: A Co-Metabolic Process Utilizing Glucose as Co-Substrate. *Proceedings of HAZMACON 1993*, Association of Bay Area Government(ABAG), Santa Clara, CA.
10. Casagrande, L. (1947). *The Application of Electro-Osmosis to Practical Problems, in Foundations and Earthworks*. Building Technical Paper No. 30, H. M. Stationary Office, London.
11. Casagrande, L. (1948). Electro-Osmosis. *Proc. 2nd Int. Conf. on Soil Mech. and Found. Eng.*, vol. 1, pp. 218–222.
12. Casagrande, L. (1952). Electro-Osmotic Stabilization of Soils. *Boston Soc. Civ. Eng.* **39**(1): 51.
13. Chilingar, G.V. et al. (1963). Possible use of electric current for increasing volumetric rate of flow of oil and water during primary and secondary recovery. *Chem. Chron.* **28**(1): 1–4.
14. Chilingar, G.V. et al. (1964). Use of direct electrical current for increasing the flow rate of reservoir fluids during petroleum recovery. *J. Canadian Pet. Tech.* **3**(1): 8–14.
15. Chilingar, G.V. et al. (1968). Possible use of direct current for augmenting reservoir energy during petroleum production. *Compass of Sigma Gamma Epsilon* **45**(4): 272–285.
16. Chilingar, G.V. et al. (1970). Effect of direct electrical current on permeability of sandstone cores. *J. Pet. Tech.* **22**(7): 830–836.
17. US EPA. (1997). *Electrokinetic Laboratory and Field Processes Applicable to Radioactive and Hazardous Mixed Waste in Soil and Groundwater*. US EPA publication 402-R-97-006, Center for Remediation Technology and Tools, Washington, DC.
18. Van Doren, E.P. and Bruell, C.J. (1987). Electro-Osmotic Removal of Benzene from a Water Saturated Clay. *Proc. of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, Nov. 17–19, 1987, Houston, TX, pp. 107–126.
19. U.S. Army Corps of Engineers. (1992). *Installation Restoration and Hazardous Control Technologies*. Prepared for US Air Force, US Navy, US Army, and US EPA, pp. 45–46.
20. Loo, W.W. (1995). Electrokinetic Treatment of Hazardous Wastes in Soil and Groundwater, HAZMACON'95 Award Winning Paper. *Proceedings of HAZMACON'95*, sponsored by the Association of Bay Area Governments, San Jose Convention Center, San Jose, CA, pp. 147–158.
21. US EPA. (1995). *In-Situ Remediation Technology: Electrokinetics*. US EPA publication 542-K-94-007, Office of Solid Waste and Emergency Response, Office of Technology Innovation Office, Washington, DC.
22. Hinchee, R.E. et al. (1989). Enhancing Bio-treatment of Petroleum Hydrocarbon Fuels Through Soil Venting. *Conference Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, Houston, TX, pp. 235–248.
23. Hinchee, R.E. et al. (1990). Enhanced Bioreclamation Soil Venting and Groundwater Extraction: A Cost-Effectiveness and Feasibility Comparison. *Conference Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, Houston, TX, pp. 147–164.
24. Miller, R.N. et al. (1990). A Field Investigation of Enhanced Petroleum Hydrocarbon Bio-treatment in the Vadose Zone at Tyndall AFB, Florida. *Conference Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, Houston, TX, pp. 339–351.
25. Loo, W.W., Wang, I.S., and Fan, K.T. (1994). Electrokinetic Enhanced Bioventing of Gasoline in Clayey Soil: A Case

History. *Proceedings of the SUPERFUND XV Conference*, Washington, DC.

26. Loo, W.W. (1994). Electrokinetic Enhanced Passive In-Situ Co-Metabolic Bio-treatment of Gasoline and Diesel in Clayey Soil and Aquifer: A Case History. *Proceedings of the SUPERFUND XV Conference*, Washington, DC.
27. Loo, W.W. (1998). Groundwater Case Closures of MtBE, Benzene & Chlorinated Solvents to Non-Detect By In-Situ Electrokinetic Processes. *Presented at the HAZMACON Conference*, Santa Clara Convention Center, Santa Clara, CA, April 1998, sponsored by the Association of Bay Area Governments.
28. Loo, W.W. (1993b). Bio-treatment of Chlorinated Solvents in Soil and Groundwater Utilizing Glucose as the Co-Substrate. *Proceedings of the 1993 HAZMACON Conference*, San Jose, CA.
29. Loo, W.W. (1994). Passive In-Situ Bio-treatment of Gasoline, Diesel and Kerosene in Soil and Groundwater. *Proceedings of the 1994 HAZMACON Conference*, San Jose, CA.
30. Loo, W.W. (1996). Experience of Soil and Groundwater Project Closures in California and Nevada. *Proceedings of SUPERFUND WEST'96, Las Vegas, Nevada*, Sponsored by Hazardous Waste Management Association, Washington, DC.
31. Loo, W.W. et al. (1991). *Soil Closure Report, submitted to Santa Ana Regional Water Quality Control Board*. Electrokinetic Enhanced Soil Remediation with Chlorinated Solvents at the Northrop ESD Site, Anaheim, CA.
32. Loo, W.W. (1993). Engineered Soil Vapor Extraction: Two Case Histories. *Proceedings of the 1993 HAZMACON Conference*, San Jose, CA.
33. Loo, W.W. and Wang, I.S. (1991). Remediation of Groundwater Aquifer by In-Situ Electrolysis and Electro-Osmosis. *Proceedings of National Research and Development Conference on the Control of Hazardous Materials*, February 20–22, 1991, Anaheim, CA, p. 163.

FIELD CAPACITY

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Storage of soil water is important to soil flora and fauna, to hydrologic processes, and to a variety of soil physical properties. One element of soil water storage is an upper limit on water that is available for plant use, referred to as "field capacity." This entry provides a history of the concept, its relation to soil water holding properties, predictive techniques for field capacity, applications, and failures of the field capacity concept.

HISTORY OF THE CONCEPT

Plant Available Water

Early researchers of plant water relations quickly realized that in water limited regions, the ultimate crop yield depended not only on the amount of rainfall received but on what portion of that rainfall was usable. Three key factors could reduce the usefulness of rainfall: runoff, drainage below the root zone, and evaporation. The net effect of rainfall, runoff, and drainage results in retention of water in the root zone. Evaporation and transpiration reduce this retained water. This retention was studied by Veihmeyer and Hendrickson (1). The concepts developed by Veihmeyer and Hendrickson provide a means to evaluate whether a soil retains sufficient water to support a particular crop. Veihmeyer and Hendrickson (2) redefined their original definition of field capacity to "the amount of water held in soil after excess water has drained away and the rate of downward movement has materially decreased, which usually takes place within 2–3 days after a rainfall event or irrigation in pervious soils of uniform structure and texture."

Field studies focused on measuring the soil water content following a heavy rainfall (that penetrated deeply into the soil). It was observed that the water content would change after the rain stopped. This change gradually slowed such that after 3 days it was difficult to observe additional changes. The inaccurate concept took hold: that after 1–3 days, drainage stopped, and the water retained in the soil at that time would then be available for transpiration. The choice of 2–3 days was partially the result of limited means to measure soil water content. However, the concept took hold that the soil stored water and an upper limit on stored water (available for plant use) could be defined. This upper limit is called "field capacity."

Correspondingly, there is a lower limit to the soil's ability to store water that plants can use. This lower limit is called the "wilting point" or "permanent wilting point." This also has a historical basis, usually limited to a particular plant but more typically taken as the volumetric water content at a matric potential of −1.5 MPa (−15 bars). The difference between field capacity and the permanent wilting point is called the "available water capacity" or the potential "plant available water." Figure 1 shows how the soil porosity (or void space) might be divided into these components. For dryland agriculture, the "available water capacity" approximates the soil's water storage ability. For irrigated agriculture, the field capacity is combined with a lower limit of water content usually set at a point where irrigation is started.

A related interpretation of the field capacity is the water held against gravity. Early attempts to transfer these ideas to the lab depended on a centrifuge to remove

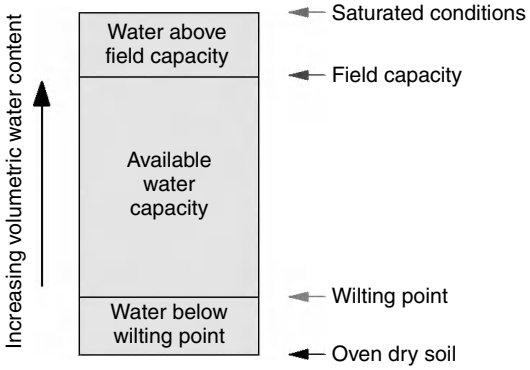


Figure 1. Naive concept of water filled soil porosity.

soil water (3–5). Some workers attempted to relate field capacity to these soil water contents (measured under specific centrifuge conditions, e.g., moisture equivalent) with limited success. Many of these early researchers were limited by their understanding of water movement.

There are several concerns in regard to the definition of field capacity proposed by Veihmeyer and Hendrickson. These include identifying when water movement ceases and the rarity of "soils of uniform structure and texture." The following section addresses the first issue, and the second is postponed to a later section.

Does Drainage Cease?

Later research into the process of drainage showed variation across soil types. Typically, sandier soils drain faster before a noticeable drop-off in water movement. More finely textured soils show a much longer decay process for changes in water content. Thus, at least sands appeared to conform to the Veihmeyer and Hendrickson concept. However, Gardner et al. (6) and Hillel et al. (7) clearly showed that water content does not approach equilibrium up to 30 days after infiltration even on a uniform sandy soil. Figure 2 shows an example of this drainage process for a sandy soil. Thus, for many soil environments, the concept of field capacity is an oversimplification and invalid (i.e., there is no well-defined drainage-induced upper limit to soil water content).

Infiltration Storage Capacity and Runoff

As indicated earlier, not all rainfall enters the soil. Depending on the infiltration characteristics of the soil and the rainfall (intensity and duration), water may pond and runoff. The ability of soils to accept rainfall (i.e., infiltration) depends on a number of soil hydraulic properties (most directly hydraulic conductivity and the soil water characteristic) as well as surface roughness. These infiltration properties may in turn correlate with properties such as field capacity. Thus, some hydrologic runoff models may require soil hydraulic properties as input parameters, which provides an indirect linkage of soil properties such as field capacity to runoff. It also creates a demand for estimates of field capacity, no matter how poorly defined it may be.

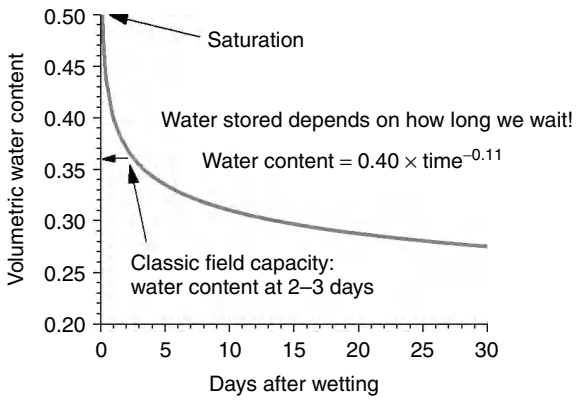


Figure 2. Example of a drainage curve for a sandy soil.

Erosion

When runoff occurs, the potential for water erosion and transport of eroded material also arises. Ponding and runoff contribute separately to the detachment of soil material (the initial process in soil erosion). Subsequent to detachment, runoff can remove the suspended material and transport it off-field or downstream. Runoff also contributes with greater velocities resulting in greater detachment. Finally, the ability of runoff to transport eroded material is also proportional to its velocity.

Field capacity influences the water erosion process through its indirect effect on infiltration. Typically, a larger field capacity results in greater infiltration rates and lower runoff velocities compared to a similar soil with smaller field capacity. These effects may be masked if the storm is very small or very large.

Wind erosion is also influenced indirectly by field capacity. The ability of wind to detach and suspend particles depends on the water content and vegetation (or plant residue) near the soil surface. The linkage between field capacity and some of these variables is weak, but some modeling efforts still rely on inputs of field capacity in their prediction algorithms.

RELATION TO WATER HOLDING PROPERTIES

The original experiments by Veihmeyer and Hendrickson (1,2) were time-consuming, labor-intensive, and not always readily adaptable to all soils and soil environments. A number of researchers looked for alternative means of estimating soil water content (or another property) that would relate to the concept of field capacity (i.e., the water content of a soil following a heavy rain and after 2–3 days of drainage). Several methods have been proposed; the most widely adopted is the use of volumetric water content at a specified matric potential. The water content is usually reported with units of $m^3\ m^{-3}$ to remove confusion with gravimetric water content. We describe three approaches to determining this water content, based on matric potential, unsaturated hydraulic conductivity, or soil water flux.

Matric Potential: The 1/10 and 1/3 Bar Criteria

A variety of workers (8,9) have examined the behavior of soil water content from field experiments meant to simulate field capacity. A broad pattern emerged suggesting that soil matric potential (a measure of the energy with which water is held by soil) provides an indicator independent of soil texture. An initial examination suggests that a range of values from -5 to -50 kPa might be reasonable; values closer to zero are used for coarse textured soils, and the more negative values are for more finely textured soils. Some researchers suggested that -10 kPa (or 1/10 bar in older units) was appropriate for sands and -33 kPa (or 1/3 bar) for all other soils. Thus, the volumetric water content at either -10 kPa or -33 kPa is commonly reported as the field

capacity. The relative simplicity of this concept resulted in the adoption of these values as standard measurements by the USDA Natural Resources Conservation Service and by most introductory textbooks. However, not all researchers have adopted these values, and for individual soils, a different matric potential may be more appropriate. Below (under the section titled Deficiencies), we mention some of the profound limitations and errors that can be introduced when using the concept of field capacity as the volumetric water content at 1/10 or 1/3 bar.

Unsaturated Hydraulic Conductivity Concept

A second approach to field capacity looks for a soil property that describes water movement. In particular, a property is desired that characterizes the point where water movement slows to an imperceptible level. Unsaturated water movement is described by a Buckingham–Darcy law where the "unsaturated hydraulic conductivity function" controls water movement. In this approach, the appropriate water content (or matric potential) is the value where the unsaturated hydraulic conductivity is reduced to some fraction of its saturated value. A variety of fractions have been proposed (0.1 or 1/e). This method is rarely used because of the difficulty currently associated with measuring unsaturated hydraulic conductivity.

Flux Concept

A third concept looks directly at water movement. The Buckingham–Darcy law can be used to predict the flux of water. The concept of field capacity is interpreted to mean the point where the flux is close to zero (10). Like the hydraulic conductivity method, just described, it relies on basic concepts of water movement, and it may set up a criterion relative to saturated flow. Unlike the hydraulic conductivity method, it uses a directly measured water movement (the flux), rather than an indirect physical property, and may provide an absolute criterion for zero flux, rather than a relative one. Meyer and Gee (10) suggest that a drainage flux of 3×10^{-7} cm/s represents field capacity.

PREDICTIONS OF WATER CONTENT AT 1/10 AND 1/3 BAR

The lack of a valid laboratory method combined with the time and expense of field methods has not reduced the desire for information about field capacity. Instead, many researchers have adopted the most convenient measurement (i.e., the volumetric water content at 1/10 bar or 1/3 bar). A number of laboratories will perform this analysis. However, water content measurements at these matric potentials is extremely sensitive to sample disturbance. This requires collecting and transporting undisturbed samples to laboratories for measurement. Handling of undisturbed samples is costly and requires special training that many laboratories do not have. The coefficient of variation for undisturbed samples has been reported as between 20 and 50% (11). Thus, laboratory measurements have clear advantages over field methods, but they are not without their own set of difficulties.

One solution to the problems just described is to develop regression or physical models to predict the water content at a specified matric potential. A variety of regression models have been proposed. Some of them are described by Acutis and Donatelli (12), Baumer and Brasher (13), Cassel et al. (14), Ritchie et al. (15), and Rawls et al. (16). More recently, Gijsman et al. (17) compared a variety of predictive techniques and found a great deal of variation among the models they tested. These authors recommend the method described by Saxton et al. (18) based on their independently obtained data set. Note that use of any of these relations does not remove the concerns expressed later in this article.

APPLICATIONS

The use of field capacity (usually as 1/10 or 1/3 bar water content) has grown beyond the original goal of understanding crop yields. In this section, we briefly look at current applications for crop yield prediction as well as a surrogate for other soil hydraulic properties that are more difficult to measure.

Agronomic/Ecological Models

Advances in computational power allow researchers to describe water movement in soils after rainfall and during plant growth by using physical transport principles. One common application of such models is the prediction of plant growth and crop yield (17,19). These models typically require the input of soil physical properties, possibly including field capacity. Input to these models is the laboratory measured water content at 1/10 or 1/3 bar as one point on a soil water retention curve that is used to predict other hydraulic properties. In other words, these models tend to be dynamic and allow soil water content to change continuously beyond the 2- or 3-day period despite the input of a so-called field capacity. In addition to crop yield/plant growth, these models may be used to develop irrigation timing strategies.

Hydrologic Models

Another area where field capacity estimates are used is in watershed modeling (20,21). These hydrologic models provide a means to describe the response of a watershed to a rainfall. A key component of these models is the infiltration process. In some cases, empirical infiltration models are used. Otherwise, physical soil water transport models (similar to agronomic models) are used. In either case, parameter inputs are typically needed either as an explicit parameter or to calculate the needed parameter (e.g., to estimate unsaturated hydraulic conductivity).

Other Applications

Field capacity (or at least the volumetric water content at 1/10 or 1/3 bar) can frequently act as a surrogate for other (less readily measured) soil properties, which, combined with its ready availability in a variety of databases, has led to its appearance in a variety of publications that are not directly tied to water movement or plant growth. In this case the use of the phrase "field capacity" refers only to a specific laboratory measured water content and has lost any "field" significance.

Examples of this use of field capacity include observations of microbial occurrence and activity (22), solute transport (23), soil strength (24,25), and soil erodibility (26).

DEFICIENCIES IN MEASUREMENTS

A variety of criticisms have been directed toward the field capacity concept by Richards (27), Baver et al. (28), Hillel (7) and Cassel and Nielsen (29). In addition to questions regarding the time when drainage ceases (mentioned earlier), there are three basic areas of concern with field capacity as a widely used concept describing water movement in field soils. The importance of changes in soil structure, soil layering, and initial conditions. We briefly discuss these issues as presented by the previously cited researchers.

Dependence on Structure and Disturbance

Field capacity measurements in the field and laboratory measurements (for matric potentials between 0 and 100 kP) are sensitive to changes in soil structure or aggregation. Changes in soil structure due to tillage, root growth, faunal activity, or freeze/thaw cycles are expected to alter soil hydraulic properties and the movement of water. Water quality (e.g., sodium or total salts) is also expected to influence aggregation and ultimately water movement.

Dependence on Soil Morphology and Internal Drainage

Soils are rarely uniform. Layers that have different hydraulic properties are typical. These layers may result in perched water tables or hindered drainage, which can be expected to extend drainage times. Equally important, drainage will not be uniform throughout the soil profile, so there will not be a single water content at a point of restricted water movement.

This existence of soil layers plays particular havoc with the use of laboratory determined values based on a specific matric potential. It may be possible to measure each soil layer independently, but the sequence of layers may be more important in controlling drainage patterns.

Dependence on Initial Conditions

The soil conditions prior to wetting (required in the basic definition of field capacity) are assumed to be unimportant. In fact, initial soil water content can influence the uniformity of wetting (30). It is not possible to measure field capacity under all possible scenarios of initial water content distribution or wetting history. Also of importance, the existence and position of the water table will influence both wetting and the drainage process. The presence of a shallow water table may act to reduce drainage. The use of laboratory methods to estimate field capacity cannot account for these conditions.

SUMMARY

The field capacity concept has been used to approximate the ability of soils to store water and to calculate an "available water capacity." However, soil water is not a static reservoir, and such a picture oversimplifies soil water movement and availability. Field representations of soil water storage require field measurements. Laboratory measurements (particularly water content at 1/10 and 1/3 bar) are popular because of their availability and seeming simplicity. Laboratory measurements can be useful for describing soils or estimating other soil hydraulic properties; however, their use as a reflection of water storage may be misleading and should be used with extreme caution. Any representation of soil water storage must be site specific and must take antecedent conditions into account.

BIBLIOGRAPHY

1. Veihmeyer, F.J. and Hendrickson, A.H. (1931). The moisture equivalent as a measure of the field capacity of soils. *Soil Sci.* **32**: 181–193.
2. Veihmeyer, F.J. and Hendrickson, A.H. (1949). Methods of measuring field capacity and wilting percentages of soils. *Soil Sci.* **68**: 75–94.
3. Briggs, L.J. and Mclane, J.W. (1907). *The Moisture Equivalent of Soils*. U.S.D.A. Bureau of Soils Bull. 45.
4. Briggs, L.J. and Shantz, H.L. (1912). *The Wilting Coefficient for Different Plants and its Indirect Determination*. U.S.D.A. Bureau Plant Indus. Bull. 230.
5. Russel, J.C. and Burr, W.W. (1925). Studies on the moisture equivalent of soils. *Soil Sci.* **19**: 251–266.
6. Gardner, W.R., Hillel, D., and Benyamini. (1970). Post irrigation movement of soil water: I. Redistribution. *Water Resour. Res.* **6**: 851–861.
7. Hillel, D., Krentos, V.D., and Stylianou, Y. (1972). Procedure and test of an internal drainage method for measuring soil hydraulic charcteristics in situ. *Soil Sci.* **114**: 395–400.
8. Coleman, E.A. (1947). A laboratory procedure for determining the field capacity of soils. *Soil Sci.* **63**: 277–283.
9. Jamison, V.C. and Kroth, E.M. (1958). Available moisture storage capacity in relation to textural composition and organic matter content of several Missouri soils. *Soil Sci. Soc. Am. Proc.* **22**: 189–192.
10. Meyer, P.D. and Gee, G.W. (1999). Flux-based estimation of field capacity. *J. Geotechnical Geoenvironmental Eng.* **125**(7): 595–599.
11. Warrick, A.W. and Nielsen, D.R. (1980). Spatial variability of soil physical properties in the field. In: *Applications of Soil Physics*. D. Hillel (Ed.). Academic Press, New York, Chap. 13.
12. Acutis, M. and Donatelli, M. (2003). *SOIL*PAR 2.00: software to estimate soil hydrological parameters and functions. *Eur. J. Agron.* **18**: 373–377.
13. Baumer, O.W. and Brasher, B.R. (1982). *Prediction of Water Content at Selection Suctions*. Am. Soc. Agric. Eng. Paper 82–2590.
14. Cassel, D.K., Ratliff, L.F., and Ritchie, J.T. (1983). Models for estimating in situ potential extractable water using soil physical and chemical properties. *Soil Sci. Soc. Am. J.* **47**: 764–769.
15. Ritchie, J.T., Gerakis, A., and Suleiman, A. (1999). Simple model to estimate field-measured soil water limits. *Trans. ASAE* **42**: 1609–1614.
16. Rawls, W.J., Gish, T.J., and Brakensiek, D.L. (1991). Estimating soil water retention from soil physical properties and characteristics. *Adv. Agron.* **16**: 213–234.

17. Gijsman, A.J., Jagtap, S.S., and Jones, J.W. (2002). Wading through a swamp of complete confusion: How to choose a method for estimating soil water retention parameters for crop models. *Eur. J. Agron.* **18**: 75–105.
18. Saxton, K.E., Rawls, W.J., Romberger, J.S., and Papendick, R.I. (1986). Estimating generalized soil-water characteristics from texture. *Soil Sci. Soc. Am. J.* **50**: 1031–1036.
19. Ittersum, M.K. et al. (2003). On approaches and applications of the Wageningen crop models. *Eur. J. Agron.* **18**: 201–234.
20. Descroix, L. et al. (2002). An experimental analysis of hydrodynamic behaviour on soils and hillslopes in a subtropical mountainous environment (Western Sierra Madre, Mexico). *J. Hydrol.* **266**: 1–14.
21. Devonec, E. and Barros, A.P. (2002). Exploring the transferability of a land-surface hydrology model. *J. Hydrol.* **265**: 258–282.
22. Nunez-Requeira, L. et al. (2002). The influence of some physicochemical parameters on the microbial growth in soils. *Thermochimica Acta* **394**: 123–131.
23. Dutt, G.R. and Tanji, K.K. (1962). Predicting concentrations of solutes in water percolated through a column of soil. *J. Geophys. Res.* **67**: 3437–3439.
24. Becher, H.H. (1998). Resistances to penetration of aggregates from loess-derived topsoils at different soil water tensions. *Soil Tillage Res.* **47**: 73–81.
25. Towner, G.D. and Childs, E.C. (1972). The mechanical strength of unsaturated porous granular material. *J. Soil Sci.* **23**: 481–498.
26. USDA. (1995). Available: http://topsoil.nserl.purdue.edu/nserlweb/weppmain/jhtml/appx1.html.
27. Baver, L.D., Gardner, W.H., and Gardner, W.R. (1972). *Soil Physics*, 4th Edn. John Wiley & Sons, New York.
28. Richards, L.A. (1960). Advances in Soil Physics. *Trans. Int. Cong. Soil Sci.* **7th Madison I**: 67–69.
29. Cassel, D.K. and Nielsen, D.R. (1986). Field capacity and available water capacity. In: *Methods of Soil Analysis*. Part 1, *Physical and Mineralogical Methods*. Agronomy Monograph #9, 2nd Edn. American Society of Agronomy, Madison, WI, Chap. 36.
30. Rickard, D.S. (1973). Plant and soil water: Information required in agronomic trials. In: *Soil Plant Water Symp. 1973*. Palmerston North, N.Z. New Zealand Dept. of Scientific and Industrial Research, Wellington, N.Z., pp. 107–112.

GROUNDWATER FLOW PROPERTIES

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Groundwater constitutes a large component of the freshwater cycle. It moves more or less continuously from areas of recharge to areas of discharge through interconnected void spaces in porous media, fractured media, and large passages. Groundwater flow results mainly from precipitation that infiltrates into the soil; it also originates from influent streams, seepage from reservoirs, artificial recharge, seepage from oceans, etc. It often augments streamflow, eventually moving through the soil to the stream channel, also referred to as baseflow, or dry-weather flow.

The driving force for groundwater movement is measured in terms of hydraulic head, which represents the fluid pressure potential and elevation potential. It is also referred to as the piezometric or potentiometric head. Contour maps of hydraulic head (piezometric or potentiometric maps), which can be constructed from water-table elevations, can be used to infer directions of groundwater flow.

The hydraulic and physical properties of a porous medium influence groundwater flow. They are porosity, hydraulic conductivity and permeability, specific storage, transmissivity and storage coefficient. A hydrologic unit (aquifer) is homogenous if its hydraulic properties are the same at every location. However, owing to the spatial and temporal variability in the geologic processes that create and modify rocks and sediments, no unit is truly homogenous.

HYDRAULIC CONDUCTIVITY

Hydraulic conductivity (K) is a measure of the ability of a fluid to move through interconnected void spaces in a sediment or rock. It is a function of both the medium and the fluid properties. A medium has a unit hydraulic conductivity if it transmits in unit time a unit volume of groundwater at the prevailing kinematic viscosity through a unit cross-sectional area, measured at right angle to the direction of flow, under a unit hydraulic gradient. The SI unit is

$$K = -\frac{q}{dh/dl} = -\frac{\text{m/day}}{\text{m/m}} = \text{m/day} \qquad (1)$$

Several factors affect hydraulic conductivity—those that pertain to the water-bearing material itself and those related to the groundwater as a fluid. The geometry of the pore spaces through which groundwater movement occurs, the grain size distribution, the surface roughness of the particles, and other secondary geologic processes such as faulting and folding, secondary deposition, and secondary solution in rock (such as limestone) are the major factors pertaining to the porous medium. The fluid characteristics that affect hydraulic conductivity are density, viscosity, and salinity. Temperature, by inversely affecting viscosity, has a direct influence on groundwater flow. The effect of salinity, on the other hand, is brought about by changes in the ionic concentrations of the groundwater and also due to the chemical effect of the saline water on the aquifer material. However, the effects of fluid characteristics on hydraulic conductivity tend to be rather less important than the effects of the aquifer characteristics.

PERMEABILITY

The term permeability (k), used synonymously with intrinsic permeability, of a porous medium defines its ability to transmit a fluid, which is a property only of the medium and is independent of fluid properties. Permeability (k) is defined as

$$K = \frac{k\rho g}{\mu} \qquad (2)$$

Table 1. Representative Values of Hydraulic Conductivity and Permeability[a]

Sediment or Rock Type	Hydraulic Conductivity (m/day)	Permeability (m^2)
Clays	10^{-7}–10^{-3}	10^{-19}–10^{-15}
Silts	10^{-4}–10^{0}	10^{-16}–10^{-12}
Fine to coarse sands	10^{-2}–10^{+3}	10^{-14}–10^{-9}
Gravels	10^{+2}–10^{+5}	10^{-10}–10^{-7}
Shales (matrix)	10^{-8}–10^{-4}	10^{-20}–10^{-16}
Shales (fractured and weathered)	10^{-4}–10^{0}	10^{-16}–10^{-12}
Sandstones (well-cemented)	10^{-5}–10^{-2}	10^{-17}–10^{-14}
Sandstones (friable)	10^{-3}–10^{0}	10^{-15}–10^{-12}
Salt	10^{-10}–10^{-8}	10^{-22}–10^{-20}
Anhydrite	10^{-7}–10^{-6}	10^{-19}–10^{-18}
Unfractured igneous and metamorphic rocks	10^{-9}–10^{-5}	10^{-21}–10^{-17}
Fractured igneous and metamorphic rocks	10^{-5}–10^{-1}	10^{-17}–10^{-13}

[a] Reference 1.

where K = hydraulic conductivity, k = permeability, ρ = fluid density, g = acceleration due to gravity, and μ = dynamic viscosity of the fluid. Table 1 presents representative values of hydraulic conductivity and permeability for a variety of sediment and rock types.

Owing to the spatial and temporal variability in the geologic processes that create and modify rocks and sediments, heterogeneity occurs in a range of spatial scales. In a porous multilayer medium, the variation in hydraulic conductivity among the depositional units can amount to five or six orders of magnitude. The groundwater analyst has to decide whether or not the homogeneity approximations are adequate, and if not, at what scale the heterogeneity should be specified. Some averaging rules can be applied to average a set of measurements to a single value of effective hydraulic conductivity (K_e) when using a homogenous medium approximation.

The effective hydraulic conductivity (K_e) depends upon the properties of the porous medium and the pattern of fluid flow. For steady-state flow, with a spatially uniform hydraulic gradient, the following averaging rules apply:

1. For a perfectly stratified medium, n layers of layer thickness d_i, and hydraulic conductivity K_i:
   (a) When flow is parallel to the layering, K_e is given by applying the arithmetic mean as

$$K_e = K_A = \sum_{i=1}^{n} \frac{d_i K_i}{\sum_{i=1}^{n} d_i} \tag{3}$$

   (b) When flow is perpendicular to the layering, K_e is given by applying the harmonic mean as

$$K_e = K_H = \sum_{i=1}^{n} \frac{d_i}{\sum_{i=1}^{n} \frac{d_i}{K_i}} \tag{4}$$

2. For a heterogeneous medium, nonstratified, and m measurements
   (a) For two-dimensional models, K_e is given by applying the geometric mean as

$$K_e = K_G = (K_1 K_2 \cdots\cdots K_m)^{1/m} \tag{5}$$

   (b) For three-dimensional models, K_e is given as,

$$K_e = (1 + \sigma^2{}_y/6) \tag{6}$$

where $\sigma^2{}_y$ is the variance of the natural logarithms of the hydraulic conductivity measurements.

TRANSMISSIVITY

Transmissivity (T) is defined as the amount of water that can be transmitted horizontally through a unit width by a fully saturated thickness of an aquifer under a unit hydraulic gradient. The transmissivity of an aquifer is equal to the hydraulic conductivity of the aquifer multiplied by the saturated thickness of the aquifer. Thus,

$$T = Kb \tag{7}$$

where T = transmissivity, K = hydraulic conductivity, and b = saturated thickness of the aquifer.

STORAGE COEFFICIENT

Specific storage (S_s) is defined as the volume of water that a unit volume of aquifer releases from storage under a unit decline in hydraulic head. Storage coefficient or storativity (S) is the product of specific storage (S_s) and aquifer thickness. It is defined as the volume of water that a permeable unit will absorb or expel from storage per unit surface area per unit change in head. It is a dimensionless quantity, and this property becomes important when an aquifer loses or gains water. Storativity is due to porosity in the aquifer and is different for confined and unconfined aquifers. For a unit decline in hydraulic head, the volume of water released from a confined aquifer is substantially less than that for an unconfined aquifer, indicating a comparative low value of the storage coefficient for a confined aquifer.

SPECIFIC YIELD (S_Y)

The storativity of an unconfined aquifer termed specific yield, is defined as the volume of water that an unconfined aquifer releases from storage per unit surface area of aquifer per unit decline in the water table, as shown in Fig. 1. Table 2 gives representative values of the specific yield for different aquifer materials.

STORATIVITY IN CONFINED AND UNCONFINED AQUIFERS

The storativity in unconfined aquifers is higher than that in confined aquifers. The higher values of storativity for unconfined aquifers (specific yield), as shown in Table 2, reflect the fact that releases from storage in unconfined aquifers represent an actual dewatering of the soil pores, whereas releases from storage in confined aquifers

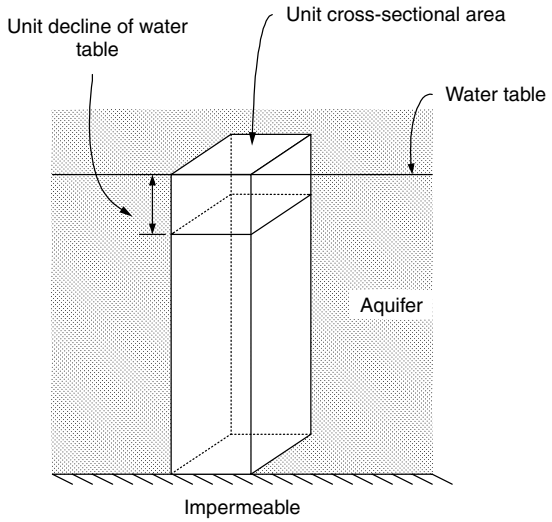


Figure 1. Schematic representation of storativity in unconfined aquifers.

Table 2. Representative Values of Specific Yield[a]

Material	Specific Yield, %
Clays	1–5
Silts	10–20
Fine sands	10–30
Sands and gravels	20–30
Sandstone	5–20
Shale	0.5–5
Limestone	0.5–20

[a] Reference 1.

represent only the secondary effects of water expansion and aquifer compaction brought about by changes in fluid pressure. In most confined aquifers, the storativity values fall in the range 0.00005 to 0.005 (2), indicating that large pressure changes over extensive areas are required to produce substantial water yields. Thus, the same yield can be realized with smaller head changes over less extensive areas in unconfined aquifers compared to confined aquifers, making them more efficient for exploitation by wells.

BIBLIOGRAPHY

1. Maidment, D.R. (1993). *Handbook of Hydrology*. McGraw-Hill, New York.
2. Todd, D.K. (1980). *Groundwater Hydrology*. John Wiley & Sons, New York.

FLUORIDE CONTAMINATION IN GROUND WATER

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Fluoride occurrence in ground water is a natural phenomenon, influenced by the local and regional geological setting and hydrogeological conditions of the region. Fluoride content much higher than the maximum permissible limit has been found in many regions throughout the world. The problem assumes more significance in India and other developing countries because a major portion of the population that lives in rural as well as urban areas have to depend on available groundwater resources for their day-to-day requirements. An estimated 62 million people in 17 out of 32 states are affected with dental, skeletal, and/or nonskeletal fluorosis in India. The extent of fluoride contamination varies from 1.0 to 48.0 mg/L.

INTRODUCTION

One of the serious health problems facing India today is the prevalence of a disease known as fluorosis. It involves millions of people and arises primarily due to an excess of fluoride in drinking waters. Fluorosis was first detected in India among cattle (bullocks used for ploughing land) by the farmers of Andhra Pradesh during early 1930s. The farmers noticed the inability of the bullocks to walk due to painful and stiff joints. During later years, the same disease was detected in human beings. Shortt et al. (1) published the first report on endemic fluorosis in India, when the disease was prevalent in four states, Andhra Pradesh, Tamil Nadu, Punjab, and Uttar Pradesh (2). During the period 1960–1986, nine more states have been identified as endemic for fluorosis. During 1990–1992, two more states, Kerala and Jammu and Kashmir have also been identified as endemic for the disease. As per the report published by Rajiv Gandhi National Drinking Water Mission (3), fourteen states and Delhi have been identified as endemic for fluorosis. Datta (4) has also reported fluoride contamination in the ground water of the National Capital Territory of Delhi. Recently, elevated levels of fluoride have been reported from the Birhum district of West Bengal and Karbi-Anglong and Nagaon districts of Assam (5–8). Thus, the total number of states endemic for fluorosis at present is seventeen: Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, and West Bengal.

Fluoride is essential for normal mineralization of bones and formation of dental enamel. About 96% of the fluoride in the body is found in bones and teeth. Calcium-rich constituents of teeth, enamel and dentine, have a strong affinity for fluoride during the formation of teeth. Fluoride combines with calcium to form calcium fluoroapatite crystals during the mineralization of teeth. The principal sources of fluoride for human physiology are water and food. At the same time, fluoride also has considerable physiological importance for humans and animals. If one is exposed to fluoride for long durations, it may pose serious health hazards. The major health problems caused by fluoride are dental caries, teeth mottling, skeletal fluorosis, and deformation of bones in children as well as in adults (9).

The Geological Survey of India has brought out considerable data that reveal that fluorite, topaz, apatite, rock phosphate, phosphatic nodules, and phosphorites are

wide-spread in India and contain high percentages of fluoride (10). As a result of rich mineral content, fluoride leaches out and contaminates water and soil, thereby contaminating agricultural crops as well. Several natural fluoride-bearing minerals identified in India include fluorides, fluorites, and cryolite; phosphates, fluorapatite, and wagnerite; silicates and topaz; and the mica group, magnesium mica and lithium mica.

The permissible limits for fluoride in drinking water have been defined by various agencies. In view of the health problems, the Bureau of Indian Standards, formerly known as Indian Standards Institution (ISI), has laid down the Indian standard of 1.0 mg/L as the desirable limit (11). The Indian Council of Medical Research (ICMR) has recommended a desirable level of 1.0 mg/L and the maximum permissible limit of 1.5 mg/L, which means that the body may tolerate fluoride up to the limit of 1.5 mg/L depending on the nutritional standards and body physiology. The World Health Organization (12) has recommended 0.5 mg/L as the maximum limit for fluoride.

In India, more than 76% of the population lives in rural areas. The problem of endemic fluorosis occurs with varying intensity in different parts of the country. An extensive survey of community water supplies has shown that around 25 million people in rural areas consume water whose fluoride content is more than the maximum permissible concentration of 1.5 mg F/L (13). According to a Sub-mission set up by the Government of India under a Technical Mission, about 25 million people are suffering from fluorosis at various stages, and another 25 million are reported to be prone to it (14,15). Jain et al. (16) have reviewed the status of fluoride contamination in groundwater and Susheela (7) reported the overall status of fluoride contamination and the suffering of the people in India. It is stated that an estimated 62 million people in 17 states out of 32 states are affected with dental, skeletal, and/or nonskeletal fluorosis.

Rajasthan is one of the states where fluorides at high levels in all 31 districts and the problem of dental and skeletal fluorosis is widespread (17). The studies carried out by the Rajasthan Voluntary Health Association (RVHA) noticed that the total number of problem villages that have high fluoride content in groundwater is 2702. About three million people are consuming water with excess fluoride, out of which one-fifth of the affected population are children below the age of 7 years, and about 35,000 people are consuming water that has more than 10 mg/L of fluoride.

As much as 90 mg/L of fluoride was found in groundwater in western Rajasthan (18). High fluoride content is attributed to the circulation of groundwater through fluorite-bearing granites and acid volcanics and basic dykes (that act as barriers and result in ample contact time for circulating water to dissolve fluorite). High fluoride content is always associated with a lower Ca/F ratio. It is an established fact that waters high in calcium are low in fluoride content, and therefore the low fluoride concentration in the eastern region can possibly be explained by the presence of high calcium in the water due to the movement of groundwater through carbonate rocks and a higher recharge from surface water to the Sukri River that possibly dilutes the fluoride content further.

The fluoride concentration in the Nagpur district of Maharashtra state varies from 0 to 44 mg/L (19). The fluoride content increases with an increase in salinity. High bicarbonate and sodium content were observed in groundwater rich in fluoride. High values of phosphorous were also observed in association with high fluoride content indicating its possible occurrence due to mineral weathering and local pollution.

Wodeyar and Sreenivasan (20) reported the occurrence of fluoride in the Bellary district in the state of Karnataka. Deeper aquifers have shown higher fluoride concentrations than shallow aquifers. A high degree of weathering and easy accessibility of circulating water to the weathered rocks due to intensive and long-term irrigation are responsible for leaching of fluoride from parent minerals in soil and rocks. Further concentration has been brought about by the arid climate of the region and the long residence time of groundwater in the aquifer. The influence of local lithology and soil, aided by other factors like very low freshwater exchange due to the arid climate of the region, is also responsible for higher concentrations of fluoride in groundwater.

Shukla et al. (21) studied the fluoride level in human teeth obtained from two different regions, Bhilai and Shillong in the state of Madhya Pradesh. They reported that the Bhilai region is fluoridated and have an average fluoride level of 1.3 ppm, whereas the Shillong region is nonfluoridated and has an average fluoride level of 0.02 ppm. The fluoride content of the teeth, it was found, increases with age, and therefore, the duration of exposure to fluoride has a significant effect on its accumulation in the dental structure. The biologically active age group of 10–30 years incorporates fluoride in teeth more rapidly compared to the passive age group of 50–70 years in both regions.

Apparao and Karthikeyan (22) reported a fluoride content of less than 1 mg/L in the drinking water of seven fluorosis-affected villages of the Nilakottai and Dindigul blocks in the state of Tamil Nadu. The poor socioeconomic groups of these villages are affected much by dental as well as skeletal fluorosis. The general nutritional status of their diet is poor, and specifically, the calcium and vitamin C intake are very low. It is surprising that people exposed to 0.51 mg/L F water are affected, and such reports are scanty in India. However, analysis of food grains grown in these areas indicated 4.0 to 4.6 mg/kg of fluoride which is a significant amount of the total fluoride intake and hence the prevalence of fluorosis in these areas. Other fluoride-affected districts include Vellore, Dharmapuri, Trichy, Karur, Salem, Namakkal, Erode, Coimbatore, and Virudhunagar (23–28). Agricultural practices and the depth to the groundwater table, it has been found, have an important impact on fluoride concentration.

Malhotra et al. (29,30) studied fluoride contamination in the groundwater of the Allahabad, Pratapgarh, Gonda, Ballia, Bareilly, and Fatehpur districts in the state of Uttar Pradesh and reported apparently high levels of fluoride. The maximum fluoride content of 6.5 mg/L was found in rural areas of Phulpur in the Allahabad district. The extent of fluoride increases in summer months,

apparently because of a drop in the water level. The evidence suggests that due to a gradual drop in the water level below the earth's crust a greater concentration of fluoride is found in the water because of greater dissolution of fluoride from rocks and soil.

Gupta et al. (31,32) and Shrivastav and Choudhary (33) reported fluoride contamination in the Agra district the highest concentration of 22 mg/L was in Bainkhera village. A significant positive correlation of fluoride with pH and negative correlation with hardness and magnesium was observed. Dental fluorosis was observed among school children in most of the villages, even where water had a fluoride concentration well within permissible limits. These observations clearly indicate the need for redefining the permissible levels of fluoride in drinking water and an exhaustive assessment of fluoride levels in foods.

Swamy (13) presented an interdisciplinary approach to understanding the problem of fluorosis against the background of present day development. Sudarshan and Reddy (2) described the pollution of fluoride in groundwater and its impact on the environment and on the socioeconomic status of the people. Mariappan et al. (28) described the occurrence and method of removing fluoride.

SOURCES OF FLUORIDE CONTAMINATION

Geological Sources

Fluoride occurrence in groundwater is a natural phenomenon, influenced by the local and regional geologic setting and hydrogeological conditions of the region. Fluoride occurs abundantly in the earth's crust as a component of rocks and minerals. The dissolution of fluoride from geologic formations occurs through the rainwater and repeated irrigation of agricultural lands. As rain water percolates through the soil, it comes in contact with the rocks and minerals in the aquifer materials. Due to the acid in the soil, dissolution of fluoride from the country rocks occurs.

The main sources of fluoride in natural water are fluorite (CaF_2), fluorapatite [$3Ca_3(PO_4)_2{-}CaF_2$], cryolite (Na_3AlF_6), magnesium fluoride (MgF_2), and as a replacement of, ions in the crystal lattice of mica and many other minerals (34,35). The other important fluoride-bearing minerals are biotite, muscovite, lepidolite, tourmaline, hornblende series minerals, glucophane riebeckite, asbestos (chrysolite, actinolite, anthophyllite), sphene, apophyllite, zinnwaldite, etc.

Dissolution of fluoride in groundwater itself may also contribute to the fluoride contamination phenomenon. The fluoride content in groundwater becomes higher in summer season due to a drop in the water level. The higher concentration of fluoride in the summer may be further attributed to the higher dissolution of fluoride, which may be due to the presence of air in the minerals/rocks cavities, which indicates that oxygen in the cavities of the geologic formation catalyzes the fluoride dissolution process. The evidence suggests that, as the ground water level gradually drops below the earth's crust, a greater concentration of fluoride is found in the water because of greater dissolution of fluoride from rocks and soil.

Industrial Sources

Industries are also a very important source of groundwater contamination. The effluents and other by-products of industries often constitute sources of groundwater pollution. Industries that release significant quantities of fluorides in process waste streams include fluorosilicone acid and fluorocarbon polymer synthesis, gasoline production; and manufacture's of coke, ceramic, cement, enamel, fiberglass, electronics, pesticides and fertilizers, surface heating operations, metal etching (with hydrofluoric acid), and wood preservatives (36).

Fluoride discharged from fertilizer manufacturing processes is typically in the form of silicon tetrafluoride, as a result of processing of phosphate rock. Power plant boiler cleaning wastes may contain fluoride due to its presence in the cleaning formulation. Both fluorspar and limestone are among the basic fluxing materials used in steelmaking. Air pollution control scrubbers water from steel manufacturing in basic oxygen, open hearth, and electric arc furnaces as well as in the sintering plant is the principal source of fluoride-containing wastewater from this industry. The primary aluminum processing industry uses the fluoride compound cryolite as a catalyst in bauxite ore reduction, The gaseous fluorides resulting from this process are discharged directly into the atmosphere or the fluorides into aqueous waste streams from wet scrubbing of the process fumes (37). Average fluoride values for aluminum reduction plants are reported as 107–145 ppm in wastewater streams. It has been observed that the number of echinocytes increases, depending on the duration of fluoride exposure among the workers in aluminum smelters (38). Fluoride concentrations ranging from 1,000–3,000 ppm have been reported for a glass manufacturing process. Glass and plating wastes typically contain fluoride in the form of hydrogen fluoride or fluoride ion, depending on the pH of the waste.

A high amount of fluoride has been reported in the groundwater in the vicinity of the aluminum industry (34,39). The main sources of fluoride in brick works are local clay and burning of coal. Malhotra et al. (30) have reported the fluoride content in groundwater in the vicinities of brickworks in Pratapgarh, Mirapur, Kechavpur, Mander, and Ahmedpur. Clarke et al. (40) have also reported fluoride contamination in groundwater due to by-products of brick kilns. Fluoride has also been detected in groundwater and air near Agra due to the 16 brick industries in the area (36).

Nonpoint Sources

Nonpoint sources of groundwater pollution also contribute fluoride to ground water to some extent. Modern agricultural practices that involve the application of fertilizers coupled with pesticides which contain about 1–3% fluoride also contribute fluoride to groundwater (41). The use of phosphatic fertilizers might also be one of the factors contributing to high fluoride concentration, which is being leached down to the groundwater by irrigation return flow (2,36). Irrigation with water containing small amounts of fluoride ion would tend to concentrate these

ions in the soil. If the calcium ions are removed as calcite, fluoride ions will either be absorbed or coprecipitated with calcite. If the carbonate concentration is high enough to precipitate calcium as calcite without concomitant removal of fluoride ions, these ions may move down to the water front and ultimately join the main groundwater body (42). The U.S. Environmental Protection Agency (43) has recommended 1 mg/L of fluoride in irrigation water for continuous use but up to 15 mg/L of fluoride for short term use (20 years) on fine soils.

The production of fly ash is another important nonpoint source of fluoride contamination. More than 150 million tonnes of fly ash one produced annually worldwide from the combustion of coal in power plants (44). At least half of this amount is disposed of by landfill, thus contributing to environmental pollution due to leaching of fluoride. In addition to this, smoke particles from the aluminum industry, brickworks, and volcanoes also contain traces of fluroride (37,39,40). Fluoride in the atmosphere has been detected near Agra, India, due to the presence of about 16 brickworks in this area (36). A possibility of groundwater contamination may exist due to traces of fluoride in the atmosphere during the rainy season. The Geological Survey of India has also brought out considerable data which reveal that fluorite, topaz, apatite, rock phosphates, phosphatic nodules and phosphorites are widespread in India and contain high percentages of fluoride. As a result of their rich mineral content, fluoride leaches out and contaminates not only the groundwater but the soil as well, thereby contaminating agricultural crops also.

Other Miscellaneous Sources

Besides water, fluoride is also found in agricultural crops and other edible items. It is well recognized that fluoride enters the human body through various foods, though the data available in India are rather scanty. The information that is available is based on the analysis of food or agricultural crops in certain regions. Thus, data, from a specific location may not be applicable to other regions due to the varying concentration of fluoride in water and soil. Chary et al. (45) and Lakdawala and Punekar (46) reported the fluoride content in some commonly used foods in the Prakasam district and Bombay (India). Nanda and Kapoor (47) found the fluoride content in pine and betel. Sengupta and Pal (48) also reported the fluoride contents of different foodstuffs. Gradien (49) reported that fluoride content generally decreased in the order: tea> cereals> vegetables> pulses> fish> meat> fruits.

In addition to foodstuffs, fluoride has also been reported in cosmetics and drugs. The use of drugs containing sodium fluoride for osteoporosis, otosteosclerosis, and dental caries is very common. Different brands of toothpaste contain excessive amounts of fluoride. Fluoride enters into the circulation directly from the oral cavity through the fine blood vessels of the mouth. Fluoride is a persistent bioaccumulator; even small amounts that enter through fluoride toothpaste one guaranteed entry in children as well as adults, and the cumulative effects of fluoride are a matter of serious concern.

CONTROLLING FACTORS AND MECHANISM

Controlling Factors

Fluoride contamination in ground water is controlled by a number of parameters. The most important are

- distribution of easily weathered fluoride-bearing minerals
- the accessibility of circulating water to these minerals
- pH of the percolating water
- calcium content of the leaching water
- temperature of the percolating water and the soil
- exchangeable ions in the percolating water
- extent of fresh water exchange in an aquifer
- evaporation and evapotranspiration
- complexing of fluoride ions with other ions
- presence of CO_2 and other chemicals in draining water
- residence time of the percolating water in soil

The pH of circulating water is an important factor that controls leaching of fluoride from fluoride-bearing minerals. Wodeyar and Sreenivasan (20) have indicated that higher alkalinity of waters promotes leaching of fluoride and thus affects the concentration of fluoride in groundwater. Alkaline water dissolves fluoride-bearing minerals under simultaneous precipitation of calcium carbonate (50). It has been reported that the degree of weathering and easy accessibility of circulating waters from weathered rocks, due to intensive and long term irrigation, are responsible for leaching fluoride from the parent minerals in soil and rocks. A high content of fluoride has been reported in black cotton soil due to excessive canal irrigation (20). Further, concentration of fluoride has been brought about by the arid climate of the region and the long residence time of groundwater in the aquifer (20,50). Very low fresh water exchange due to the arid climate of the region is also responsible for higher concentration of fluoride in groundwater (20).

The fluoride concentration in groundwater, it was found, is positively correlated with calcium content but with a very low degree of validity (14,15). This observation is similar to that reported by Somani et al. (51), but there is no agreement to that report by Gupta et al. (31,32). This departure from the normal trend may be due to an irregular distribution of fluoride-bearing minerals in the soil, their solubilization characteristics, the nature of the product with soil, and other environmental conditions (51). Generally, waters of high calcium contents are low in fluoride content (52). The presence of carbon dioxide also affects the fluoride dissolution process in rocks.

Fluoride in soil and ground water is also concentrated by evaporation and evapotranspiration due to arid and semiarid atmospheric conditions following scanty rainfall. The overwithdrawal of groundwater may also have favorable effects on fluoride concentration in groundwater. The combined effect of evapotranspiration and long-term contact of the water in the aquifer (due to low hydraulic conductivity of the weathered zone) activates the process

of dissolution (50). Ion exchange of the different elements in the soil and circulating water during the weathering process help in dissolving of fluoride from rocks and minerals (17,50). Besides, the formation of ion pairs such as $CaSO_4$, $CaHCO_3$ and complexing of fluoride with aluminium, beryllium, ferric ions, and series of mixed fluoride hydroxide complexes with boron affect fluoride contamination (35). The temperature also plays a crucial role in the fluoride content of groundwater because the amount of fluoride ingested by living beings is influenced primarily by air temperature (20). Besides, the dissolution of fluoride from minerals/rocks is a physicochemical process that is also controlled by the temperature of the water and the soil itself. Chand (36) presented a correlation of ambient temperature with fluoride content.

Mechanism

During the process of chemical weathering, dissolution of fluoride species in natural water is controlled by calcium ions and governed by thermodynamic principles. The $CaCO_3$ equilibrium in groundwater plays an important role in this process. The equilibrium constant of calcite can be evaluated from the following reactions (53).

$$CaCO_3 + H^- \Longleftrightarrow Ca^{2+} + HCO_3^-$$

$$K_{CaCO3} = [Ca^{2+}][HCO_3^-]/[H^+] = 97 \text{at } 25\,^\circ\text{C} \qquad (1)$$

($CaCO_3$ is constant)

The fluoride equilibrium is given by (54):

$$CaF_2 \Longleftrightarrow Ca^{2+} + 2F^-$$

$$K_{CaF2} = [Ca^{2+}][F^-]^2 = 10^{-10.58} \text{ at } 25\,^\circ\text{C} \qquad (2)$$

(CaF is constant)

Dividing the first equation by the second, the solubility of calcite and fluorite can be represented by a third constant K:

$$K = \frac{[HCO_3^-]}{[H^+][F^-]^2}$$

$$\text{or} \quad [F^-]^2 = K' \frac{[HCO_3^-]}{[H^+]} \text{ (where } K' = 1/K)$$

$$\text{or} \quad [F^-] \propto [HCO_3^-]/[H^-]$$

It is evident that the activity of fluoride is directly proportional to the bicarbonate ion at constant pH. Thus, according to the principle of ionic product, if the concentration of calcium and fluoride in water exceeds the solubility product of fluorite ($10^{-10.58}$ at 25 °C), CaF_2 precipitates. Before reaching saturation the calcium ion has a positive correlation with fluoride ion, and after this stage, there will be a negative correlation between calcium and fluoride ions. In fact, the total concentration of fluoride in a solution will be somewhat greater due to the presence of other electrolytes (ionic strength and complexing effects). But it appears that a high fluoride concentration is more likely to occur in water of low calcium concentration. Handa (55), Das (56), and Gupta et al. (57) summed up the characteristics of ground water whose fluoride content is from dissolved minerals, as follows:

- negative correlation of calcium and fluoride ions
- positive correlation of bicarbonate and fluoride ions
- close of saturation with respect to calcium fluoride
- saturated with calcium carbonate

Thus, the dissolution mechanism of fluoride from its minerals and rocks can be explained on the basis of the solubility product. The dissolution mechanism is physicochemical and, therefore, is governed by thermodynamic parameters, too. The important parameters are temperature, pH, ionic strength, and pressure.

REMEDIAL MEASURES

There are two types of remedial measures to control fluoride contamination. The first is to control fluoride contamination in groundwater, and the second includes removal of fluoride from fluoride-containing water. The control of fluoride contamination in groundwater is very difficult because the contamination of fluoride in groundwater is controlled by a number of hydrogeologic and physicochemical parameters. However, various artificial recharge techniques, including the aquifer storage recovery (ASR) technique may be applied to improve the quality of water by dilution.

The ASR technique is being followed in many parts of the world. In this technique, water is stored underground in wells when it is available, and this water is recovered from the same wells when needed to meet peak, long-term, and emergency water needs. The technique is being applied in United States, Canada, England, Australia, Israel, and other countries. The technique has proved to be a viable, cost-effective option for storing large volumes of fresh water not only in fresh, but also in brackish and other nonpotable aquifers at depths as low as 900 m. Most ASR sites store drinking water in confined aquifers containing water that is brackish or contains constituents such as nitrates, fluorides, iron, manganese, and hydrogen sulfide, all unsuitable for drinking purposes except following treatment. Mixing between the drinking water and the native water in the aquifer can be controlled in most situations by the proper design and operation of ASR wells, so that recovered water has acceptable quality. The operation includes development of a buffer zone surrounding the ASR well to contain the stored water and development of a target storage volume for each well so that recovered water will meet flow, volume, and water quality criteria with acceptability. This technique, however, still remains to be tried in India.

Excess withdrawal of groundwater should be avoided to the extent possible. Aquifers should be recharged periodically so that air cannot enter the aquifer. In addition, only those types of raw materials should be used in industries, which do not release fluoride into the environment. In addition to this, contamination through nonpoint sources should also be minimized by checking

man-made activities and the use of fluoride-containing fertilizers and pesticides.

The second type of remedial measure includes removal of fluoride from fluoride-containing water (28,58). There are several methods that have been advocated for defluoridation of drinking water. These methods can be broadly divided into two categories, those based upon the addition of some chemical to the water during the softening or coagulation processes and those based upon ion exchange or adsorption processes. Adsorption or ion exchange processes are recommended for treating low concentrations. These processes are performed by using lime and alum, bone char and synthetic bone, activated carbon and bauxite, ion exchange, activated alumina, and reverse osmosis.

CONCLUSION

The problem of high fluoride concentration in groundwater resources has now become one of the most important health-related geoenvironmental issues in India influenced by the regional and local geological and hydrological conditions of the region. It is high time that an affordable solution is found to minimize fluoride contamination to maintain the health of the large population of the country. There is an immediate need to defluoride the water system either by community or by domestic defluoridation techniques. Demonstration-cum-awareness camps for the purpose should be arranged in fluorosis endemic areas. There is a need to carry out detailed fluoride mapping, hydrological studies for existing water sources to show flow lines, and hydrogeochemical surveys where fluorosis is endemic. In the affected areas, the government should apply firm guidelines for using groundwater, so that tube wells and/or hand pumps in high fluoride zones can be discouraged. Short-term solutions to minimize the fluoride level in drinking water could be using domestic defluoridation equipment or filters.

BIBLIOGRAPHY

1. Shortt, H.E. (1937). Endemic fluorosis in the Madras presidency. *Ind. J. Med. Res.* **25**: 553–561.
2. Sudarshan, V. and Reddy, B.R. (1991). Pollution of fluoride in groundwater and its impact on environment and socio-economic status of the people—a case study in Sivannagudem area. *Indian J. Environ. Prot.* **11**(3): 185–192.
3. *Rajiv Gandhi National Drinking Water Mission*. (1994). New Delhi, Vol. 1, p. 20
4. Datta, P.S. (1996). Fluoride in ground water in Delhi area. *J. Contam. Hydrol.* **24**(1): 85–96.
5. Sengupta, A. (1999). *Proc. Workshop on Ground Water Pollution and Protection with Special Reference to Arsenic Contamination*. Central Ground Water Board, Science City, Calcutta, pp. 69–74.
6. Chakraborti, D. and Bhatta, A. (1999). *The Statesman*. 22 August 1999, pp. 8–9.
7. Susheela, A.K. (1999). Fluorosis management programme in India. *Curr. Sci.* **77**(10): 1250–1256.
8. Chakraborti, D. et al. (2000). Fluorosis in Assam, India. *Current Science* **78**(12): 1421–1423.
9. Susheela, A.K., Kumar, A., Bhatnagar, M., and Bahadur, R. (1993). Prevalence of endemic fluorosis with gastro-intestinal manifestation in people living in some north Indian village. *Fluoride* **26**(2): 94–104.
10. Vasavada, B.J. (1998). Excessive fluoride in Gujarat—a perspective plan of solution. *J. Indian Water Works Assoc.* **30**(3): 191–198.
11. BIS. (1991). Drinking Water—Specifications. Bureau of Indian Standards, New Delhi.
12. WHO. (1996). Guidelines for Drinking Water Quality, Vol. 2. World Health Organization, Geneva.
13. Swamy, N.K. (1990). Control of fluorosis—An interdisciplinary approach. *Indian J. Environ. Prot.* **10**(3): 181–185.
14. Garg, V.K., Dahiya, S., Chaudhary, A., and Shikha, D. (1998). Fluoride distribution in under ground water of Jind district, Haryana, India. *Ecol. Env. & Cons.* **4**(1–2): 19–23.
15. Garg, V.K., Sharma, I.S., and Bishnoi, M.S. (1998). Fluoride in ground water of Ulkana town, district Hisar. Haryana. *Poll. Res.* **17**(2): 149–152.
16. Jain, C.K., Ali, I., and Sharma, M.K. (1999). Fluoride contamination in ground water—Indian scenario. *Indian J. Environ. Prot.* **19**(4): 260–266.
17. Agrawal, V., Vaish, A.K., and Vaish, P. (1997). Groundwater quality: Focus on fluoride and fluorosis in Rajasthan. *Curr. Sci.* **73**(9): 743–746.
18. Gupta, S.C. and Vijeya, R.P. (1988). Some inherent problems of groundwater quality in western Rajasthan. *Trans. Isdt.* 97–103.
19. Gupta, S.C. (1991). Chemical characteristics of ground waters in Nagpur district, Rajasthan. *Indian J. Environ. Hlth.* **33**(3): 341–349.
20. Wodeyar, B.K. and Sreenivasan, G. (1996). Occurrence of fluoride in the ground water and its impact in Peddavankahalla basin, Bellary district, Karnataka—a preliminary study. *Curr. Sci.* **70**(1): 71–73.
21. Shukla, N., Moitra, J.K., and Trivedi, R.C. (1995). Fluoride level in exfoliated human teeth from 2 contrast environmental regions in India. *Indian J. Environ. Prot.* **15**(12): 903–905.
22. Apparao, B.V. and Karthikeyan, G. (1986). Permissible limits of fluoride in drinking water in Indian rural environment. *Indian J. Environ. Prot.* **6**(3): 172–175.
23. Mariappan, P., Vasudeven, T., and Yegnaraman, V. (1998). Surveillance of ground water in Thiruppathur block of Sivagangai district. *Indian J. Environ. Prot.* **19**(4): 250–254.
24. Mariappan, P., Vasudeven, T., and Yegnaraman, V. (1999). Fluoride distribution in ground waters of Salem district. *Indian J. Environ. Prot.* **19**(9): 681–683.
25. Mariappan, P., Yegnaraman, V., and Vasudeven, T. (1999). Correlation between fluoride and alkalinity in ground waters of fluorosis endemic—Salem district. *Indian J. Environ. Prot.* **20**(3): 182–187.
26. Mariappan, P., Yegnaraman, V., and Vasudeven, T. (1999). Control of fluoride content in the ground water—Scope for an interdisciplinary approach. *Poll. Res.* **20**(6): 421–426.
27. Mariappan, P., Yegnaraman, V., and Vasudeven, T. (2000). Correlation between water table and fluoride content in the ground waters of Salem district, Tamil Nadu. *Poll. Res.* **20**(3): 182–187.
28. Mariappan, P., Yegnaraman, V., and Vasudeven, T. (2000). Occurrence and removal of fluoride in ground water. *Poll. Res.* **19**(2): 165–177.
29. Malhotra, S.K., Verma, M., Verma, A.N., and Kulshreshtha, K. (1997). Fluoride and fluorosis in India—3. Osteo-dental fluorosis in school going children in Allahabad city (U.P.). *Chemistry & Biology of Herbal Medicine*: 203–210.
30. Malhotra, S.K., Verma, A.N., and Kulshreshtha, K. (1998). Fluoride and fluorosis in India—I. Drinking water source contamination in Utter Pradesh. *Poll. Res.* **17**(4): 311–315.

31. Gupta, M.K., Singh, V., Rajwanshi, P., Srivastava, S., and Dass, S. (1994). Ground water fluoride levels in a rural area of district Agra. *Indian J. Environ. Prot.* **14**(5): 370–372.
32. Gupta, M.K., Singh, V., Rajwanshi, P., Srivastava, S., and Dass, S. (1994). Fluoride in ground water at Agra. *Indian J. Environ. Hlth.* **36**(1): 43–46.
33. Shrivastav, R. and Choudhary, B. (1997). Drinking water quality in an average Indian city: A case study of Agra (U.P.). *Poll. Res.* **16**(1): 63–65.
34. Das, S., Mehta, B.C., Das, P.K., Srivastava, S.K., and Samanta, S.K. (1998). Source of high fluoride in ground water around Angul, Dhenkenal district, Orissa. *Poll. Res.* **17**(4): 385–392.
35. Das, S., Mehta, B.C., Das, P.K., Srivastava, S.K., and Samanta, S.K. (1999). Sources of high fluoride in ground water around Angul, Dhenkenal district, Orissa. *Poll. Res.* **18**(1): 21–28.
36. Chand, D. (1999). Fluoride and human health—cause for concern. *Indian J. Environ. Prot.* **19**(2): 81–89.
37. Samal, U.N. (1988). Dental fluorosis in school children in the vicinity of aluminium factory in India. *Fluoride* **21**(3): 137–141.
38. Susheela, A.K. (1991). *Prevention and Control of Fluorosis. Technical Information for Training cum Awareness Camp for Doctors, Public Health Engineers and other Officers*. Published by National Technology Mission of Drinking Water, New Delhi.
39. Sun, Z., Cheng, Y., Zhou, J., and Wei, R. (1998). Research on the effect of fluoride pollution in atmosphere near an aluminium electrolysis plant on regional fall wheat growth. *Proc. Annu. Meet., Air Waste Manag.*, Assoc. 91st TPE 09/P1-TPE 09P/7.
40. Clarke, M.L., Harvey, D.G., and Humphrevs, D.J. (1981). *Veterinary Toxicology*, 2nd Edn. Bailliere Tindal & Cassle Ltd., London, pp. 48–54.
41. Suresh, T. (1996). Fluoride in ground water of Chiknaya Kanahalli Taluk, Tumkur district, Karnataka. *Proc. Workshop on Challenges in Groundwater Development*, Madras, pp. 185–187.
42. Handa, B.K. (1979). Effect of return irrigation flows from irrigated land on the chemical composition of ground water from shallow unconfined aquifers. *Prog. Water Tech.* **11**: 337–349.
43. EPA Report. (1976). *National Interim Primary Drinking Water Regulation*. EPA Publication No. EPA-570/9-76-003.
44. Piekos, R. and Paslawska, S. (1998). Leaching characteristics of fluoride from coal fly ash. *Fluoride* **31**(4): 188–192.
45. Chary, V., Rao, R.J., and Naidu, M.G.C. (1975). Fluoride content of some raw vegetable foods available at Podile, Prakasam district, Andhra Pradesh. *Proc. Symp. Fluorosis*, Hyderabad, India, pp. 144–150.
46. Lakdawala, D.R. and Punekar, B.D. (1973). Fluoride content of water and commonly consumed foods in Bombay and supply of dietary intake. *Ind. J. Med. Res.* **16**: 1679–1687.
47. Nanda, R.S. and Kapoor, K (1971). Fluoride content of pine and betel and its constituents. *Ind. J. Med. Res.* **59**: 1966–1968.
48. Sengupta, S.R. and Pal, B. (1971). Iodine and fluoride contents of foodstuffs. *Ind. J. Nutr. Dicter.* **8**: 66–71.
49. Gradien, P. (1992). Cancer incident and mortality in workers exposed to fluoride. *J. Mat. Cancer Inst.* **184**: 1903–1909.
50. Rao, N.S., Rao, J.P., Rao, B.N., Babu, P.N., Reddy, P.M., and Devadas, D.J. (1998). A preliminary report on fluoride content in ground water of Guntur area, Andhra Pradesh, India. *Curr. Sci.* **75**(9): 887–888.
51. Somani, I.C., Gandhi, A.P., and Palwal, K.V. (1972). Note on toxicity of fluorine in well waters of Nagpur and Jaipur districts of Western Rajasthan. *Ind. J. Agric. Sci.* **48**(2): 752–754.
52. Maithani, P.B., Gurjar, R., Banerjee, R., Balaji, K.B., Ramachandran, S., and Singh, R. (1998). Anomalous fluoride in ground water from western part of Sirohi district, Rajasthan and its crippling effects on human health. *Curr. Sci.* **74**(9): 773–776.
53. Hem, J.D. (1970). *Study and Interpretation of the Chemical Characteristics of Natural Waters*. USGS Water Supply, Paper 1475, pp. 363–369.
54. Brown, D.W. and Roberson, C.E. (1977). Solubility of natural fluorite at 25 °C. *USGS J. Res.* **5**(4): 506–517.
55. Handa, B.K. (1975). Geochemistry and genesis of fluoride containing ground water in India. *Ground Water* **13**(3): 275–281.
56. Das, D.K. (1985). Incident of high fluoride in deep ground water in Betwa basin, Madhya Pradesh, Central India. *G.S.I. Res.* **116**(2): 23–30.
57. Gupta, S.C., Doshi, C.S., and Paliwal, B.L. (1986). Occurrence and chemistry of high fluoride ground water in Jalore district of Western Rajasthan. *Annal of Arid Zone* **25**(4): 255–265.
58. Jain, A.K. (1997). *Akalanka's Water Supply and Treatment: Central Public Health and Environmental Engineering Organizations: Manual on Water Supply and Treatment*. Akalank Publications, New Delhi, India, pp. 203–208.

ROCK FRACTURE

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INTRODUCTION

From their origin, rocks are more or less disturbed by forces acting within the lithosphere. When a mass of rock is not strong enough to resist forces that are tending either to compress it or to stretch it, the rock is deformed. The change of form is brought about by flow in the deeper parts of the lithosphere and fractures in the upper parts (1). Fractures in rocks are either joints or faults.

JOINTS

The term joint is most commonly used in reference to relatively continuous and through-going fractures that are reasonably planar and along which there has been imperceptible movement. Joints may form as a result of either diastrophism or contraction.

Classification of Joints

Theoretically, joints may be classified according to whether they have been formed by compression or tension. Joints due to compression are (1) diagonal joints, (2) irregular cracks induced by the expansion of rocks consequent upon chemical alteration, and (3) probably a majority of the regular joint system in stratified rocks. Tension joints include (1) irregular cracks formed in the shrinkage accompanying certain kinds of rock alteration; (2) cross-joints in igneous rocks; (3) hexagonal columnar structures and associated fractures due to cooling; (4) small local

fractures; (5) fractures clearly associated with tension faulting; and (6) cracks due to drying of muds, clays, and argillaceous limestones.

Description of Joints

1. A series of parallel joints is called a "joint set."
2. Two or more joints intersecting each other produce a "joint system."
3. A persistent joint or set that may be horizontal or vertical is called a "master joint."

Probably all consolidated rocks and a good share of unconsolidated deposits contain joints. Although not well recognized by most individuals involved in groundwater problems, joints exert a major control on water movement and chemical quantity. Characteristically, joints are open and serve as major conduits or pipes. Water can move through them quickly, perhaps carrying contaminants, and, being open, the filtration effect is lost. It is a good possibility that the outbreak of many waterborne diseases that can be traced to groundwater supplies result from the transmission of infectious agents through fractures to wells and springs.

Most joints, at least initially, are tight fractures, but because of weathering, the joint may be enlarged into an open fissure; this is especially common in limestone regions.

Effect of Joints

Knowledge of joints is important in many kinds of geologic studies. Quarry operations, especially those involved in obtaining blocks of certain dimensions and sizes, are obviously greatly influenced by joints. Closely spaced horizontal joints are obviously of great concern in tunneling. A large joint dipping into a highway cut is the site of a potential landslide. Wells drilled in granites for water supply are more productive in highly jointed rocks than in less jointed rocks (2).

If joints are too numerous (i.e., more sets), closely spaced, and of great magnitude, then such a fractured site will be physically too weak to withstand the stresses of dams and bridges. Saturation with water along with the accompanying decay of rocks will make the site more unsuitable for foundations.

Value of Joints

Although joints are often difficult to interpret, they are nonetheless very important structures. For ages, quarry workers have taken advantage of joint-controlled planes of weakness in removing building blocks of granite and limestones from bedrock. These fracture weaknesses exert profound control on weathering and erosion and, thus, on fashioning landscape. Many scenic attractions owe much of their uniqueness to weathering and erosion of horizontal layers of systematically broken up, steeply dipping joints.

Beyond their scenic value, joints constitute structures, of indisputable geologic and economic significance. Joints invite circulation of fluids, including rain and groundwater, hydrothermal mineralizing solutions, and oil and gas. As cracks in rocks, joints can be thought of as structures that significantly contribute to the bulk porosity and permeability of rocks.

Explorers appreciate the benefits of the circulation of fluids through jointed rocks. Petroleum geologists evaluate the nature and degree of development of joints as one guide to the reservoir quality of sedimentary formations. To increase the yield of reservoir rocks in oil and gas fields where production is waning, it is common practice to "crack" the rocks artificially, either by explosives or by high-pressure pumping of fluids into wells.

Joints can serve as sites of deposition of metallic and nonmetallic minerals. In almost all hydrothermal deposits, a part of the mineralization is localized in and around joints. The minerals are deposited either through open-space filling of joints or through selective replacement of chemically favorable rocks adjacent to the joint surfaces along which hydrothermal fluids once circulated.

FAULTS

A fault may be defined as a fracture along which there has been slipping of contiguous masses against one another. Points formerly in contact have been dislocated or displaced along the fracture. Solid rocks or unconsolidated sands, gravel, etc. may be dislocated in this way. Faulting may result from compression, tension, or torsion. Some faults in loose or weakly consolidated clays, sands, and gravels are produced by the removal of a support.

Faults are most common in the deformed rocks of mountain ranges, suggesting either lengthening or shortening of the crust. Movement along a fault may be horizontal, vertical, or a combination. The most common types of faults are called normal, reverse, and lateral (Fig.1). A normal fault, which indicates stretching of the crust, is one in which the upper or hanging wall has moved down relative to the lower or foot wall. The Red Sea, Dead Sea, and the large lake basins in the East African highlands, among many others, lie in a graben, which is a block bounded by normal faults. A reverse or thrust fault implies compression and shortening of the crust. It is distinguished by the fact that the hanging wall has moved up relative to the foot wall. A lateral fault is one in which the movement has been largely horizontal. The San Andreas Fault, extending some 600 miles from San Francisco Bay to the Gulf of California, is the most notable lateral fault in the United States. Movement along this fault produced the 1906 San Francisco earthquakes.

Recognition of Faults in the Field

To recognize faults in the field, a number of criteria are used. The faults may be directly seen in the field, particularly in artificial exposures such as river cuttings and road cuttings. In most of cases, faults are recognized by stratigraphic and physiographic evidence such as (2)

1. repetition or omission of strata,
2. discontinuity of structures,
3. features characteristic of fault planes,
4. silicification and mineralization,

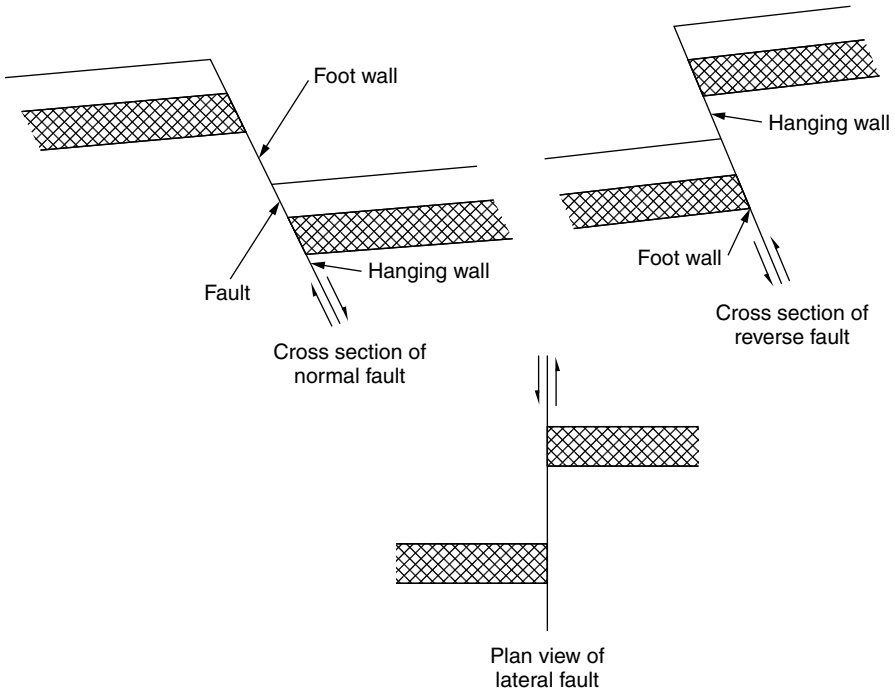


Figure 1. Cross sections of normal, reverse, and lateral faults.

5. sudden changes in sedimentary facies, and
6. physiographic data.

Effects of Faulting

Faulted areas are neither safe nor stable for the foundation of civil engineering works because of the various harmful effects produced by faults. Some important effects of faulting follow (3):

1. Faults cause considerable fracturing and shattering of rocks along fault zones, which means that they are not compact, massive, or strong. Such places are reduced to physically very weak grounds and hence are unfit as foundation sites to withstand heavy loads of structures such as dams.
2. When such porous and fractured zones are saturated with water, their strength is reduced further.
3. The same fractures act as channels for movement of groundwater, which may cause severe groundwater problems in tunnels and leakage problems in reservoirs.
4. The most dangerous features of faulting are its possible recurrence at the same place, which means that the faulted ground is unstable as long as faulting remains active there. Vertical, lateral, or rotational movements are likely to take place at the time of renewed faulting. Naturally, under such conditions, any civil engineering structure cannot have a safe or stable foundation. And if constructions are made, they are likely to collapse when renewed ground movements occur.
5. The fault plane itself is a very prominent fracture plane in the fault zone and therefore may act as a severe source of water leakage. When such percolated water reaches underground, it decomposes the shear zone or fault zones. Such weathering further reduces the competence of rocks.

BIBLIOGRAPHY

1. Lahee, F.H. (1987). *Field Geology*. CBS, New Delhi, p. 222.
2. Billings, M.P. (1984). *Structural Geology*. Prentice-Hall of India, New Delhi, pp. 140–200.
3. Kesavulu, N.C. (1997). *Textbook of Engineering Geology*. Macmillan India, New Delhi, pp. 241–242.

GEOCHEMICAL MODELS

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INTRODUCTION

A geochemical model, like any other model, is an abstract representation of a given reality, normally reduced to a set of master variables and described by mathematical equations, which aim at representing natural processes that occur in a system. The output data of these models are a quantitative representation of an outcome that can be observable in the natural system or subject to experimental validation. This operational definition of a geochemical model suggests that a model is nothing more than a set of mathematical equations, which is not strictly true. Any set of equations representing a process must be bounded within limits imposed by nature; otherwise the outcome of these models may be totally unrealistic. Thus, the modeler is called to

set proper initial and boundary conditions such that the natural system is correctly represented, and to feed the model with the correct parameters, most of them previously determined experimentally. The quality and self-consistency of the thermodynamic data used, as well as other parameters, such as kinetic ones, are of fundamental importance for the outcome of geochemical models. This issue is considered one of the most critical in any geochemical model. When using any of the available computer programs for geochemical modeling, the choice of the thermodynamic database is left to the modeler. Several compiled thermodynamic databases are available, but this does not mean that all data is internally self-consistent. It is, however, possible to find some databases that are self-consistent relative to some set of chemical species.

Geochemical models have been extensively reviewed in the literature, such as Yeh and Tripathi (1), Mangold and Tsang (2), Appelo and Postma (3), Nordstrom and Munoz (4), and Nordstrom (5). Some textbooks on aqueous geochemistry or geochemical modeling also discuss and include several examples and case studies where specific geochemical computer models have been used (6–8). Of relevance is also the book of Albarède (9), which provides a wealth of mathematical methods and extensive examples on how to build and develop geochemical models in a truly wide range of applications.

COMPONENTS OF GEOCHEMICAL MODELS

Geochemical models may have several components that can be combined in different configurations. These components may be coupled within the model or may imply certain feedback loops.

An essential component of these models is chemical reactions, and these determine, for example, the chemical speciation in solution or the saturation states relative to solid phases. Within these reactions, biological processes may be involved, which take active part in certain reactions, boosting their kinetics (catalysts), hindering the formation of certain compounds (inhibitors), or just transforming chemical compounds (such as the biodegradation of organic pollutants).

Chemical species and compounds in solution are carried away with the water by advection and disperse through the medium by molecular diffusion. These are the components of transport of chemical elements in solution, which determine their spreading in the system.

Transport of chemical elements are thus a function of water velocity and, consequently, of fluid flow in the system. Physical parameters of the system, such as porosity and permeability, determine the patterns of fluid flow and velocity variations in space and time. In the coupled reactive transport models, precipitation/dissolution of mineral phases can reduce/increase the porosity and permeability of the medium and change fluid flow patterns.

In certain systems, such as large-scale sedimentary basins, it is necessary to consider heat transport. Heat can increase the kinetics of several chemical reactions and induce fluid flow along thermal gradients.

TYPES OF GEOCHEMICAL MODELS

The description of the different types of geochemical models is not extensive and outlines only their main characteristics, as presented by Zhu and Anderson (8). Geochemical models are generally grouped according to their level of complexity. The simplest ones are the speciation-solubility models. These models are meant to compute the thermodynamic equilibrium of species in a system at a given temperature and pressure. Therefore, the output comprises the concentration and activity of the various ionic and molecular species in a solution. It also includes the saturation state of the solution relative to several minerals and the distribution of stable species on surfaces or ion-exchange sites in equilibrium with the aqueous solution.

Reaction-path models calculate the sequence of equilibrium states of a system in response to incremental additions (or subtractions) of mass to the system, change in temperature and/or pressure, and mass transfer between phases in the system. The configuration of these models can be diverse and includes the addition of a reactant (such as a titration), fixation of the activity of a chemical species modeling a buffered system, incremental feeding of a reactant solution (as in a continuous stirred tank reactor), and kinetic controls of heterogeneous reactions.

Another group of models corresponds to inverse mass balance models. These specialized models derive the initial composition of a water solution from its actual final composition, which takes into account the reactions and mass transfer between water and solid and/or gas phases, in agreement with the available data of a system. Thus, the initial composition of the water is determined by subtracting the amount of dissolved species caused by reaction with minerals and other phases in the system from its final composition. Inverse mass balance calculations may also involve the determination of the fractions of different waters that have, at some given time, mixed completely.

Finally, coupled reaction-transport models are the most complex. In these models, both the partial differential equations describing the advection-dispersion transport and the set of algebraic equations describing the chemical equilibrium are solved. These models can also include heat transfer and fluid flow, thus increasing the number of equations to be solved. The level of complexity depends also on the details of chemical reactions considered. These details can include multicomponent reactive transport, which accounts for the kinetics of mineral dissolution and precipitation; adsorption onto mineral surfaces; and radioactive decay, to name but a few.

FINAL REMARKS: MODEL VALIDATION AND USEFULNESS

The outcome of geochemical models can be either observable in nature or subject to experimental testing. Both processes are fundamental for model validation, and they are surely the ultimate test that a model must face. However, the process is not as simple as it may seem. Usually, geochemical models may adequately describe several processes and mechanisms in nature, but nature's

inherent complexity puts a limit to model precision and accuracy, which limits considerably its proper validation. Normally, the number of variables assumed within a model is limited and corresponds to a fraction of the ones found in nature. In such complex models, slight variations in parameters may induce diverse outcomes, such as in climate modeling. Thus, models are not only helpful tools to gain insight into the workings of nature, but they also must have some sort of predictive power. A model outcome may not be accurate enough to make a prediction relative to contaminant dispersion in a groundwater system, for example. However, it may give enough confidence to help make decisions on regulatory issues.

BIBLIOGRAPHY

1. Yeh, G.T. and Tripathi, V.S. (1989). A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* **25**: 93–108.
2. Mangold, D.C. and Tsang, C.-F. (1991). A summary of subsurface hydrological and hydrochemical models. *Rev. Geophys.* **29**: 51–79.
3. Appelo, C.A.J. and Postma, D. (1993). *Geochemistry, Groundwater and Pollution*. A.A. Balkema, Rotterdam.
4. Nordstrom, D.K. and Munoz, J.L. (1994). *Geochemical Thermodynamics*, 2nd Edn. Blackwell, Boston, MA.
5. Nordstrom, D.K. (2004). Modeling low-temperature geochemical processes. In: *Treatise on Geochemistry—Surface and Ground Water, Weathering, and Soils*. J.I. Drever (Ed.). Vol. 5, pp. 37–72.
6. Langmuir, D. (1996). *Aqueous Environmental Geochemistry*. Prentice-Hall, Upper Saddle River, NJ.
7. Drever, J.I. (1997). *The Geochemistry of Natural Waters*, 3rd Edn. Prentice-Hall, Upper Saddle River, NJ.
8. Zhu, C. and Anderson, G. (2002). *Environmental Applications of Geochemical Modeling*. Cambridge University Press, Cambridge, UK.
9. Albarède, F. (1996). *Introduction to Geochemical Modeling*. Cambridge University Press, Cambridge, UK.

GEOCHEMICAL MODELING-COMPUTER CODES

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An important share of geochemical studies increasingly relies on the use of computer programs[1] to model diverse geochemical systems. Most of these programs are freely available to the general public, or at a symbolic cost for educational and research purposes. Although developing open source and/or precompiled codes is markedly important, their regular maintenance should not be dismissed. Programming languages evolve, as well as operating systems and computer hardware, which means that codes without regular revision become outdated and eventually useless as their compiled versions may stop working properly under new operating systems.

All geochemical models rely very much on the availability of good quality, self-consistent thermodynamic data. This data is stored in database files that are accessed by the program while it is executed, making it one of its core elements. In the absence of specific data in the database for the problem to be modeled, some programs allow the incorporation of the data in simulations or, alternatively, the database can be modified by incorporation of new data. As new and improved experimental thermodynamic measurements are continuously being made, thermodynamic databases should also be regularly revised and updated.

The description that follows is meant to address mainly those computer programs most readily accessible and does not pretend to be an exhaustive list of all available programs. Although presenting the address of websites where these programs and codes are stored and may be obtained, one should be aware that this information will potentially become out of date rather quickly.

USGS CODES

The USGS supports various projects for developing software, including aqueous geochemistry computer programs, which include the chemical speciation program WATEQ4F (1), well suited for processing large numbers of water analyses. The most recent upgrades include the revision of the thermodynamic data on uranium and arsenic species. The most complete computer programs available are the ones from the PHREEQC (2) family (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/).
PHREEQC is a program that performs chemical speciation calculations, reaction-path modeling, one-dimensional transport, and inverse geochemical calculations. Currently, it contains a basic interpreter allowing a very flexible use of the program, meeting each one's needs, especially for modeling kinetic data. The latest revisions (February–April 2003) include isotope fractionation modeling (3). PHREEQC uses its own thermodynamic database, and also the LLNL and WATEQ4F databases, which are still updated and corrected regularly. Two graphical user interfaces (GUI) were developed: PHREEQCI by USGS and PHREEQC for Windows by Vincent Post from the Vrije Universiteit Amsterdam (http://www.geo.vu.nl/users/posv/phreeqc). The latter allows the graphical display of the output, which is unavailable in the original program, which is rather achieved by using the PHRQCGRF program. PHAST is a three-dimensional multicomponent reaction-transport model that simulates transient groundwater flow, that may or may not include geochemical reactions. PHAST combines the HST3D simulator (4) for the transport calculations with PHREEQC for geochemical calculations. PHRQPITZ is specially designed to use with brines, as it implements Pitzer's equation for the calculation of activity coefficients.

[1]We will use the term "computer code" as a set of written instructions aiming at solving a set of specific problems, and computer program to a compiled code to be executed as a standalone application under a given operating system.

Other computer programs include OTIS (5), used for the geochemical modeling solute transport in streams and rivers. Recently, Bowser and Jones (6) presented a Microsoft® Excel spreadsheet for a mineral-solute mass-balance model in order to study and understand the mineralogical controls on water composition in surface and groundwater systems dominated by silicate lithologies. All of these programs, and others, are available from USGS webpages at http://water.usgs.gov/software/geochemical.html.

USEPA CODES

The USEPA has a series of supported computer codes, the most popular of which is the MINTEQA2/PRODEFA2 (last release in 1999 is version 4.0), widely used in environmental geochemistry problems (7), which is a chemical equilibrium computer model that is able to calculate chemical speciation, solubility equilibrium, titration, and surface complexation modeling. It also includes the Gaussian model for the interaction of dissolved organic matter (DOM) with cations. However, it lacks database maintenance. Gustafsson (8) has been developing VisualMINTEQ, a GUI version of this program that also presents other improvements, such as the NIST database, adsorption with five surface complexation models, ion-exchange, and inclusion of both the Stockholm Humic Model and the NICA-Donnan model for metal-DOM complexation to name only a few.

The program BIOPLUME III (9) is a 2-D finite difference model that accounts for advection, diffusion, adsorption, and biodegradation in groundwater systems to model natural attenuation of organic contaminants. BIOCHLOR (10) and BIOSCREEN (11) are both Microsoft® Excel spreadsheet-based codes that model natural attenuation of chlorinated solvents and petroleum-derived hydrocarbons in water systems, respectively.

CHEMFLO-2000 (12) is a model that simulates water flow and chemical transport and fate in the vadose zone. CHEMFLO-2000 is a program that is written in Java®, which makes it platform-independent. All of these programs can be obtained from http://www.epa.gov/ada/csmos/models.

OTHER CODES

The set of computer codes known as EQ3/6 (13) supported by Lawrence Livermore National Laboratory (LLNL) was originally developed to model water-rock interactions in hydrothermal systems. It is currently one of the most complete programs applied to several problems, including municipal and industrial waste situations, and has been used to assess natural and engineered remediation processes. Unlike the programs presented until now, it must be purchased from LLNL. Closely related but mostly used for a range of high temperature and pressure is SUPCRT92 (14). This program has been discontinued, but still available on request to the authors.

The Geochemist Workbench® (15) is a commercial software with a range of capabilities similar to EQ3/6 and PHREEQC. It is available for Windows® only, but taking advantage of this environment makes it user friendly, with graphical capabilities included that are normally absent from most of these programs.

The Windermere Humic Aqueous Model (WHAM) version 6 (16) models the ion–humic substances interaction in surface waters using surface complexation. It also incorporates cation exchange on clays. However, precipitation and dissolution of solids as well as oxidation-reduction reactions cannot be simulated. This program must also be purchased for use. Alternatively, WinHumicV is a freely available GUI version of WHAM with model V implemented (17).

Steefel and Yabusaki (18) developed the GIMRT/OS3D codes for 2-D and 3-D multicomponent coupled reactive-transport modeling for flow in porous media. Both of these programs were superseded by the program CRUNCH (http://www.csteefel.com/CrunchPublic/WebCrunch.html), which can be obtained from the developer (C. I. Steefel) on request.

ORCHESTRA (19) (http://www.meeussen.nl/orchestra/) represents a new class of computer programs for use in geochemical reactive-transport modeling. This program is actually a framework where chemical speciation models can be implemented by the user and combine them with kinetic and transport processes. It is written in Java® and takes advantage of object-oriented programming. In the same class of programs is MEDIA (http://www.nioo.knaw.nl/homepages/meysman/), to simulate the biogeochemistry of marine and estuarine sediments.

BIBLIOGRAPHY

1. Ball, J.W. and Nordstrom, D.K. (1991). *User's Manual for WATEQ4F, with Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters*. U.S. Geological Survey, Open-File Report 91-183, Washington, DC.
2. Parkhurst, D.L. and Appelo, C.A.J. (1999). *User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. U.S. Geological Survey Water-Resources Investigations Report 99-4259. Washington, DC, p. 312.
3. Thorstenson, D.C. and Parkhurst, D.L. (2002). *Calculation of Individual Isotope Equilibrium Constants for Implementation in Geochemical Models*. U.S. Geological Survey Water-Resources Investigation Report 02-4172. Washington, DC, p. 129.
4. Kipp, K.L. (1987). *HST3D—A Computer Code for Simulation of Heat and Solute Transport in Three-dimensional Groundwater Flow Systems*. U.S. Geological Survey Water-Resources Investigations Report 86-4095. Washington, DC, p. 517.
5. Runkel, R.L. (1998). *One Dimensional Transport with Inflow and Storage (OTIS): A Solute Transport Model for Streams and Rivers*. U.S. Geological Survey Water-Resources Investigation Report 98-4018. Washington, DC, p. 73.
6. Bowser, C.J. and Jones, B.F. (2002). Mineralogic controls on the composition of natural waters dominated by silicate hydrolysis. *Amer. J. Sci.* **302**: 582–662.
7. Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. (1991). *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. U. S. Environmental Protection Agency, Washington, DC, p. 107.

8. Gustafsson, J.P. (2004). Visual MINTEQ ver. 2.30. Available: http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm.
9. Rafai, H.S., Newel, C.J., Gonzales, J.R., Dendrou, S., Kennedy, L., and Wilson, J.T. (1998). *BIOPLUME III—Natural Attenuation Decision Support System, User's Manual Version 1.0. EPA/600/R-98/010*. USEPA, Washington, DC, p. 282.
10. Aziz, C.E., Newel, C.J., Gonzales, J.R., Haas, P., Clement, T.P., and Sun, Y. (2000). *BIOCHLOR—Natural Attenuation Decision Support System*, User's Manual, Version 1.0. EPA/600/R-00/008. USEPA, Washington, DC, p. 46.
11. Newel, C.J., McLoed, R.K., and Gonzales, J.R. (1996). *BIOSCREEN—Natural Attenuation Decision Support System*, User's Manual, Version 1.3. EPA/600/R-96/087. USEPA, Washington, DC, p. 65.
12. Nofziger, D.L. and Wu, J. (2003). *CHEMFLO-2000—Interactive Software for Simulating Water and Chemical Movement in Unsatured Soils*. EPA/600/R-03/008. USEPA, Washington, DC, p. 69.
13. Wolery, T.J. (1992). *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)*. (UCRL-MA-110662 PT I).
14. Johnson, J.W., Oelkers, E.H., and Helgeson, H.C. (1992). SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput. Geosci.* **18**: 899–947.
15. Bethke, C.M. (1996). *Geochemical Reaction Modeling, Concepts and Applications*. Oxford University Press, New York.
16. Tipping, E. (1998). Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aqua. Geochem.* **4**: 3–48.
17. Gustafsson, J.P. (1999). WinHumicV. http://www.lwr.kth.se/english/OurSoftWare/WinHumicV/.
18. Steefel, C.I. and Yabusaki, S.B. (1996). *OS3D/GIMRT, Software for Multicomponent—Multidimensional Reactive Transport*. User manual and programmer's guide. PNL-11166. Battelle, Richland, WA.
19. Meeussen, J.C.L. (2003). ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. *Environment. Sci. Technol.* **37**: 1175–1182.

READING LIST

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A. (1988). *A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines: U.S. Geological Survey Water-Resources Investigations Report 88-4153*. Washington, DC, p. 310.

GEOCHEMICAL MODELING—COMPUTER CODE CONCEPTS

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INTRODUCTION

This article is focused on geochemical models in aqueous systems. The applications for these models have grown over the last 20 years as the capabilities and flexibility of the codes has increased in conjunction with the increased speed of personal computers. Many earlier computer models were designed for specific questions related to aqueous speciation (1,2). Many earlier models have been discontinued or superseded by newer programs that incorporate new features and capabilities, increased flexibility, and improved input and output options. This change has been driven by the wider use of geochemical modeling and the increase in modeling as a component of environmental studies. Some more important recent applications include modeling high-level radioactive waste disposal, environmental issues associated with mining, landfill leachate, injection of hazardous wastes into deep wells, water resources issues, and artificial recharge to aquifers (3).

All available models use the same basic approach, that of calculating the thermodynamic equilibrium state of a specified system that can include water, solutes, surfaces, and solid and gas phases. These models comprise four major components. They are as follows:

1. Input: specific information that defines the system of interest such as concentrations of solutes, temperature, partial pressure of gases, and composition of solid phases.
2. Equations that are solved by the model.
3. Equilibrium and kinetic formulations between solutes of interest.
4. Output: in tabular or graphic form.

CAPABILITIES AND METHODS

The computer codes require initial input constraints that generally consist of water chemistry analyses, units of the measurement, temperature, dissolved gas content, pH, and redox potential (Eh). The models work by converting the chemical concentrations, usually reported in wt./wt. or wt./volume terms such as mg/kg or mg/L, to moles, and then solving a series of simultaneous nonlinear algebraic equations (chemical reaction, charge balance, and mass balance equations) to determine the activity-concentration relationship for all chemical species in the specified system. The models usually require electrical balance and will force charge balance with one of the components (can be designated), as they solve the matrix of nonlinear equations. The capabilities of modern codes include calculation of pH and Eh, speciation of aqueous species, equilibrium with gases and minerals, oxidation and reduction reactions (redox), kinetic reactions, and reactions with surfaces.

The nonlinear algebraic equations are solved with an iterative approach by the Newton–Raphson method (4). The equations to be solved are drawn from a database that contains equations in the standard chemical mass action form. In theory, any reaction such as sorption of solute to surface that can be represented in this form can be incorporated into the model. These equations represent chemical interactions with reactants on the right and products on the left. Reactions are assumed to reach

equilibrium (the point of lowest free energy in the system) when there is no change in concentration on either side.

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3{}^{2-}$$

Note that the arrow in the calcite dissolution example above goes in both ways; that is, the reaction as written is reversible. Once a mineral reaches equilibrium with a solution, adding more mineral will not increase the dissolved concentration because we have already saturated the solution. But removing ions from the right side (e.g., lowering the concentration by dilution with distilled water) will cause more solid to dissolve.

We express this in a mathematical form where, at equilibrium, the ratio of the concentration of reactants (on the bottom) and products (on the top) is equal to K, known as the proportionality constant or distribution coefficient or equilibrium constant.

$$K_{calcite} = \frac{[Ca^{2+}][CO_3{}^{2-}]}{[CaCO_3]}$$

Kinetic reactions, those involving time, are included by assuming that the chemical reaction will proceed to equilibrium, but at a specified rate. The available kinetic reactions include mineral dissolution and precipitation, redox reactions and microbial growth, and metabolism of solutes. The rate laws used in the codes vary, but all codes with kinetic capabilities include simple first-order rate laws, and they may include more complex rate formulations such as cross-affinity, Michaelis–Menten, and Monod formulations (5).

THERMODYNAMIC BACKGROUND

The formalism that allows us to relate mass actions equations (balanced chemical reactions) to actual solutions is called chemical thermodynamics or, more precisely, equilibrium thermodynamics. The basic idea is that elements, molecules, and compounds all contain some internal energy and that all systems try to reach a state where that energy is minimized (equilibrium). Natural systems, particularly low-temperature systems, do not always reach equilibrium, but they do move in that direction. The internal energy of an element, molecule, or compound is expressed as its enthalpy or internal heat. The free energy of an element is an element, molecule or compound is the sum of its internal heat and its internal tendency toward disorder (entropy).

$$G = H - TS$$

Assuming constant T and P, we get

$$\Delta G = \Delta H - T\Delta S$$

The total free energy of a component in the system is dependent on this inherent energy of an element, molecule, or compound and the amount (concentration). When two or more elements, molecules, and compounds are combined, the result is a reaction that minimizes the energy of the new system, lowering the ΔG. The free energy of a reaction is calculated by

$$\Delta G^0 \text{ rxn.} = \sum \Delta G^0 \text{ products} - \sum \Delta G^0 \text{ reactants}$$

The ΔG^0 values (standard free energy) for many compounds can be found in the back of textbooks such as Drever (6). This way we can calculate a ΔG value for any reaction that for which we can write a balanced chemical equation. The minimum energy state (equilibrium) between the reactants and products is related to the ΔG value by

$$\log K_{rxn.} = \frac{-\Delta G^0 \text{ rxn}}{2.303\, RT}$$

where R is the universal gas constant in kJ/mole; T is the temperature in Kelvin; and K is the equilibrium constant for the reaction.

COMPUTER MODELS

The computer models are divided into two basic types, speciation models and reaction-path models. In both cases, the models are fundamentally static; that is, no explicit transport function exists; however, some forms of transport can be simulated by manipulation of the models. More complex reaction-transport models that explicitly incorporate transport are briefly described below.

The equilibrium models are speciation models in that they can calculate the speciation (distribution) of aqueous species for any element or compound included in the database. Speciation models calculate activities (chemically reactive concentration), species distribution for elements in the database, saturation indices, and ion ratios at the specified conditions of pH and redox potential (ORP or Eh). Most models allow selection of method of activity calculation (Davies, Debye-Huckel, extended Debye-Huckel, Pitzer). Some models incorporate adsorption, solid phase solutions, and kinetics. Only one model, PHREEQC, has the inverse modeling option. This features uses mass balance constraints to calculate the mass transfer of minerals and gases that would produce an ending water composition given a specified starting water composition (7). This method does not model mass transport; it only calculates and provides statistical measures of fit for possible solutions to the mass balance between starting and ending water compositions.

The next step in complexity is the reaction path (mass transfer) models. The reaction path models use speciation calculation as a starting point and then make forward predictions of changes along the specified reaction path (specified change in T, P, pH, addition of new reactants such as another fluid or solid). The program makes small incremental steps with stepwise addition or removal of mass (dissolution or precipitation), and it can include changes in temperature or pressure along the reaction path. Typical questions posed by modelers include:

- If I change a variable (pH, pe, P_{CO2}), how does system change?
- What happens if I mix water A with water B?
- What is concentration of A^+ in water saturated with mineral AB?

- What happens to the water chemistry *A* if I react the water with mineral *B*?

Limitations exist with any model. The field input data may be corrupt with bad analysis, missing parameter, or electrical imbalance. Speciation models assume equilibrium conditions, which may not be the case. The databases are also a source of uncertainty. They do not always contain all elements or species of interest; the data have some uncertainty, and some data may be inaccurate data (6). Some available codes try and minimize this problem by including several of the most popular databases such as the MINTEQ database (EPA-approved database specializing in metals), WATEQ (USGS database specializing in minerals), and the LLNL database (the most complete database available that is compiled and maintained by Lawrence Livermore National Laboratory). For environmental applications, the limited data for organic compounds remain a concern.

Other limitations include the redox reactions that are of particular importance in metal transport. These reactions are difficult to model correctly because redox reactions may have different rates producing natural systems that are not in redox equilibrium (8). This problem can be addressed by modeling redox reactions as rate-limited (kinetic) formulations if the data are available.

The most complex models explicitly incorporate transport and reaction. The codes couple and solve both the partial differential equations of flow using the advective-dispersion equation and the nonlinear algebraic equations of chemical equilibrium. The general approach is to solve for the reaction term in each cell with the chemical module of the code, and then separately solve for the effects of transport (split-operator approach). The effects of adsorption are solved in the transport module with the retardation portion of the equation (3,8,10). These models are much more complex than are the reaction path models. Presently, only three commonly used models have transport capabilities, HYDROGEOCHEM2, PHREEQC (1D) and the related PHAST (3D) code, and Geochemist's Workbench.

Table 1 lists the most common programs, their sources, and some of the most useful capabilities. The list is not meant to be exhaustive; rather, it offers an overview to serve as a starting point for further investigation. Details of the capabilities of each program can be found on the listed websites or in the manuals. More detailed comparison of these and other models are available in related publications (1,11,12).

BIBLIOGRAPHY

1. Nordstrom, D.K. et al. (1979). Comparison of computerized chemical models for equilibrium calculations in aqueous systems; chemical modeling in aqueous systems; Speciation, sorption, solubility, and kinetics. *ACS Symposium Series* **93**: 857–892.
2. Allison, J.D., Brown, D.S., and Novac-Gradac, K.J. (1991). *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. U.S. EPA, Athens, GA.
3. Zhu, C. and Anderson, G. (2002). *Environmental Applications of Geochemical Modeling*. Cambridge University Press, Cambridge, UK.
4. Bethke. (1996).
5. Bethke. (2002).
6. Drever, J.I. (1997). *The Geochemistry of Natural Waters*, 3rd Edn. Prentice-Hall, Englewood Cliffs, NJ.
7. Garrels, R.M. and Mackenzie, F.T. (1967). *Origin of the Chemical Compositions of Some Springs and Lakes in Equilibrium Concepts in Natural Waters*. American Cancer Society, Washington, DC, pp. 222–242.
8. Lindberg, R.D. and Runnels, D.D. (1984). Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* **225**: 925–927.
9. Appelo, C.A.J. and Postma, D. (1993) *Geochemistry, Groundwater and Pollution*. A. A. Balkema, Rotterdam.
10. Parkhurst, D. and Appelo, C.A.J. (1999). *USER'S Guide to PHREEQC (VERSION 2)—A Computer Program for Speciation, Batch-Reaction, One-dimensional Transport and Inverse Geochemical Calculations*. Water-Resources Investigations Report 99-4259.
11. Engesgaard, P. and Christensen, T.H. (1988). A review of chemical solute transport models. *Nordic Hydrol.* **19**(3): 183–216.
12. Mangold, D.C. and Tsang, C.-F. (1991). A summary of subsurface hydrological and hydrochemical models. *Rev. Geophys.* **29**(1): 51–79.

Table 1. Comparison of Selected Codes' Capabilities and Features

Program	Source	Speciation	Reaction Path	Tabular Output	Graphic Output	Surface Rxns.	Kinetics	Inverse	Transport	Multiple Databases
EQ3/6	LLNL	yes	yes	Yes	no	no	yes	no	no	no
GWB	Rockware*	yes	yes	Yes	yes	yes	yes	no	yes	yes
HYDROGEOCHEM2	SSG*	yes	yes	Yes	no	yes	yes	no	yes	no
MINTEQ	EPA	yes	no	yes	no	yes	no	no	no	no
MINEQL+	ERS*	yes	no	yes	some	no	no	no	no	no
PHREEQC	USGS	yes	yes	yes	no	yes	yes	yes	yes	yes

*Commercial programs; others are freeware.
EQ3/6—http://www.earthsci.unibe.ch/tutorial/eq36.htm
GWB—Rockware—http://www.rockware.com
HYDROGEOCHEM—http://www.scisoftware.com/environmental_software/software.php
MINEQL+—http://www.mineql.com/
MINTEQ—http://soils.stanford.edu/classes/GES166_266items%5Cminteq.htm
PHREEQC—http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

READING LIST

Glynn, P.D., Engesgaard, P., Kipp, K.L., Mallard, G.E., and Aronson, D.A. (1991). *Two Geochemical Mass Transport Codes; PHREEQM and MST1D, Their Use and Limitations at the Pinal Creek Toxic-Waste Site*. U.S. geological survey toxic substances hydrology program. Abstracts of the technical meeting, Monterey, CA, March 11–15, 1991. Open-File Report—U.S. Geological Survey OF 91-0088.

Grove, D.B. and Stollenwerk, K.G. (1987). Chemical reactions simulated by ground-water-quality models. *Water Resour. Bull.* **23**(4): 601–615.

GEOLOGICAL OCCURRENCE OF GROUNDWATER

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The occurrence, movement, and storage of groundwater are controlled by geology. The geologic factors that control groundwater are petrography, stratigraphy, structure, geomorphology, lithology, and thickness (1). The petrography of a given rock type controls the porosity and permeability. Porosity defines the storage capacity of an aquifer. There are two types of porosity: primary and secondary. Primary porosity, such as pores between sand grains, is created when rocks are formed. The shape, sorting, and packing of grains determine primary porosity. Sedimentary rocks are poorly sorted when the grains are not the same size creating spaces between the larger grains that are filled by smaller grains. Secondary porosity such as joints, fractures, and solution opening, is formed after the rock has been deposited. The number and arrangement of fracture openings and the degree to which they are filled with fine-grained material control secondary porosity.

Aquifers (1) are classified as unconfined and confined. An unconfined aquifer has the water table as its upper boundary (2). Recharge to unconfined aquifers is primarily by downward seepage through the unsaturated zone. The water table in an unconfined aquifer rises or declines in response to rainfall and changes in stream stage. When a well that tap an unconfined aquifer is pumped, the water level is lowered, gravity causes water to flow to the well, and sediments near the well are dewatered. Unconfined aquifers are usually the uppermost aquifers and, therefore, are more susceptible to contamination from activities at the land surface.

A confined (artesian aquifer) contains water under pressure greater than that of atmospheric. Rocks of permeability lower than the aquifer overlie a confined aquifer. The low-permeability layer that adjoins a confined aquifer is called a confining bed. A confining bed has very low permeability that restricts the movement of groundwater either into or out of the aquifer. Confining beds are thus poorly transmissive to groundwater flow. Because the water is under pressure, water levels in wells rise above the base of the confining bed. If the water level in a well that taps a confined aquifer stands above the land surface, the well is called a flowing artesian well. In some cases, a fault (fractures along which rocks have moved) will allow the passage of water from a confined aquifer to the surface, resulting in a spring.

Sand and gravel aquifers are the source of most of the groundwater pumped in many parts of the world, including North America, The Netherlands, France, Spain, and China. Sand and gravel aquifers are common near large to moderately sized streams. Rivers or the meltwater from glaciers formed these aquifers.

Limestone aquifers are the sources of some of the largest well and spring yields because limestone is soluble in water. Openings that existed when the rocks were formed are frequently enlarged by solution (dissolved by water), providing highly permeable flow paths for groundwater (3).

Basalt and other volcanic rocks are some of the most productive aquifers. Basalt aquifers contain water-bearing spaces in the form of shrinkage cracks, joints, and lava caves. Lava tubes are formed when tunneling lava ceases to flow and drains out, leaving a long, cavernous formation.

Fractured igneous and metamorphic rock aquifers are the principal sources of groundwater for people who live in mountainous areas. Where fractures are numerous and interconnected, these rocks can supply water to wells and can be classified as aquifers. Wells are commonly 50 to 100 feet deep (15 to 30 meters). Granite and metamorphic rocks have not been extensively developed as aquifers. Groundwater movement in these rocks is irregular, which makes exploration for a water supply difficult (4).

Sandstone aquifers are formed by the cementation of sand. Their porosity ranges from 5–30%. Their permeability is largely a function of the amount of cement (clay, calcite, and quartz). Sandstone is an important source of groundwater in Libya, Egypt (Nubian), Britain (the Permo-Triassic sandstones), the north central United States (St. Peter-Mount Simon Sandstone), and in the west central United States (the Dakota Sandstone).

BIBLIOGRAPHY

1. Meinzer, O.E. (1923). *The occurrence of ground water in the United States, with a discussion of principles*. U.S. Geol. Survey Water Supply Paper 489.
2. Lohman, S.W. et al. (1972). *Definitions of selected ground-water terms-revisions and conceptual refinements*. U.S. Geol. Survey Water Supply Paper 1988.
3. Heath, R.C. (1983). *Ground water regions of the United States*. U.S. Geol. Survey Water Supply Paper 2220.
4. Moore, J. E. et al. (1995). *Groundwater, a Primer*. American Geological Institute, Alexandria, VA, p. 53.

GEOPHYSICS AND REMOTE SENSING

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When data cannot be gathered by direct observation, such as observing an outcrop or taking a physical sample,

information can often be obtained by using remote sensing techniques. Remote sensing methods measure physical properties of materials by measuring changes in the flux of various forms of energy using natural or transmitted fields. The science of applying these methods to earth materials is called geophysics

Geophysics is commonly used to obtain subsurface information for a variety of resource development and engineering applications. A partial list of applications for which geophysical methods can be used includes mapping aquifers, mapping water quality, mapping geologic structure, measuring flowing fluids, finding buried objects for engineering and archeological purposes, and measuring *in situ* soil and rock properties. The major energy fields used include magnetic fields (magnetometry), electrical fields (electrical resistivity and spontaneous potential), electromagnetic fields (electromagnetic induction and ground-penetrating radar), propagation of seismic waves (seismic reflection, seismic refraction, passive acoustic emission monitoring, and spectral analysis of surface waves), the gravitational field (gravimetry), gamma-ray radiation (gamma-ray spectroscopy), and heat transfer (geothermal). Other physical properties can be measured by bombarding the material with gamma rays (electron density) or high-energy neutrons (hydrogen content). Less commonly, properties such as thermal conductivity, electrical chargeability, or magnetic resonance are also measured.

The methods can be broadly classified in several ways. Most commonly, methods are classified by their mode of deployment. Surface methods are commonly applied from the ground surface. Borehole methods are used within boreholes or wells. Several techniques can also be applied using airborne or marine systems. Methods can also be classified as active or passive measurement. Methods that measure variations in natural fields, such as gravimetry or magnetometry, are called passive methods because they use natural fields propagating through the earth. Other methods are called active methods because the measurement is based on the response of earth material to some form of transmitted energy. Active methods include most seismic methods and most electrical methods.

There are many types of geophysical methods; each has specific advantages and limitations. The choice of the proper method requires understanding the target body, the matrix material, and the environment in which the survey is to be conducted. The following is a brief outline of the most common geophysical methods with a summary of the characteristics of each method. The list is by no means complete.

SURFACE METHODS

Electrical Methods

Electrical Resistivity. The electrical resistivity method uses two electrodes planted at the surface to pass an electric current through the ground. A second pair of electrodes is used to measure the potential difference between two points. The measured potential and the applied current are used to calculate the electrical resistance per unit length (resistivity) of the subsurface. The depth of measurement is changed by changing the relative position and spacing of the electrodes. Several newer systems use cables with multiple electrodes connected to a switching system to select the electrode pairs. The field data produce an apparent resistivity value, which is a function of all materials penetrated by the current. The data must be modeled to obtain the unique resistivity and thickness of each layer for a nonuniform subsurface.

Applications

Can distinguish saturated from unsaturated materials.
Can distinguish sandy material from clay-rich material.
Can distinguish high-conductivity groundwater (inorganic contaminants) from low-conductivity groundwater.
Less susceptible to cultural interference than electromagnetic (EM) methods.
Better vertical resolution for resistive targets than EM methods.

Limitations

Requires electrical coupling with the surface, which can be difficult in dry soils.
Generally requires three to five times the surface array length to the depth of investigation.
Field acquisition generally slower than EM methods.
Poorer lateral resolution than EM methods at depths of more than a few meters.
Relatively insensitive to changes in the resistivity of highly conductive bodies.
Highly resistive near-surface material can mask conductive bodies at depth.
Can be affected by strong EM fields such as from high-voltage power lines.
Interpretation of field data produces nonunique solutions (i.e., many possible solutions can fit data nearly as well as actual conditions).

Spontaneous Potential. The SP method uses two nonpolarizing electrodes and a high-impedance voltmeter to measure natural voltages between two points generated by several natural processes. Anomalies can be due to variations in the geochemical properties of soils, fluids, or moving groundwater. Although its origins are in the mining industry for finding sulfide ore bodies, the method is principally a profiling technique to find seepage pathways such as for a dam investigation.

Applications

Relatively fast and simple data acquisition and interpretation.
Can detect zones of high groundwater flow.
Can detect oxidizing metal bodies.

Limitations

Requires special nonpolarizing electrodes for accurate voltage measurements.

Susceptible to interference from near-surface soil conditions.
Interpretation is qualitative and can be ambiguous.

Induced Polarization. The IP method measures a property known as chargeability, which is the ability of subsurface materials to hold a charge after an electrical current is shut off. It is basically a modification of the electrical resistivity method that measures induced electrical polarization between two electrodes caused by an applied low-frequency alternating current. Measurements are typically made by measuring the decay of voltage with time after the applied current is shut off, called the time domain method, or by measuring the suppression of voltage relative to the frequency of the applied external current, called the complex resistivity method. IP surveys have been used to determine the clay content of the subsurface or the geochemical properties of several minerals in the subsurface. The surveys can be conducted as profiles or as depth soundings.

Applications

Can be used to estimate the clay content of the subsurface and thereby infer hydraulic conductivity.
Can be acquired simultaneously with electrical resistivity data.
Can be used to detect organic contamination of soils under certain conditions, primarily sites that have 6% to 12% clay content.
Can be used to measure the *in situ* oxidation state of some inorganic compounds.

Limitations

Requires surface electrodes and better electrode coupling than standard resistivity surveys.
Requires higher currents than electrical resistivity—potentially dangerous.
Ability to convert IP soundings to depth sections is limited.
IP response is relatively insensitive to increases in clay content above 7% to 10%.
Interpretation is qualitative and can be ambiguous.

Azimuthal Resistivity. The azimuthal resistivity method is a modification of the standard electrical resistivity method that measures electrical resistivity versus azimuthal orientation at one location. The method is used to identify areas of fractured till or bedrock and determine the orientation of the principal fracture set. Several specialized electrode arrays have been developed to reduce the number of readings required, including the tripotential array and the square array.

Applications

Can determine the fracture orientation and fracture porosity from the surface.
Uses standard resistivity equipment.

Limitations

Data acquisition can be relatively slow and require a relatively large area of open land.
Limited ability to determine location of individual fractures.
Steeply dipping or irregular bedrock surfaces can skew data.
Cannot distinguish clay-filled from fluid-filled fractures.
Interpretation is quantitative for uniformly fractured materials with no overburden; quantitative interpretation is more limited for more common cases such as discrete fracture zones with overburden.

Seismic Methods

Seismic Refraction. The seismic refraction method uses the principle of refraction (bending) of sound energy across a boundary between two materials that have different sound velocities. The travel time of sound energy from a seismic source, such as a hammer blow or explosive, to a line of ground motion detectors, called geophones, is measured by a device called a seismograph. The travel time versus distance between the source and the geophones is used to calculate the thickness and depth of the geologic layers present. The method can resolve only layered systems in which each layer has a higher sound velocity than the layer above it. A layer that is too thin or whose velocity is lower than the layer above it cannot be detected and will introduce an error in the depth calculation of deeper layers. The shape of dipping or undulating surfaces can be resolved if several source locations are used in different positions relative to the geophone string.

Applications

Relatively simple and fast.
Requires less interpretation than other seismic methods.
Directly measures the seismic velocity of the materials present.
Measured velocities can be used to determine the type of bedrock or soil.
Can provide information on depth to bedrock to within about 10%.
Can determine the slope and shape of a bedrock surface.
Can map dense till sheets beneath softer sediments.
Can identify larger faults under the right conditions.

Limitations

Typically requires three to five times the surface array length to the depth of penetration.
Practical depth limit approximately 150 to 200 feet without a strong seismic source such as explosives.
Cannot detect low velocity layers beneath high velocity layers (i.e., sand beneath clay).
Limited ability to measure changes in velocity along a layer.
Cannot resolve steep dips.
Water table mapping only possible in coarse, sandy soils.
Sensitive to vibrations from cultural features such as highways.

Seismic Reflection. The reflection methods uses a string of geophones connected to a seismograph to measure

direct reflections of sound energy from geologic boundaries between layers with contrasting acoustic impedance values (density times sound velocity). After significant processing, the data are typically plotted as a time section that shows the two-way travel time to major reflectors that is analogous to a geologic cross section, except that the depth axis is presented in travel time, which is not linear with depth. The method is typically used for deeper, more detailed studies than the refraction method, and the limitation of increasing velocity with depth does not apply. Faults, geologic structure, and dipping or truncating beds are commonly mapped by reflection.

Applications

The depth of penetration can be several times the surface array length.
More sophisticated interpretation and processing techniques are available.
Produces a continuous image of the subsurface that provides a time cross section that can be converted into a depth cross section.
Lateral resolution is much better than refraction.
Can tolerate steeper dips than refraction.
Can accurately map small faults.
Can be used onshore or offshore.
Can handle low velocity layers beneath high velocity layers.

Limitations

Requires more sophisticated field equipment, processing, and field procedures.
Data acquisition and processing are more intensive than refraction.
Requires sophisticated analysis and accurate seismic velocity data from an independent source to convert from time to depth cross section.
Difficult to apply to shallow exploration targets (i.e., above approximately 50 to 100 feet).
Interpretation of data subjective and requires experienced interpreter.
Sensitive to vibrations from cultural sources such as highways.

Gravitational Methods

Gravimeter Surveys. The gravitational method uses a sensitive balance, called a gravimeter, to measure variations in the force of gravity at the surface caused by variations in the density of the subsurface. A common modification of the method is called the microgravity method. Microgravity uses a more sensitive gravimeter to detect small near-surface features, such as voids or cavities.

Applications

Can be used to detect buried bodies of contrasting density.
Can be used to detect bedrock valleys, faults, cavities, and other geologic structures.
Data acquisition relatively simple.
Forward modeling can easily be used to predict the success of the method for a given target.

Limitations

Requires a series of complex data corrections requiring precise locations and elevations at points of measurement and surrounding topography.
Materials of similar density do not produce a measurable anomaly (e.g., granite and quartzite)
Large anomalies at depth can mask shallow, smaller anomalies.
Interpretation of data produces a nonunique solution.
Can be difficult to collect accurate data around buildings or in areas of highly irregular topography.

Magnetic Methods

The magnetic method measures variations in the intensity of the earth's magnetic field caused by material of high magnetic susceptibility such as ferrous iron. Measurements can be made with single sensor units, so-called total field magnetometers, that measure the total magnitude of the magnetic field at a given point. Other types of magnetometers make simultaneous measurements at two elevations and compute the vertical gradient of the magnetic field, which increases the sensitivity to shallow targets and decreases the interference from adjacent objects. Some magnetometers measure only the vertical component of the magnetic field, which also reduces interference from adjacent objects. Three types of magnetometers are currently available: (1) Proton precession instruments measure the total field and commonly use two sensors to measure the vertical gradient. Proton precession magnetometers are commonly available and relatively inexpensive, but they are sensitive to steep magnetic gradients from cultural sources, such as power lines and large metal bodies, and do not provide reliable data in many highly developed sites. (2) Flux gate magnetometers measure only a single (usually vertical) component of the magnetic field. The readings are slower, and the sensor must be properly oriented, making data acquisition slower; but the sensor functions well in the presence of steep vertical gradients and is less sensitive to horizontal fields from adjacent objects. The units are less common and more expensive, but they work on sites where proton procession units do not. (3) Cesium magnetometers make fast, very accurate total field measurements, and two sensors are commonly used to make vertical gradient measurements. The sensors can handle steep magnetic gradients and operate at a higher data acquisition rate than other magnetometers. The sensor has an axial blind spot of about 30° that may produce erroneously low readings if the sensor is not properly aligned with the target bodies. The units are more common than flux gate systems but more expensive than proton systems.

Applications

Field acquisition is fast and relatively easy.
Can readily detect buried ferrous objects (e.g., buried drums, tanks, and pipelines).

Can be used to detect geologic structures where materials of contrasting magnetic susceptibility are present (e.g., igneous vs. sedimentary rock).

Limitations

Large masses of ferrous objects can have coalescing anomalies that prevent precise location of individual targets.
Susceptible to interference from surface metallic objects such as fences or strong electromagnetic fields from power lines.
Does not detect material of low magnetic susceptibility (e.g., nonferrous objects such as aluminum or fiber barrels).
Interpretation of data produces nonunique results.

Electromagnetic Methods

Frequency Domain Electromagnetic Induction. Frequency domain EM systems use a two-coil system to transmit an electromagnetic field to induce "eddy" currents in the subsurface and measure the resultant magnetic field, which is a product of the primary field and the induced fields. In some systems, the receiver coil is coincident with the transmitter coil. Systems typically operate at a single frequency that can be selected by the operator. Some systems use a sweep across a range of frequencies. The depth of investigation is controlled by changing the separation between the coils or the frequency of the transmitted field. Two components of the magnetic field are measured, the in-phase or quadrature component and the out of phase component. Some units are designed to operate in low-conductivity soils and use the quadrature term to set the coil spacing. These units are called low induction number systems and generally provide a direct reading of subsurface conductivity. They are easier to use in the field but do not make accurate measurements in soils above a few hundred millimhos per meter. Other systems require measuring the coil spacing independently. These systems make an accurate measurement of subsurface conductivity over a broader range of conditions, but the data must be processed to provide a conductivity measurement. The in-phase component of these units can be used as a direct indicator of high induction number material, such as metal, in the subsurface. Both types of systems produce an apparent conductivity measurement that must be modeled to obtain individual layer conductivity and thickness for a nonuniform subsurface.

Applications

No electrodes required; can be used on surfaces where electrode plants would be impossible.
Data acquisition is fast and efficient.
Can be conducted through freshwater.
Different coil orientations and intercoil spacing can be used to accommodate different depths of investigation.
Lateral resolution much better than electrical resistivity techniques.
Can be used to detect buried metal.
Detects nonferrous metal (e.g., copper, aluminum, brass, bronze).
Sensitive to inclined conductive sheets such as faults or fracture zones.
Can be used for azimuthal surveys to map fracture density and orientation.
Simple profiling instruments can be used by relatively inexperienced operator (e.g., Geonics EM34 or EM31).
Multiple-frequency systems can make vertical depth soundings.

Limitations

Depth interpretation of sounding data requires an experienced interpreter.
Vertical resolution generally poorer than with electrical resistivity.
More sensitive to cultural interference (pipelines, metal fences, power lines, etc.) than electrical resistivity.
Relatively insensitive to changes in the conductivity of highly resistive targets.
Highly conductive surface material limits depth of penetration.
Cannot be used through reinforced concrete.
Problem of nonunique interpretation greater than with resistivity method.

Very Low Frequency Induction. The VLF method uses low-frequency radio waves from one of several military transmitters as a plane wave source. The instrument measures the magnetic field generated by induced eddy currents. Some instruments use a pair of electrodes to measure the phase shift of the electric field. The depth of penetration of the system is limited by the frequency of the military transmitter and the conductivity of the subsurface. Penetration may be limited in areas of clay-rich soils, and the method is generally incapable of detecting features that are aligned perpendicularly to the direction of propagation of the plane wave. The method is generally used for profiling to detect fractures in bedrock, although it does have some limited depth sounding capabilities.

Applications

Simple instrumentation and operation.
Very rapid and efficient.
Sensitive to inclined conductive sheets such as faults or fracture zones.
Can map lateral variations in conductivity such as conductive plumes, changes in soil type, or landfill boundaries.

Limitations

Limited range in transmitted frequencies available that limits choices of the depth of investigation.
Certain transmitters are out of service periodically.
Relatively insensitive to changes in conductivity in highly resistive targets.
Highly conductive surface materials limit the depth of penetration.

Location of transmitters makes it difficult to detect linear conductive bodies oriented approximately perpendicularly to the direction of propagation of the plane wave.
Long, narrow, near-surface conductors (such as pipelines, fences, or groundwater-filled bedrock depressions) produce strong anomalies that can mimic or mask deeper anomalies.
Depth of investigation is totally dependent on subsurface conductivity for a given transmitter frequency.
Interpretation is largely qualitative and nonunique.

Magnetotellurics. The magnetotelluric (MT) method uses plane waves from natural electromagnetic fields generated by oscillations in the earth's ionosphere as transmitter signals or from transmitters positioned remote from the area of investigation. The magnetic and electric fields are measured in two horizontal components using two orthogonal electrode dipoles and two orthogonal magnetometers. The intensity and phase of electric and magnetic fields are used to determine the conductivity of the subsurface. The method is commonly used to map conductive targets at depths of hundreds or thousands of meters, where other EM methods are impractical. The magnitude and frequency range of the natural EM signals are variable, and data collection often is limited to the later afternoon or evenings. Deep studies require very low source frequencies that can require hours of data collection to record a single sounding. Shallower studies frequently require a remote transmitter to provide enough EM energy in the audio-frequency range, known as a controlled source audio-frequency magnetotelluric (CSAMT) survey. Interference from power lines and other utilities is common in developed areas. Modern MT systems generally can collect both natural source MT and CSAMT data in a single sounding to provide a broader spectrum of frequencies.

Applications

Can find conductive anomalies at depths of a few hundred to a few thousand meters.
A large area can be surveyed with a single transmitter setup (CSAMT) or with no transmitter (MT).

Limitations

The natural source is often biased toward low frequency, which seriously limits the sensitivity of the method to shallow features without a CSAMT transmitter.
Relatively insensitive to small, near-surface targets.
Relatively insensitive to highly resistive targets.
Sensitive to interference from cultural features such as power lines and buried utilities.
Interpretation is nonunique

Time Domain Electromagnetic Induction. The TEM (or TDEM) method uses a loop of wire to pass a current of several amps. The current is shut off almost instantaneously to create a broad-frequency-pulsed EM source. Typical transmitter loops are square or rectangular and a few meters to a few hundred meters on a side. The receiver uses a small magnetic coil to measure the magnetic field over a series of time windows following the shutoff of the current in the transmitter coil. The magnetic field measured at the receiver is a function of the induced eddy currents, which are a function of the conductivity of the subsurface. The data produce a sounding that can be modeled to determine the change in electrical conductivity versus depth. Several systems are available that cover a range in exploration depths of a few tens of meters to a few hundred meters.

Applications

Well suited to map conductive bodies at depths of a few tens of meters to a few hundred meters.
Often used to map zones of saline groundwater.
Vertical resolution significantly better than most multiple-frequency FDEM methods.
Can be used to find resistive targets under favorable circumstances.

Limitations

Practical upper limit of method is approximately 10 to 20 meters, depending on near-surface conductivity.
Interpretation produces nonunique results.
Sensitive to interference from linear conductors such as power lines, fences, or pipelines within distances of one or two times the depth of investigation from the transmitter loop.

Metal Detectors. Metal detectors are essentially specialized FDEM or TEM devices designed to find buried metal objects. The FDEM instruments use the high response of metal objects to distinguish them from natural materials. TEM instruments take advantage of the relatively long duration of the eddy currents induced in metal bodies. In most instruments, the depth of penetration is related to the coil size, transmitter frequency, and the surface area and shape of the metal target. The depth of penetration is generally unaffected by soil type over the conductivity range of typical soils. The instruments have high lateral resolution, but the vertical resolution of the depth of the target is generally limited.

Applications

Ease of use.
Very portable.
High lateral resolution.

Limitations

Limited depth of investigation.
Response of target related to the surface area of the target rather than the volume of metal.

Ground Penetrating Radar. GPR uses a high-frequency pulse of EM energy to probe the subsurface. The EM energy is reflected off boundaries of contrasting dielectric constant (the ability of a material to separate an electric charge), so the instrument can find nonmetallic or metallic

targets. The output is a time versus amplitude plot that is generally displayed as a series of plots along a transect line. The field plots are analogous to cross sections, except that the vertical access is in two-way travel time, not depth. The data can be processed similarly to seismic reflection data to produce depth sections. The instruments are configured with single transmitter/receiver antennas or with separate transmitter and receiver antennas that can be offset to collect data at different separations to increase the data processing that can be conducted. Under ideal conditions, the GPR method provides very high-resolution images of buried bodies, stratigraphic structure, or areas of disrupted soils.

The penetration of the method is determined by the conductivity of the subsurface and the degree of scattering from rubble or other small targets. Penetration is severely limited in highly conductive soils or in areas with lots of buried rubble or other discontinuous reflectors. The depth of penetration can be increased to some degree by using a lower frequency antenna but at the cost of resolution of the target.

Applications

Resolution can be of the order of a few centimeters.
Provides a cross section of subsurface in the field.
Can detect buried, ferrous or nonferrous targets.
Can detect disturbed soil zones.
Sophisticated data processing techniques available (similar to seismic reflection processing).

Limitations

Equipment is somewhat cumbersome; usually requires a relatively flat surface.
Depth of penetration is seriously limited by conductive material such as clay or water. Penetration through moist clay can be less than 1 foot.
Decreasing transmitter frequency to increase penetration decreases resolution.
Penetration and resolution limited by scattering effects at sites with buried cobbles or rubble.

Geothermal Techniques

The geothermal method uses soil temperature measurements to detect zones of anomalous flow at depth. Soil temperature is measured by using a shallow probe driven a few feet below the surface or a dedicated monitoring probe installed in a shallow borehole. Surface temperature variations diminish with depth below the surface. Daily temperature variations penetrate less than 1 or 2 meters, whereas seasonal temperature variations generally penetrate only about 10 meters. Below a depth of a few meters, soil temperature variations are largely a function of heat flow from within the earth. On a local scale, variations in heat flux often indicate zones of anomalous groundwater flow. Geothermal methods have been used to find permeable zones at depths of a few meters to over 100 meters using probes at depths of less than 1 meter to approximately 15 meters. A principal advantage of the method is that it detects anomalous flow instead of some other less directly related property, such as electrical resistivity. The method is susceptible to thermal interference by infiltration from shallow sources or from small features near the probes.

Applications

Identifies areas of high groundwater flow such as bedrock fractures or clean sand and gravel deposits.
One of the few methods that can directly detect moving groundwater from the surface.
Can pinpoint location of maximum permeability.
Can detect permeable features at depths of more than 100 feet beneath probes.

Limitations

Requires relatively uniform soils above target interval.
Small sand lenses near probes can create false anomalies or mask deeper anomalies.
Interpretation is qualitative.
Probe installation is relatively labor-intensive.

GROUNDWATER GEOPHYSICS—BOREHOLE METHODS

Most of the geophysical measurements made at the surface can also be made in a borehole using sensors lowered down the hole on a cable connected to up-hole recording equipment. Borehole measurements tend to be more accurate and precise because the borehole environment tends to be more predictable and less prone to noise. The field of measurement is typically only a few inches to a few feet around the borehole. Due to the small scale of the measurement, borehole methods tend to produce excellent vertical resolution. The combination of high resolution and greater accuracy make most borehole methods suitable for quantitative measurements and small-scale correlation of stratigraphic properties.

Borehole measurements are commonly used to determine the physical properties of the formation and formation fluids. The measurements can be used to measure directly or interpret several properties such as lithology, porosity, water quality, borehole diameter or alignment, borehole flow, formation or fluid temperature, mineralogy, and other properties of interest.

A variety of logging tools are available. Each tool has specific requirements for the borehole environment. Some tools can measure through casing; most cannot. Some tools require a fluid-filled hole; others operate in air, water, or drilling mud.

Electrical Logs

Spontaneous Potential Log. The SP log measures the electrical potential between a surface reference electrode and an exposed electrode that is raised up or down the borehole. The SP response is caused by a difference in resistivity between the borehole fluid and the formation fluid.

Applications

Quick and inexpensive.
Can be a good sand versus shale indicator.
Can be used to estimate total dissolved solids (TDS) of formation fluid.

Limitations

If borehole fluid and formation fluid have similar resistivity (typical for a water well), there is no SP response.
Works only in uncased fluid-filled boreholes.

Single Point Resistance Log. The SPR log measures the resistance between a grounded surface electrode and an electrode that is moved up or down the borehole. The tool measures the resistance of the total thickness of the formation between two electrodes. As a result, the measurement is in units of resistance, which is not a material property. The log is used primarily to detect changes in the formation but is not appropriate for quantitative analysis of the physical properties of the formation or the formation fluid.

Applications

Quick and inexpensive.
Good indicator of formation contacts.

Limitations

Measures resistance, not resistivity.
Works only in uncased fluid-filled boreholes.

Resistivity Log. Resistivity logs use two or more potential electrodes in the borehole to measure the change in potential difference along the borehole across a fixed electrode separation. Both current electrodes can be located on the down-hole sonde, or more commonly, one current electrode is on the sonde, and the other is planted at the surface. The depth of penetration of the current can be controlled by using different electrode spacings. Typically, a short electrode spacing is used to provide a high-resolution measurement of formation changes, and one or more longer electrode spacings are used for more accurate measurements of the bulk formation resistivity. Some sondes use additional current electrodes to focus the electrical field into the formation. The data can be corrected for borehole effects to provide a quantitative measurement of the bulk formation resistivity which is a function of the resistivity of the formation and formation fluid.

Applications

Measures bulk resistivity of formation.
Can be used to determine the formation lithology, porosity, and fluid resistivity.

Limitations

Works only in uncased fluid-filled boreholes.

Induction Log. Induction logs use a frequency domain electromagnetic (EM) sonde to measure the conductivity of the formation around the borehole. Some tools include a short spacing electrode tool to measure the conductivity of the borehole fluid independently.

Applications

Can be run in fluid-filled or air-filled borehole.
Can be run in open hole or through PVC casing.
Can be run with shallow or deep depths of investigation (dual induction) to determine the invasive effects of borehole fluids.

Limitations

More expensive than electrode logs.
Response of highly resistive materials (freshwater aquifers) is small, so the sensitivity of the tool is reduced.
Cannot be run in highly conductive borehole fluids.

Passive Radioactivity Log

Natural Gamma Log. Natural gamma logs use a sensor that measures the gamma-ray energy emitted by the formation. In most formations, gamma-ray emissions are almost entirely produced by shale minerals. As a result, the gamma-ray response is a good indicator of the concentration of clay in the formation.

Applications

Good clay indicator
Can be run in cased or uncased, fluid-filled or air-filled boreholes.

Limitations

Gamma-ray units (API units or counts per second) are arbitrary units and do not relate directly to clay mineral content.
Raw data must be corrected for borehole diameter effects before making direct comparisons.

Spectral Gamma Log. A spectral gamma log separates gamma-ray energy by frequency to measure the spectrum of gamma rays emitted by the formation. The frequency spectrum of gamma rays emitted by the formation is diagnostic of the radioactive isotopes in the formation.

The gamma-ray spectrum is commonly used to determine the concentrations of potassium, uranium, and thorium in the formation (KUT logs), but full spectrum tools are available that allow identifying additional elements.

Applications

Can be used to perform "complex formation analysis," where the mineral content and groundwater flow history of formation are estimated.
Can be used to detect uranium or radium-enriched zones of sandstone aquifers.
May have application to radioactive contamination problems.

Limitations

Equipment is significantly more expensive than natural gamma tools.

Porosity Log

Several logging tools have been developed to measure the porosity of a formation. Porosity is a useful property

to measure, but it does not always relate directly to permeability, which is generally the property of greatest interest. If more than one porosity tool is used, the data can be cross-plotted to identify formation type directly and correct the porosity measurement for lithologic effects. Most porosity tools require the use of a radioactive source in the tool. The use of radioactive sources requires special licensing and is prohibited in water wells in some states. The following sections describe the most common types of porosity tools.

Neutron Density Log. Neutron density logs use a radioactive source to bombard a formation with high-energy neutrons and records gamma-ray energy "bounced back" from the formation. The tool measures the hydrogen content of a formation, which is equivalent to the water content of the formation if no hydrocarbons are present. The water content of the formation is equivalent to the porosity below the water table and the soil moisture content above the water table. Some tools do not compensate for changes in borehole diameter and produce erroneously high estimates of porosity in washouts in the borehole. Compensated tools can accommodate some degree of variation in borehole diameter, but erroneous data can be recorded in zones with rough borehole walls. Bound water in shale zones produces erroneously high values of measured porosity.

Applications

Directly measures water content of formation. Can be related to porosity of nonshale units.
Measures porosity below water table and moisture content above water table.
Can be run in a cased or uncased hole.

Limitations

Sensitive to variations in borehole diameter.
Will see "bound water" in shale zones as porosity and give unrealistically high values.
Presence of hydrocarbons (pure product) erroneously suppresses calculated porosity.
Stringent licensing requirements to make a log due to the radioactive source.
Application to cased holes is limited.

Gamma Density Log. Gamma density tools use a radioactive source to bombard a formation with high-energy gamma rays. The tool has a sensor that records gamma rays "scattered" back to the detector. The magnitude of the backscattered gamma rays is a measurement of the electron density of formation that is related directly to bulk density. Given a bulk density measurement, the formation porosity is calculated for an assumed rock matrix (sandstone or limestone).

Applications

Will record accurate porosity values in shale zones.
Can be run in cased or uncased boreholes.

Limitations

Sensitive to variations in borehole diameter.
Presence of hydrocarbons causes erroneously high porosity values.
Stringent licensing requirements to make a log due to the radioactive source.

Sonic Log. Sonic logs use a source of high-frequency sound and one or more detectors on the down-hole sonde to measure the transit time of sound across a known distance of the formation. By comparing the measured velocity of sound in the formation to the known sound velocity for the rock type, the percentage of void space (porosity) can be calculated. Sonic tools do not require a radioactive source. The measurement is sensitive to irregular hole conditions. Specialized versions of the tool record the full waveform of the sound energy transmitted and can be used to detect poor bonds between the casing and grout or find voids behind the casing.

Applications

Porosity can be calculated for a given matrix (sandstone or limestone).
Modified sonic log can be used to inspect the bond of the cement grout to the casing (cement bond log).
Full waveform sonic logs can be run to measure the engineering properties of the formation.

Limitations

Sensitive to borehole diameter and roughness of borehole wall.
Works only in a fluid-filled uncased hole (except the cement bond log).

Borehole Condition Log

Several types of logs have been developed to measure the physical condition of the borehole, rather than measuring the properties of the surrounding formation. These tools can be used to determine the integrity of a borehole, determine if the hole is straight, or determine if flow is occurring between different zones. The following section describes several of the more common logs.

Down-Hole Televising Log. Down-hole televising logs use a down-hole video camera to inspect a borehole visually. Most cameras provide a fish-eye, forward-looking view with a depth reading on the image. Some cameras offer a side-looking view that looks directly at the borehole wall and can be rotated 360°.

Applications

Produces a visual record of a well bore on VCR tape or DVD.
Can be used to inspect borehole irregularities or obstructions.
Can be used to inspect the casing.
Can be used to detect fractures or solution cavities.
Shows small-scale stratigraphic layering with more resolution than other logs.

Valuable tool in assessing options to recover lost logging tools or drilling equipment.

Limitations

Requires clear borehole fluid. May have to add clear water to flush the hole if the water is cloudy.
Produces a qualitative record. Does not measure any physical property in calibrated units.
Most tools do not provide an oriented image.

Caliper Log. Caliper tools use spring-loaded arms that scrape along the borehole wall to record the variation in diameter. Simple tools that use two arms tend to turn so that the tool always measures the maximum hole diameter. Three-arm tools average the diameter at three points and provide better measurements of the average hole diameter. Four-arm caliper tools are available that provide oriented independent measurements in two coordinates in the horizontal plane that provide additional information on the shape of the hole.

Applications

Can identify ledges or washouts that can identify incompetent zones or fractures.
Can be used to calculate volumes of grout or backfill.
Can be measured in x and y planes (four-arm caliper) to estimate the shape of the borehole.

Limitations

Two-arm caliper measures only maximum hole diameter. Can be misleading in elliptical boreholes.
Does not measure alignment of borehole.

Alignment Log. Alignment tools measure the deviation of the center of the borehole from vertical. Simple alignment tools use a weighted plumb bob suspended from a tripod. The deflection of the plumb bob is measured by crosshairs at the surface. More sophisticated alignment tools use cameras with targets mounted on a system of gimbals or gyroscopes and magnetometers to measure the deviation of the borehole.

Applications

Can identify deviations in a borehole that can limit the size of the casing or pump that can be installed.
Can be used to calculate actual well depth and actual lateral position of a borehole.

Limitations

Must be combined with a caliper log to determine the shape of the hole accurately.
Large washouts can cause erroneous alignment readings unless the diameter of the hole is taken into account.
Sharp doglegs or extreme deviations can cause a surface line to "hold up" on the side of a borehole for simple tripod and crosshair systems and make measurements from below impossible.
Alignment tools that use magnetometers do not work inside a metal casing.

Acoustic Televiewer. Produces a high-resolution image of a borehole wall using a high-frequency sonic tool that is rotated to scan the hole. The log produces an image that shows relief on the borehole wall as shading or color patterns. Standard log formats show the borehole wall from 0 to 360° on the horizontal axis and depth on the vertical axis. The tools are generally oriented with respect to true directions. Televiewer logs are often used to map fractures and plot their strike and dip. The tool requires a fluid-filled hole, but water can be added to raise the water level artificially for logging.

Applications

Can measure the aperture, strike, and dip of fractures.
Can operate in either mud- or water-filled boreholes.

Limitations

Does not operate in air-filled holes.
Measures only the surface of the borehole; does not penetrate scale or casing.
The resolution of the tool is limited to several millimeters by the wavelength of the sonic source.
Scrapes or washouts from the drilling process can obscure true fractures.

Optical Televiewer. Produces a high-resolution image of the borehole wall using an optical scanning tool that is rotated to scan the hole. The log produces an image of the borehole wall in true color. Standard log formats show the borehole wall from 0 to 360° on the horizontal axis and depth on the vertical axis. The tools are generally oriented with respect to true directions. Optical televiewer logs are often used to map fractures, plot their strike and dip, and image small-scale stratigraphic features. The tool requires a clear borehole, either air or clear water.

Applications

Can measure the aperture, strike, and dip of fractures.
Can image individual grains and other fine stratigraphic features.

Limitations

Does not operate in mud-filled holes, cloudy water, or dusty air-filled holes.
Measures only the surface of the borehole; does not penetrate scale or casing.
Scrapes or washouts from the drilling process can obscure true fractures.

Flowmeter Log. Flowmeter tools are used to measure the flow within a borehole that develops from head differences between different zones or while pumping. Spinner tools are simple flowmeters that use small impellers to measure the flow past the tube. The tools are usually trolled up or down the borehole to overcome the frictional resistance of the impeller and its bearings.

For stronger flows, the tool can be held stationary to measure the absolute flow velocity past the tool without correcting for the speed of the tool in the borehole. Heat pulse tools can be used to measure lower flow rates. Heat pulse tools use a heating element to create a small pulse of heated water, and temperature sensors are placed at known distances above and below the heating element. The tool measures the time required for the pulse of heated water to move upward or downward to the sensor and calculates the flow velocity and direction. A modification of the heat pulse flowmeter has been used to measure horizontal flow in boreholes. The diameter of the hole must be known before the flow velocity can be converted into a volumetric flow rate. Specialized tools have been developed to detect flow behind a casing.

Applications

Can measure the flow up or down a borehole.
Can be used to estimate the head difference and transmissivity of different zones of a borehole.

Limitations

The friction of the bearings and inertial mass of the impeller impose a lower limit of flow that can be measured by a spinner tool.
Heat pulse tools have an upper limit of flow rate that can be accurately measured.

Temperature Logs

Down-Hole Temperature Log. Temperature logs use down-hole thermistors or thermocouples to measure the variation in the temperature of the borehole fluid with depth. Temperature variations in the hole can be used as indicators of flow. The data can be plotted as absolute temperature or as a differential temperature that removes the effect of the geothermal gradient from the plot.

Applications

Provides direct measurement of fluid temperature.
Can be used to detect zones of increased fluid flow within a borehole or between two boreholes.
Directly measures the geothermal gradient.

Limitations

Geothermal gradient causes a continuous drift in borehole temperatures that can mask thermal variations within the borehole.
Requires temperature and head variations between units to create a thermal anomaly to detect permeable zones within a borehole.
Flow within a borehole during or after drilling can mask geothermal gradient measurements.

GEOPHYSICAL SURVEY DESIGN

When designing a geophysical survey, several factors must be considered, including the physical properties of the target, the desired resolution, the physical properties of the matrix around the target, the ambient noise in the survey area, and the physical access at the site. To be detected, the feature you are trying to find must have some physical property that has sufficient contrast with the surrounding matrix. A variety of physical properties can be remotely sensed by geophysical methods. Some targets, such as buried pipes in sand, present obvious contrasts of a number of properties. Some targets, such as excavations backfilled with native soils, present less obvious contrasts or can be identified only by contrasts of related features, such as disruption of macropore drainage structures causing perched soil moisture over old graves.

Geophysical methods each have characteristic resolution limits that are a function of the wavelength of the fields used for measurement and the limitations of the equipment. The resolution of the various geophysical methods varies from several tens of feet for deep studies using electromagnetic induction methods to fractions of an inch using ground penetrating radar with high-frequency antennas. The resolution of the geophysical method used must match the physical dimensions of the target body if the target is to be detected. The magnitude and size of the anomaly must be predicted with reasonable accuracy, typically by forward modeling, to determine the minimum grid size that can be used for a reasonable probability of detection.

Site conditions also play an important role in determining the ultimate success of the survey. Surface and subsurface conditions can create a noisy environment that can easily obscure the signal from the target body. Noise sources are different for each method. For instance, ground vibrations from traffic or machinery can be a major source of noise for seismic or gravity methods but do not affect other methods such as electromagnetic induction or magnetics.

Physical conditions at a site also affect the utility of geophysical methods. Major obstructions such as buildings or developed land often limit the area where data can be gathered and create inherent limitations on the geophysical survey. Buildings, parked cars, dumpsters, overhead power lines, buried utilities, fences, buried rubble, and other cultural features are not often considered when designing a geophysical survey. In addition, subsurface conditions such as soil type, uniformity, and other factors affect the propagation of energy and can limit the performance of most methods. Surface conditions, such as paved surfaces, heavy vegetation, frozen ground, rough topography, and surface debris, must be considered when designing a survey.

Assuming that the site conditions are acceptable, it is still necessary to select a method that can detect the target body. The following is a partial list of typical survey objectives with some suggestions of methods to consider.

1. Locating optimal well locations (bedrock fractures or sand and gravel deposits)
   a. EM
   b. Electrical resistivity

c. Azimuthal EM
d. Azimuthal resistivity
e. Geothermal

2. Determining depth to bedrock and mapping bedrock surface
   a. Seismic refraction
   b. Gravity
   c. Seismic reflection
   d. GPR
3. Locating preferred pathways for groundwater flow (bedrock fractures, voids, seepage paths, or sand and gravel lenses)
   a. EM
   b. Electrical resistivity
   c. Azimuthal EM
   d. Azimuthal resistivity
   e. Geothermal
   f. SP
   g. GPR
4. Finding buried metal bodies (tanks, drums, Buicks, etc.)
   a. Magnetometer
   b. Electromagnetic induction (EM)
   c. Ground penetrating radar (GPR)
   d. Metal detectors
5. Mapping conductive ground water plumes (inorganics in the range of hundreds of ppm)
   a. EM
   b. Electrical resistivity
   c. GPR
6. Mapping continuity of till sheets or clay layers
   a. Seismic refraction
   b. EM
   c. Electrical resistivity
   d. Seismic reflection
7. Determining the lateral extent or thickness of refuse
   a. EM
   b. Electrical resistivity
   c. Magnetometer
8. Detecting fractures in tills
   a. Azimuthal EM
   b. Azimuthal resistivity
9. Finding abandoned well casings
   a. Magnetometer
   b. EM
10. Detecting voids
    a. Gravity
    b. GPR
    c. Resistivity
11. Direct detection of hydrocarbons
    a. GPR (LNAPLS, DNAPLS, or biodegrading plumes)
    b. Electrical resistivity (biodegrading plumes)
    c. Induced polarization (bound only to clay)

GEOTHERMAL WATER

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Geothermal water has a temperature appreciably higher than that of the local average annual air temperature. However, in general, a spring is considered hot when its temperature is about 12.2 °C higher than mean annual ambient temperature (1). The relative terms geothermal water, warm springs, and hot springs are common.

From earliest times, hot geothermal water or geothermal springs have been used for bathing and cooking. The first technological success in using geothermal energy was in Italy in 1904 where the worlds first geothermally driven electrical plant was opened and operated. Today, applications of low- and moderate-temperature (100 to 300 °F) geothermal waters have expanded enormously to include heating large tracts of homes and buildings (district heating), heating greenhouses for growing vegetables and flowers, fish farming (aquaculture), drying foods and lumber, and many other uses. In the United States alone, there are 17 district heating systems, 38 greenhouse complexes, 28 fish farms, 12 industrial plants, and 218 spas that use geothermal waters to provide heat. The district heating system in Boise, Idaho, has been operating since the 1890s and continues to provide heat today. In Iceland, most of the homes and other buildings are connected to geothermal district heating systems, and in the Paris basin in France, many homes are heated by bringing geothermal water to the surface. Geothermal greenhouses are prominent in Italy and in the western United States.

Worldwide, there are about 12,000 thermal megawatts of installed direct uses of geothermal fluids in nearly 30 countries, replacing the combustion of fossil fuels equivalent to burning 830 million gallons of oil or 4.4 million tons of coal per year. This illustrates the trend of countries switching to alternative energy sources such as geothermal energy.

Geothermal water discharges from numerous springs located mostly in mountainous or plateau areas. The springs are connected by faults to deeply buried reservoirs that contain geothermal water, which moves upward along the fault zones to discharge at the land surface. Much geothermal water discharges as hot springs that flow steadily instead of erupting at intervals.

Hydrothermal phenomena involving the release of water and steam are nearly always associated with volcanic rocks and tend to be concentrated in regions where large geothermal gradients occur. By implication, aquifers must also be present that permit water to percolate to great depths—often 1500 to 3000 m (2). One theory used to explain how geothermal water becomes heated in areas that are underlain by complex geologic structures is that when precipitation falls in highland areas, it recharges the aquifer system. Some of the water moves downward along faults and fracture zones to great depths. As the water descends, it becomes heated because of the geothermal gradient. At some depth, the heated water becomes lighter

than the overlying water and then moves upward along faults to discharge as spring flow.

Deeply circulating groundwater can also become heated by cooling magma (molten igneous rock) at great depths in the crust of the earth. The water warms as it descends, possibly along fault zones that overlie the magma chamber, until it absorbs enough heat to become lighter than overlying water. The warm water then rises to the surface. The mechanism for circulating the water is the same, regardless of whether the water becomes heated by the geothermal gradient or by the buried cooling magma. It can also be heated through mantle decay of radioactive elements such as U, Th, and Ra, tectonic activity, metamorphic processes, and exothermic reactions of minerals.

More than 10,000 individual thermal features, including geysers, hot springs, mud pots, and fumaroles (steam vents), have been identified. Geysers are the best known and certainly the most spectacular features. They are a type of hot spring that periodically emits sudden, violent eruptions of stream and hot water. Water from surface sources and/or shallow aquifers drains downward into a deep vertical tube where it is heated above the boiling point. As the pressure increases, the steam pushes upward; this releases some water at the surface, which reduces the hydrostatic pressure and causes the deeper superheated water to accelerate upward and to flash into stream. The geyser then surges into full eruption for a short interval until the pressure is dissipated; thereafter, the filling begins, and the cycle is repeated (2). The explosive release of pressure can cause a column of steam and hot water to rise 200 feet or more into air. The period between eruptions depends on several factors, including the volume of steam and water that is ejected and how rapidly ground water refills the tubes and chambers. A mud pot, results when only a limited supply of water is available. Here, water mixes with clay and undissolved particles brought to the surface, forming a muddy suspension from the small amount of water and steam that continues to bubble to the surface. A fumarole, meaning smoke, is an opening through which only steam and other gases such as hydrogen sulfide and carbon dioxide discharge. These features are normally found on hillsides above the level of flowing thermal springs; water can often be heard boiling underground (3).

Excessive concentration of certain dissolved minerals in geothermal water poses water quality problems. The most common of these minerals are dissolved fluoride, arsenic, and iron. Concentration of dissolved fluoride in excess of 4 milligrams per liter can cause mottling of teeth, especially children's, and can cause bones to become brittle. Dissolved iron is not detrimental to human health, but concentrations in excess of 200 micrograms per liter can cause staining of kitchen and bathroom fixtures and can cause clogging of well-screen openings and pumps. Concentrations of dissolved arsenic in excess of 30 micrograms per liter are toxic to humans. Sodium, calcium, magnesium, and their salts are nontoxic to human beings. Chloride salts of these metals in higher concentrations may be toxic to plants because of their chloride ions rather than the metals. A chloride ion concentration of >300 mg/L is in general toxic to vegetation and results in defoliation, chlorosis, bronzing, and burning of plants (4). Boron in trace quantities is necessary for plants, but it is toxic to certain plants in concentrations as low as 1 to 2 mg/L.

Natural steam that always contains some noncondensable gases, such as hydrogen sulphide, and ammonia, presents the greatest potential hazard. Ammonia affects primarily the upper respiratory tract and causes coughing, vomiting, and redness of the mucus membranes of the mouth, nose, lips, and pharynx (4). In geothermal operations, ammonia is not likely to present a direct toxic hazard except possibly in the immediate vicinity of the power plant. Hydrogen sulphide, which is a noticeable geothermal effluent, is much more toxic than commonly realized. A concentration of more than 600 ppm hydrogen sulfide can cause death within 1 hour. It can also paralyze the respiratory center.

High values of total dissolved solids in geothermal water sometimes interfere with the usefulness of water as a source of energy. Rain, the prime source of meteoric water, which feeds the geothermal reservoir, is practically devoid of chemical ingredients. But after entering the atmosphere, it picks up gases such as CO_2, O_2, SO_2, and dust particles. As it falls to the ground, its concentration of chemical constituents may be up to 40 mg/L (5). Other important factors are climatic conditions and the state of weathering of rocks and their mineralogical compositions. Thus, even before entering the geothermal reservoir, water is considerably rich, chemically. Groundwaters whose salt content is around 1000 mg/L are not uncommon. The major cations in groundwater are Ca, Mg, Na, and the anions are HCO_3, SO_4 and Cl. Geothermal water commonly contains large concentrations of silica (if the water has moved through limestone or other calcite-rich rocks).

Along with these radicals, gases dissolved in meteoric water such as CO_2, O_2, He, and Ar also enter the reservoir. The chemistry of meteoric water is modified in the geothermal reservoir due to rock–water interaction under the influence of temperature, contributions from magmatic sources, mixing of different types of waters, and decay of U, Th, and Ra. Closer to the surface, within the zone of oxidation, air can also enter thermal waters. In that case, the nitrogen and oxygen content will be high, and their mutual ratio may also match that of the atmosphere. Some geothermal waters may be brines, for example, the Salton Sea area, California, whose salinity is 30% (6); others may be as pure as distilled water, for example, the Rajgir thermal spring of Bihar, India (7).

Microorganisms can thrive in geothermal waters, even at boiling temperature (8). Extremely thermophilic bacteria that survive at 350 °C have also been found (9). Fortunately, these microorganisms do not survive in animal systems. Pathogenic organisms can enter thermal waters through soil and air and also through contamination by animal/man in thermal water pools. Thermal springs of various kinds are found throughout the world. Notable areas exist in the United States, Iceland, New Zealand, the Kamchatka Peninsula of the former Soviet Union, Brazil, Argentina, Ethiopia, Zambia, China, Tibet, India, Thailand, Taiwan, and Japan. Yellowstone National Park in Wyoming, United States, that contains literally thousands of hydrothermal features possesses the greatest

concentration of thermal springs in the world (10). This area marks the site of an enormous volcanic eruption 600,000 years ago. Today, a temperature of 240 °C exists only 300 m below the ground surface.

As economies expand and population grows, energy demand worldwide is increasing rapidly. If we are to increase our energy consumption while simultaneously reducing environmental pollution, we must change our fuel mix, which today relies heavily on fossil and nuclear fuels. The use of geothermal energy has enormous environmental advantages over the use of fossil or nuclear fuels. Among these advantages are far fewer and more easily controlled atmospheric emissions, maintenance of groundwater quality, and much smaller dedicated land requirements. The small quantities of gases emitted from geothermal power plants are naturally occurring and result from geologic processes. Because the earth is porous and permeable, these gases would eventually find their way to the surface, even in the absence of geothermal power development.

BIBLIOGRAPHY

1. Alfro, C. and Wallace, M. (1994). Origin and classification of springs and historical review with current applications. *Environ. Geol.* **24**(2): 112–124.
2. Todd, D.K. (1995). *Ground Water Hydrology*. Wiley, Toronto, Canada, p. 51.
3. Poland, J.F. (1972). *Glossary of Selected Terms Useful in Studies of the Mechanics of Aquifer Systems and Land Subsidence due to Fluid Withdrawl*. U.S. Geological Survey Water-Supply Paper 2025, p. 9.
4. Pandey, S.N. and Srivastava, G.C. (1996). In: *Environmental Hazards of Indian Geothermal Fields*. U.L. Pitale and R.N. Padhi (Eds.). *Geol. Surv. India*, Spl.Vol. 45, pp. 375–378.
5. Hawkes, H.E. and Webb, J.S. (1962). *Geochemistry in Mineral Exploration*. Harper and Row, New York.
6. Werner, H.H. (1975). Contribution to mineral extraction from superheated geothermal brines, Salton Sea Area, California. *Geothermics* **2**: 1651–1657.
7. Geological Survey of India Special Publication. (1991). Geothermal Atlas of India, p. 106.
8. Yun, Z. (1986). Thermophilic microorganisms in the hot springs of Tengencheng geothermal area, West Yunan, China. *Geothermics* **15**: 347–358.
9. Baross, J.A. and Dening, J.W. (1983). Growth of "black smoker" bacteria at a temperature of at least 250 °C. *Nature* **303**: 423–426.
10. Keefer, W.R. (1971). *The Geologic Story of Yellowstone National Park*. U.S. Geological Survey Bull. Publ. No. 1347, p. 92.

GHIJBEN–HERZBERG EQUILIBRIUM

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THE ORIGINAL PAPERS

In 1889 a note was published in The Hague (The Netherlands), which dealt with a suitable location for a new borehole for the pumping of drinking water for the city of Amsterdam. The authors, Drabbe and Badon Ghijben (1), outline in length the different geological formations, their extension and their connection with each other, and especially their connection with various saline surface water bodies in that region. In the final part, salinity becomes the subject of their consideration. The authors describe that saltwater is found in the subsurface, when there is a hydraulic gradient from the surface water into the aquifer and contrast this to the situation in the dunes at the North Sea coast. There, a freshwater lens can be observed on top of the salt water. In one sentence, the topic of this contribution can be summarized: If the height of the groundwater table above the mean sea level is denoted by a, the equilibrium between saltwater and freshwater is reached at a depth of $a/0.0238 = 42a$, when the seawater weight exceeds the freshwater weight by a factor of 1.0238. A simple calculation example follows using the given formula and a reference to an even earlier communication of Conrad in 1881, who is cited to have used factors between 40 and 50 in analogy to the proposed 42.

Twelve years later, the other note (2) appeared, in which the Ghijben–Herzberg equilibrium (GHE) is named. Herzberg, an engineer from Berlin (Germany), in a talk in Vienna on behalf of the annual meeting of the German Association of Gas- and Water-Specialists, was concerned with the water supply of villages on the German North Sea coast. More specifically, he was interested in the water supply on the North Sea islands, which, due to a rise in tourism, had an increasing demand for drinking water in the summer season. Compared with his Dutch counterpart, Herzberg provided a much more detailed derivation of the equilibrium rule. In order to illustrate his arguments, Herzberg presented a figure, which is reproduced in Fig. 1.

In Herzberg's version, t denotes the elevation of the groundwater table above mean sea level and is thus identical to Badon Ghijben's a; h is the depth of the freshwater boundary below mean sea level. A saltwater column of length h has the same weight as a freshwater column of length $H = t + h$, when the condition

$$h \cdot 1.027 = h + t \tag{1}$$

is fulfilled, and when it is taken into account that the specific weight of saltwater exceeds that of freshwater by a factor of 1.027. Solving Eq. 1 for h delivers

$$h = 37t \tag{2}$$

In both studies it is shown that a wide freshwater lens is to be expected in coastal regions. The extension of this length is roughly 40 times the elevation of the groundwater table above the seawater level. For practical purposes—the authors' main concern was water supply—one conclusion is that quite a large amount of fresh groundwater is available, as the lens extends much deeper into the subsurface than above the seawater horizon. Another conclusion is that the occurrence of freshwater at greater depth does not rely on the existence of an additional freshwater source in deeper horizons.

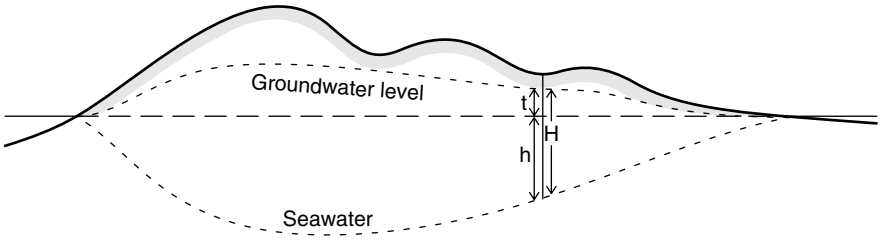


Figure 1. Illustration concerning the freshwater–saltwater equilibrium. Adapted from Reference 2.

Following the Ghijben note, a strong dispute took place in the beginning of the twentieth century in The Netherlands with respect to the maximum amount of pumping by the water works, as reported by de Vries (3). Proponents of the GHE argued in favor of such a regulated maximum.

In both publications the density difference is recognized as the major factor concerning the conditions of subsurface water near the sea coast. Freshwater is lighter than saltwater, and in order to reach an equilibrium (i.e., equal pressure), the freshwater column must extend further into the subsurface. The general situation with freshwater salinity ρ_f and water of elevated salinity ρ_s in the deeper subsurface, in current formulation, would be written as

$$h_f = -\frac{\rho_s - \rho_f}{\rho_f} z \tag{3}$$

where h_f denotes the elevation of freshwater above sea level, while z measures the depth of the interface below that level. As both extend in different directions from the zero sea level, they have different signs.

The equilibrium formulas given above can be taken as rule of a thumb. In most textbooks the formula is used with a factor of 40. The deviation of the factor in the formulation of Badon Ghijben (42) from the one given by Herzberg (37) stems from different assumptions concerning the relative weight of saltwater in relation to the freshwater. According to current knowledge, the density of seawater ρ_s lies between 1.02 and 1.029 g/m^3, depending on salinity and temperature. For a mean salinity of 35 ppt and a temperature of 10 °C (typical for subsurface water), the density is 1.027 g/m^3 (4), which is the value used by Herzberg. In real situations, it has to be taken into account that, due to mixing, dissolution, or precipitation, the subsurface saltwater may have a different salinity than seawater and that freshwater may have a slightly elevated density too.

CONDITIONS

The Ghijben–Herzberg equilibrium (GHE) has proved to be valid in several coastal systems all around the world. In both original publications, correspondence with observations is stressed. Herzberg describes that he already used the equilibrium formula for predictions concerning the depth of the saltwater in the sandy subsurface of several North Sea islands and that he obtained a good confirmation of the rule by measurements in boreholes. De Vries (3) lists field measurements and laboratory experiments, performed by Pennink in The Netherlands at the beginning of the twentieth century. However, the formula is linked to several conditions.

In the derivation it is assumed that the transition from the fresh to saline water appears quite rapidly. When the scale of the transition zone is very small in relation to the scale of the depth of the aquifer, one speaks of a *sharp interface*, which is a common term in the current literature; see, for example, Reference 5. One condition for a sharp interface is small dispersion, more specifically small transverse dispersion, as the flow direction coincides more or less with the interface (see below). But the tides and seasonal fluctuations in groundwater recharge and/or in the amount of groundwater being withdrawn also have an influence on the width of the transition zone. Extended descriptions have been derived nowadays, which are valid for situations with transition zones (see below).

Herzberg demanded caution concerning the transfer of his results obtained for the islands to cities near the coast, pinpointing the different scale, especially concerning the water supply. In a remark to Herzberg in Vienna, Halbertsma, another Dutchman, stated that the situation along the Dutch coast is quite different from one place to the other, but in some parts it is very similar to the situation described by Herzberg. As a counterexample he reports a situation where a confining impermeable clay layer can be found near the surface, which separates the freshwater on top from the saline water.

Custodio (6) illustrates several different situations, concerning the position of one or more clay layers, which disturb the ideal situation assumed for the GHE, showing that the GHE may over- or underestimate the position of the interface depending on local circumstances. In atoll islands a permeable layer below the upper strata of low hydraulic conductivity also results in a different situation, and the GHE can surely not be applied on coastlines of volcanic rock.

In the very vicinity of the coastline the GHE is mostly not valid. The GHE predicts that both fresh and saltwater heads (see below) should approach zero. But at many locations submarine groundwater discharge of freshwater has been observed (see Fig. 2). Kooi and Groen (7) provide an overview of the phenomenon and interpretations using different sharp-interface approaches.

The original formulation is given for phreatic aquifers and for the hydrostatic situation, that is, where flow in the freshwater zone as well as in the saltwater zone is neglected. Various different extensions have been made since the first formulations. Thus it is possible to use the generalizations of the Ghijben–Herzberg relation in situations for which the simple formula was not stated originally. In that sense, it is possible to use GHE as a

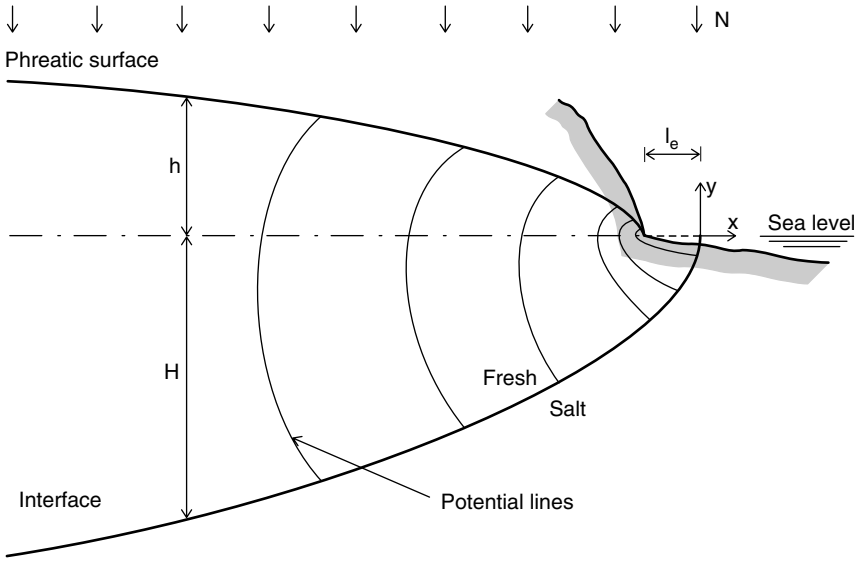


Figure 2. Schematic view of flow in an unconfined aquifer near the coast, describing submarine groundwater discharge. Adapted from Reference 12.

principle for confined aquifers, for dynamic situations, and for a dispersed transition zone, as described in the following.

When the amount of water withdrawal becomes a significant part of the entire water budget of a coastal system, the Ghijben–Herzberg formula should be questioned. Hydrostatics then has to be replaced by a quantification of the hydrological balance of the system.

GENERALIZATIONS

The original derivation assumes hydrostatic conditions, while the real situation is hydrodynamic in all cases. The authors were aware of that: in the report Badon Ghijben describes that under the North Sea dunes there is a relatively strong freshwater flow, recharged by infiltrating rainwater in the upper part, directed toward the sea, while there is a very weak flow of saltwater in the opposite direction in the lower part. In-between there is a transition from inflow to outflow.

However, the hydrostatic state can be taken as a limiting case from which the dynamic situation deviates only slightly as long as the groundwater velocities are small. The GHE idea of an equilibrium between freshwater and saltwater can then be transferred to dynamic situations. Hubbert (8) introduced the variable of *freshwater head*, defined as

$$h_f = \frac{\rho}{\rho_f} h - \frac{\rho - \rho_f}{\rho_f} z \tag{4}$$

where ρ and h denote density and head, measured at depth z. As outlined in the overview papers by Reilly and Goodman (9) and Cheng and Quazar (10), the freshwater head was used also by Muskat (11) in a description of the interface between oil and water in the subsurface. For $h = 0$ (stagnant saltwater) and $\rho = \rho_s$, the Ghijben–Herzberg formula (Equation 3) results for the interface position at depth z.

With the help of the freshwater head h_f, descriptions of situations with an interface can be simplified. A solution for freshwater head distribution is determined first; the location of the interface is calculated on the basis of the GHE afterward. This procedure is followed in many publications concerning different situations with fluids of different densities.

van der Veer (12) presents a simple formula for the one-dimensional flow in a coastal aquifer and a complex solution for flow in a vertical cross section, both based on the GHE. It is shown that distant from the shore both solutions coincide; that is, the use of the simpler solution is justified. But when the coastline is approached, the differences between both solutions increase. With the two-dimensional solution, it is possible to describe the submarine groundwater discharge into the sea.

Strack (13,14) uses the GHE and freshwater head to construct analytical solutions for shallow interface flow in confined and unconfined situations. In the case of the confined situation, the piezometric head h is the relevant variable, not the water table in the confined layer. Using these solutions the regional flow in coastal aquifers toward wells can be calculated in a two-dimensional horizontal domain.

The cross-sectional view, given in Fig. 3, depicting schematically the flow in the confined situation, is adapted from Strack (14). Due to pumping of freshwater in the upper part of the aquifer, the interface between saltwater and freshwater rises. Such an upconing may lead to severe problems, when the interface comes close to the well filter, as the salinity of the pumped water may increase above limits, which makes the water unsuitable for the drinking water supply, irrigation, or other purposes.

According to the static GHE, the interface rise exceeds the water table decline by a factor of 40 in coastal aquifers. Recent experience in Sweden shows that the GHE overestimates the rise of the interface (15). Dynamic approaches using well-known formulas for single wells were combined with the GHE by Wang (16) and by Motz (17). In regard to saltwater upconing, the GHE today

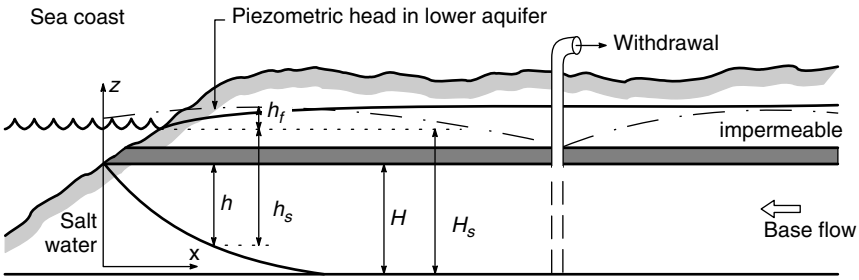


Figure 3. Schematic view of flow in a confined coastal aquifer with groundwater withdrawal. Adapted from Reference 14.

is often applied in combination with finite differences or finite elements (18,19).

The mentioned analytical solutions are valid for horizontal flow in an aquifer with a sharp interface, but vertical fluxes cannot be treated correctly by freshwater heads. As a further generalization of the GHE, Lusczynski (20) showed that for the general three-dimensional case in variable density flow, the gradients of freshwater head are responsible for horizontal groundwater flow, while for flow in the vertical direction the so-called environmental water head h_e is responsible. h_e is a generalization of Eq. 3:

$$h_e = \frac{\rho}{\rho_f} h - \frac{\rho - \rho_a}{\rho_f} z \tag{5}$$

where ρ_a denotes the average density in the column between position z and sea level.

Note that for the latter extensions of the GHE the condition of a sharp interface has been dropped. But with ρ_a another parameter is introduced, which cannot be estimated easily without any knowledge of the mean position of the interface: remember that the principal purpose of the Ghijben–Herzberg formula was to deliver an estimate for that position.

In fact, saltwater intrusion is a problem of density-driven flow (21), in which flow and transport processes are coupled and cannot be calculated independently. Naturally, the flow in the aquifer determines the salt distribution, but on the other hand the salinity influences the flow via density and possibly via viscosity.

In order to treat such complex interactions, computer models are often used today. An overview on numerical approaches, codes, and applications, concerning saltwater intrusion, is given by Sorek and Pinder (22). Henry (23) presented a widely discussed solution for the miscible displacement in a confined aquifer, which has been used by numerous modelers as a test case. Figure 4 represents the solution in a vertical cross section, calculated with the new FEMLAB code (24) for multiphysics simulations. Depicted are streamlines extending from the left freshwater boundary to the seawater boundary on the right-hand side. On the seaside, streamlines enter in the lower part and return to the seaside after a u-turn. Along the paths salinity changes due to dispersion and diffusion. The grey pattern visualizes salinity, which is high in the lower right corner.

The Henry solution and with it the penetration of the saltwater wedge and its dispersion depends on various flow and transport parameters: the ambient freshwater flow and the dispersivities—dependencies that cannot be predicted by the GHE, which is based on water densities only.

CONCLUSION

The history of the GHE offers some more peculiarities. According to Carlston (25), the static equilibrium condition

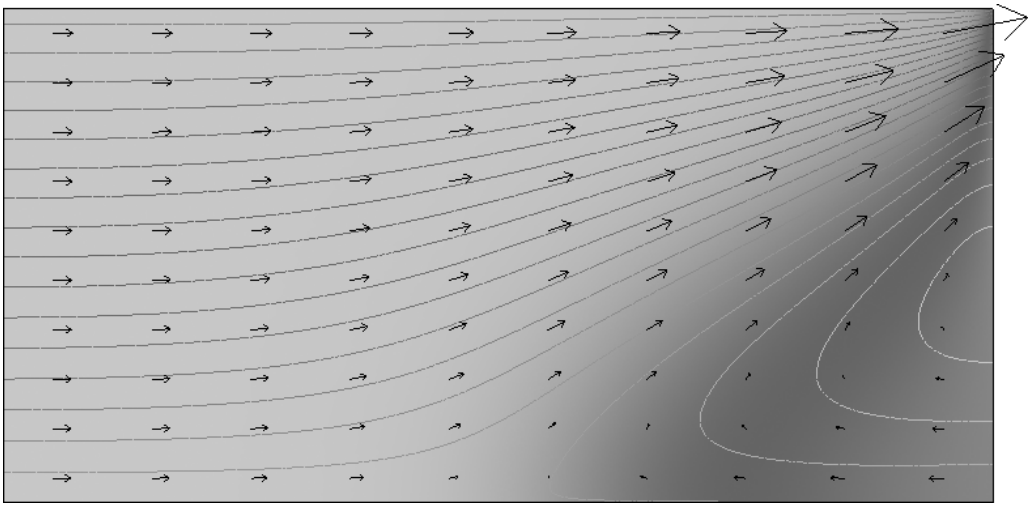


Figure 4. The solution for saltwater intrusion presented by Henry (23).

for saltwater and freshwater was formulated long before the referenced authors. Du Commun (26) already envisaged a U-tube that is filled with fluids of different density on both sides. The equilibrium in that tube was characterized by different fluid levels in both ends of the tube, and the height difference could be calculated from the density difference between the fluids. Du Commun did not provide a formula (like Badon Ghijben) but illustrated the calculation by an example. The background for his derivations was a practical problem: on the ground of a distillery in New Brunswick (New Jersey) a water well had been drilled. At that time, where not much was known about groundwater, the water level in the well and its fluctuations with the tide became the subject of a newspaper dispute (25).

Acknowledgment
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BIBLIOGRAPHY

1. Drabbe, J. and Badon Ghijben, W. (1889). *Nota in verband met de voorgenomen putboring nabij Amsterdam*. Tijdschrift van het Koninklijk Institut voor Ingenieurs, The Hague, 8–22.
2. Herzberg, A. (1901). Die Wasserversorgung einiger Nordseebäder. *J. Gasbeleuchtung Wasser.* **44**: 815–819, 842–844.
3. De Vries, J.J. (2004). From speculation to science: the founding of groundwater hydrology in the Netherlands. In: *Dutch Pioneers of the Earth Sciences*. R.P.W. Visser and J.L.R. Touret (Eds.). Koninklijke Nederlandse Akademie van Wetenschappen, Amsterdam, pp. 139–164.
4. Fofonoff, P. and Millard, R.C., Jr. (1983). Algorithms for computation of fundamental properties of seawater. *Unesco Tech. Pap. Mar. Sci.* **44**: 53.
5. Bear, J., Cheng, A.H.-D., Sorek, S., Quazar, D., and Herrera, I. (Eds.). (1999). *Seawater Intrusion in Coastal Aquifers—Concepts, Methods and Practices*. Kluwer Academic Publ., Dordrecht, the Netherlands, pp. 163–191.
6. Custodio, E. (2002). Coastal aquifers as important hydrogeological structures. In: *Groundwater and Human Development*. E. Bocanegra, D. Martines, and H. Massone (Eds.). 1905–1918.
7. Kooi, H. and Groen, J. (2001). Offshore continuation of coastal groundwater systems; predictions using sharp-interface approximations and variable-density flow modelling. *J. Hydrol.* **246**: 19–35.
8. Hubbert, M.K. (1940). The theory of ground-water motion. *J. Geol.* **XLVIII**(8): 785–938.
9. Reilly, T.E. and Goodman, A.S. (1985). Quantitative analysis of saltwater–freshwater relationships in groundwater systems—a historical perspective. *J. Hydrol.* **80**: 125–160.
10. Cheng, A.H.-D. and Quazar, D. (1999). Analytical solutions. In: *Seawater Intrusion in Coastal Aquifers—Concepts, Methods and Practices*. J. Bear, A.H.-D. Cheng, S. Sorek, D. Quazar, and I. Herrera (Eds.). Kluwer Academic Publ., Dordrecht, the Netherlands, pp. 163–191.
11. Muskat, M. (1937). *The Flow of Homogeneous Fluids Through Porous Media*. McGraw-Hill, New York.
12. van der Veer, P. (1977). Analytical solution for steady interface flow in a coastal aquifer involving a phreatic surface with precipitation. *J. Hydrol.* **34**: 1–11.
13. Strack, O.D.L. (1976). A single-potential solution for regional interface problems in coastal aquifers. *Water Resour. Res.* **12**(6): 1165–1174.
14. Strack, O.D.L. (1989). *Groundwater Mechanics*. Prentice-Hall, Englewood Cliffs, NJ.
15. Bäckblom, G. (2002). *Experience on Grouting to Limit Inflow to Tunnels*. Research and development and case studies from Sweden, Working Report 2002-18, Posiva Oy, Helsinki, Finland.
16. Wang, F.C. (1965). Approximate theory for skimming well formation in the Indus plain of West Pakistan. *J. Geophys. Res.* **70**(20): 5055–5063.
17. Motz, L.H. (1992). Salt-water upconing in an aquifer overlain by a leaky confining bed. *Groundwater* **30**(2): 192–198.
18. Wirojanagud, P. and Charbeneau, R.J. (1985). Saltwater upconing in unconfined aquifers. *J. Hydrol. Eng.* **111**(3): 417–434.
19. Reilly, T.E., Frimpter, M.H., LeBlanc, D.R., and Goodman, A.S. (1987). Analysis of steady-state salt-water upconing with application at Truro well field. *Groundwater* **25**(2).
20. Lusczynski, N.J. (1961). Head and flow of ground water of variable density. *J. Geophys. Res.* **66**(12): 4247–4256.
21. Holzbecher, E. (1998). *Modeling Density-Driven Flow in Porous Media*. Springer, Heidelberg, Germany.
22. Sorek, S. and Pinder, G.F. (1999). Numerical modelling issues. In: *Seawater Intrusion in Coastal Aquifers—Concepts, Methods and Practices*. J. Bear, A.H.-D. Cheng, S. Sorek, D. Quazar, and I. Herrera (Eds.). Kluwer Academic Publ., Dordrecht, the Netherlands, pp. 399–461.
23. Henry, H.R. (1964). Effects of dispersion on salt water enroachment in coastal aquifers. Geol. Surv. Water-Supply Paper 1613-C.
24. FEMLAB. (2004). Version 3.1, COMSOL AB, Tegnérgatan 23, SE-111 40, Stockholm, Sweden.
25. Carlston, C.W. (1963). An early American statement of the Badon Ghyben–Herzberg principle of static fresh-water–salt-water balance. *Am. J. Sci.* **261**: 88–91.
26. DuCommun, J. (1828). On the causes of fresh water springs, fountains, etc. *Am. J. Sci.* **14**: 174–176.

GROUNDWATER BALANCE

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INTRODUCTION

Rapid industrial development, urbanization, and increase in agricultural production have led to freshwater shortages in many parts of the world. In view of increasing demand of water for various purposes like agricultural, domestic, and industrial, a greater emphasis is being placed on a planned and optimal utilization of water resources. The water resources of the basins remain almost constant while the demand for water continues to increase.

As a result of uneven distribution of rainfall both in time and space, the surface water resources are unevenly distributed. Also, increasing intensities of irrigation from surface water alone may result in an alarming rise

of the water table, creating problems of waterlogging and salinization, affecting crop growth adversely and rendering large areas unproductive, which has resulted in increased emphasis on development of groundwater resources. The simultaneous development of groundwater, especially through dug wells and shallow tubewells, will lower the water table and provide vertical drainage, which can prevent waterlogging and salinization. Areas that are already waterlogged can also be reclaimed.

On the other hand, continually increased withdrawals from a groundwater reservoir in excess of replenishable recharge may result in regular lowering of the water table. In such a situation, a serious problem is created resulting in drying of shallow wells and increasing pumping head for deeper wells and tubewells, which has led to an emphasis on planned and optimal development of water resources. An appropriate strategy will be to develop water resources with planning based on conjunctive use of surface water and groundwater.

For a sustainable development of water resources, it is imperative to make a quantitative estimation of the available water resources. For this, the first task would be to make a realistic assessment of the surface water and groundwater resources and then plan their use in such a way that full crop water requirements are met and neither waterlogging nor excessive lowering of the groundwater table occurs. It is necessary to maintain the groundwater reservoir in a state of dynamic equilibrium over a period of a time, and the water level fluctuations have to be kept within a particular range over the monsoon and nonmonsoon seasons.

A complexity of factors, hydrogeological, hydrological, and climatological, control the groundwater occurrence and movement. The precise assessment of recharge and discharge is rather difficult, as no techniques are currently available for their direct measurements. Hence, the methods employed for groundwater resource estimation are all indirect. Groundwater, being a dynamic and replenishable resource, is generally estimated based on the component of annual recharge, which could be subjected to development by means of suitable groundwater structures.

For quantification of groundwater resources, proper understanding of the behavior and characteristics of the water-bearing rock formation, known as an aquifer, is essential. An aquifer has two main functions: (a) to transit water (conduit function) and (b) to store water (storage function). The groundwater resources in unconfined aquifers can be classified as static and dynamic. The static resources can be defined as the amount of groundwater available in the permeable portion of the aquifer below the zone of water level fluctuation. The dynamic resources can be defined as the amount of groundwater available in the zone of water level fluctuation. The replenishable groundwater resource is essentially a dynamic resource that is replenished annually or periodically by precipitation, irrigation return flow, canal seepage, tank seepage, influent seepage, etc.

The methodologies adopted for computing groundwater resources are generally based on the hydrologic budget techniques. The hydrologic equation for groundwater regime is a specialized form of water balance equation that requires quantification of the components of inflow to and outflow from a groundwater reservoir, as well as changes in storage therein. Some of these are directly measurable, few may be determined by differences between measured volumes or rates of flow of surface water, and some require indirect methods of estimation.

Water balance techniques have been extensively used to make quantitative estimates of water resources and the impact of man's activities on the hydrological cycle. The study of water balance requires the systematic presentation of data on the water supply and its use within a given study area for a specific period. The water balance of an area is defined by the hydrologic equation, which is basically a statement of the law of conservation of mass as applied to the hydrological cycle. With the water balance approach, it is possible to quantitatively evaluate individual contribution of sources of water in the system over different time periods and to establish the degree of variation in water regime because of changes in components of the system.

A basinwise approach yields the best results where the groundwater basin can be characterized by prominent drainages. A thorough study of the topography, geology, and aquifer conditions should be employed. The limit of the groundwater basin is controlled not only by topography but also by the disposition, structure and permeability of rocks and the configuration of the water table. Generally, in igneous and metamorphic rocks, the surface water and groundwater basins are coincident for all practical purposes, but marked differences may be encountered in stratified sedimentary formations. Therefore, the study area for groundwater balance study is preferably taken as a doab, which is bounded on two sides by two streams and on the other two sides by other aquifers or extension of the same aquifer. Once the study area is identified, comprehensive studies can be undertaken to estimate for selected period of time, the input and output of water, and change in storage to draw up the water balance of the basin.

The estimation of groundwater balance of a region requires quantification of all individual inflows to or outflows from a groundwater system and change in groundwater storage over a given time period. The basic concept of water balance is:

Input to the system − outflow from the system = change in storage of the system (over a period of time)

The general methodology of computing groundwater balance consists of the following:

- Identification of significant components,
- Evaluating and quantifying individual components, and
- Presentation in the form of water balance equation.

The groundwater balance study of an area may serve the following purposes:

- As a check on whether all flow components involved in the system have been quantitatively accounted for,

and what components have the greatest bearing on the problem under study.

- To calculate one unknown component of the groundwater balance equation, provided all other components are quantitatively known with sufficient accuracy.
- As a model of the hydrological processes under study, which can be used to predict the effect that changes imposed on certain components will have on the other components of groundwater system.

GROUNDWATER BALANCE EQUATION

Considering the various inflow and outflow components in a given study area, the groundwater balance equation can be written as:

$$R_r + R_c + R_i + R_t + S_i + I_g = E_t + T_p + S_e + O_g + \Delta S \quad (1)$$

where R_r = recharge from rainfall
R_c = recharge from canal seepage
R_i = recharge from field irrigation
R_t = recharge from tanks
S_i = influent seepage from rivers
I_g = inflow from other basins
E_t = evapotranspiration from groundwater
T_p = draft from groundwater
S_e = effluent seepage to rivers
O_g = outflow to other basins
ΔS = change in groundwater storage

Preferably, all elements of the groundwater balance equation should be computed using independent methods. However, it is not always possible to compute all individual components of the groundwater balance equation separately. Sometimes, depending on the problem, some components can be lumped and account only for their net value in the equation.

Computations of various components usually involve errors, because of shortcomings in the estimation techniques. The groundwater balance equation, therefore, generally does not balance, even if all its components are computed by independent methods. The resultant discrepancy in groundwater balance is defined as a residual term in the balance equation, which includes errors in the quantitative determination of various components as well as values of the components that have not been accounted in the equation.

The water balance may be computed for any time interval. The complexity of the computation of the water balance tends to increase with increase in area. This is because of a related increase in the technical difficulty of accurately computing the numerous important water balance components.

DATA REQUIREMENTS FOR A GROUNDWATER BALANCE STUDY

For carrying out a groundwater balance study, the following data may be required over a given time period:

Rainfall Data

Monthly rainfall data of sufficient number of rainguage stations lying within or around the study area, along with their locations, should be available.

Land Use Data and Cropping Patterns

Land use data are required for estimating the evapotranspiration losses from the water table through forested area. Cropping pattern data are necessary for estimating the spatial and temporal distributions of groundwater withdrawals, if required. Monthly pan evaporation rates should also be available at a few locations for estimation of consumptive use requirements of different crops.

River Data

Monthly river stage and discharge data along with river cross sections are required at a few locations for estimating the river-aquifer interflows.

Canal Data

Monthly water releases into the canal and its distributories along with running days during each month are required. To account for the seepage losses through the canal system, the seepage loss test data are required in different canal reaches and distributories.

Tank Data

Monthly tank gauges and water releases should be available. In addition, depth vs. area and depth vs. capacity curves should also be available for computing the evaporation and seepage losses from tanks. Field test data are required for computing infiltration capacity to be used to evaluate the recharge from depression storage.

Water Table Data

Monthly water table data (or at least premonsoon and postmonsoon data) from a sufficient number of well-distributed observation wells along with their locations are required. The available data should comprise reduced level (RL) of water table and depth to water table.

Groundwater Draft

For estimating groundwater withdrawals, the number of each type of well operating in the area, their corresponding running hours each month, and discharge are required. If a complete inventory of wells is not available, then this can be obtained by carrying out sample surveys.

Aquifer Parameters

Data regarding the storage coefficient and transmissivity are required at a sufficient number of locations in the study area.

ESTIMATION OF GROUNDWATER BALANCE COMPONENTS

The various inflow/outflow components of the groundwater balance equation may be estimated through appropriate field experiments or other methods, as discussed below.

Recharge from Rainfall (R_r)

Rainfall is the major source of recharge to groundwater. Part of the rain water that falls on the ground is infiltrated into the soil. A part of this infiltrated water is used in filling the soil moisture deficiency, whereas the remaining portion percolates down to reach the water table, which is termed as *rainfall recharge* to the aquifer. The amount of rainfall recharge depends on various hydrometeorological and topographic factors, soil characteristics, and depth to water table. The methods for estimation of rainfall recharge involve the empirical relationships established between recharge and rainfall developed for different regions, groundwater balance approach, and soil moisture data-based methods.

Empirical Relationships. Several empirical formulae have been worked out for various regions on the basis of detailed studies. For example, Kumar and Seethapathi (1) conducted a detailed seasonal groundwater balance study in Upper Ganga Canal command area (India) for the period 1972–1973 to 1983–1984 to determine groundwater recharge from rainfall. It was observed that as the rainfall increases, the quantity of recharge also increases, but the increase is not linearly proportional. The recharge coefficient (based on the rainfall in monsoon season) was found to vary between 0.05 to 0.19 for the study area. The following empirical relationship was derived by fitting the estimated values of rainfall recharge and the corresponding values of rainfall in the monsoon season through the nonlinear regression technique.

$$R_r = 0.63\ (P - 15.28)^{0.76} \tag{2}$$

where R_r = Groundwater recharge from rainfall in monsoon season (inch)
P = Mean rainfall in monsoon season (inch)

The relative errors (%) in the estimation of rainfall recharge computed from the proposed empirical relationship was compared with groundwater balance study. In almost every years, the relative error was found to be less than 8%. Therefore, Eq. (2) can conveniently be used for better and quick assessment of natural groundwater recharge in Upper Ganga Canal command area.

It is to be noted that the relationships, tentatively proposed for specific hydrogeological conditions, have to be examined and established or suitably altered for application to other areas. If adequate data of groundwater levels are not available, rainfall recharge may be estimated using the rainfall infiltration method. The same recharge factor may be used for both monsoon and nonmonsoon rainfall, with the condition that the recharge because of nonmonsoon rainfall may be taken as zero, if the rainfall during nonmonsoon season is less than 10% of annual rainfall. An additional 2% of rainfall recharge factor may be used in areas where watershed development with associated soil conservation measures are implemented. This additional factor is separate from contribution because of water conservation structures, such as check dams, nalla bunds, percolation tanks, etc., for which the norms are defined separately.

Groundwater Balance Approach. In this method, all components of the groundwater balance Eq. (1), except the rainfall recharge, are estimated individually. The algebraic sum of all input and output components is equated to the change in groundwater storage, as reflected by the water table fluctuation, which in turn yields the single unknown in the equation, namely, the rainfall recharge. A prerequisite for successful application of this technique is the availability of very extensive and accurate hydrological and meteorological data. The groundwater balance approach is valid for the areas where the year can be divided into monsoon and nonmonsoon seasons, with the bulk of rainfall occurring in former.

Groundwater balance study for monsoon and nonmonsoon periods is carried out separately. The former yields an estimate of recharge coefficient and the latter determines the degree of accuracy with which the components of water balance equation have been estimated. Alternatively, the average specific yield in the zone of fluctuation can be determined from a groundwater balance study for the nonmonsoon period, and using this specific yield, the recharge because of rainfall can be determined using the groundwater balance components for the monsoon period.

Soil Moisture Data-Based Methods. Soil moisture data-based methods are the lumped and distributed model and the nuclear methods. In the lumped model, the variation of soil moisture content in the vertical direction is ignored and any effective input into the soil is assumed to increase the soil moisture content uniformly. Recharge is calculated as the remainder when losses, identified in the form of runoff and evapotranspiration, have been deducted from the precipitation with proper accounting of soil moisture deficit. In the distributed model, variation of soil moisture content in the vertical direction is accounted for, and the method involves the numerical solution of partial differential equation (Richards equation) governing one-dimensional flow through unsaturated medium, with appropriate initial and boundary conditions.

Soil Water Balance Method. Water balance models were developed in the 1940s by Thornthwaite (2) and revised by Thornthwaite and Mather (3). The method is essentially a bookkeeping procedure that estimates the balance between the inflow and outflow of water. When applying this method to estimate the recharge for a catchment area, the calculation should be repeated for areas with different precipitation, evapotranspiration, crop type, and soil type. The soil water balance method is of limited practical value, because evapotranspiration is not directly measurable. Moreover, storage of moisture in the unsaturated zone and the rates of infiltration along the various possible routes to the aquifer form important and uncertain factors. Another aspect that deserves attention is the depth of the root zone, which may vary in semiarid regions between 1 and 30 meters. Results from this model are of very limited value without calibration and validation, because of the substantial uncertainty in input data.

Nuclear Methods. Nuclear techniques can be used for the determination of recharge by measuring the travel of

moisture through a soil column. The technique is based on the existence of a linear relation between neutron count rate and moisture content (% by volume) for the range of moisture contents generally occurring in the unsaturated soil zone. The mixture of Beryllium (Be) and Radium (Ra) is taken as the source of neutrons. Another method is the gamma ray transmission method based on the attenuation of gamma rays in a medium through which it passes. The extent of attenuation is closely linked with moisture content of the soil medium.

Recharge from Canal Seepage (R_c)

Seepage refers to the process of water movement from a canal into and through the bed and wall material. Seepage losses from irrigation canals often constitute a significant part of the total recharge to groundwater system. Hence, it is important to properly estimate these losses for recharge assessment to groundwater system. Recharge by seepage from canals depends on the size and cross section of the canal, depth of flow, characteristics of soils in the bed and sides, and location as well as level of drains on either side of the canal. A number of empirical formulae and formulae based on theoretical considerations have been proposed to estimate the seepage losses from canals.

Recharge from canals that are in direct hydraulic connection with a phreatic aquifer, underlaid by a horizontal impermeable layer at shallow depth, can be determined by Darcy's equation, provided the flow satisfies Dupuit assumptions.

$$R_c = K\frac{h_s - h_l}{L}A \tag{3}$$

where, h_s and h_l are water-level elevations above the impermeable base, at the canal, respectively, and at distance L from it. For calculating the area of flow cross section, the average of the saturated thickness $(h_s + h_l)/2$ is taken. The crux of computation of seepage depends on correct assessment of the hydraulic conductivity, K. Knowing the percentage of sand, silt, and clay, the hydraulic conductivity of undisturbed soil can be approximately determined using the soil classification triangle showing relation of hydraulic conductivity to texture for undisturbed sample (4).

A number of investigations have been carried out to study the seepage losses from canals. United States Bureau of Reclamation (USBR) recommended the channel losses based on the channel bed material as given below:

Material	Seepage Losses (Cumec Per Million Square Meter of Wetted Area)
Clay and clay loam:	1.50
Sandy loam:	2.40
Sandy and gravely soil:	8.03
Concrete lining:	1.20

These values are valid if the water table is relatively deep. In shallow water table and waterlogged areas, the recharge from canal seepage may be suitably reduced. Specific results from case studies may be used, if available. The above norms take into consideration the type of soil in which the canal runs while computing seepage. However, the actual seepage will also be controlled by the width of canal (B), depth of flow (D), hydraulic conductivity of the bed material (K), and depth to water table. Knowing the values of B and D, the range of seepage losses (R_{c_max} and R_{c_min}) from the canal may be obtained as

$$R_{c_max} = K(B + 2D) \quad \text{(in case of deeper water table)} \tag{4a}$$

$$R_{c_min} = K(B - 2D) \quad \text{(in case of water table at the level of channel bed)} \tag{4b}$$

However, the various guidelines for estimating losses in the canal system are only approximate. The seepage losses may best be estimated by conducting actual tests in the field. The methods most commonly adopted are:

Inflow-Outflow Method. In this method, the water that flows into and out of the section of canal under study is measured using current meter or Parshall flume method. The difference between the quantities of water flowing into and out of the canal reach is attributed to seepage. This method is advantageous when seepage losses are to be measured in long canal reaches with few diversions.

Ponding Method. In this method, bunds are constructed in the canal at two locations, one upstream and the other downstream of the reach of canal with water filled in it. The total change in storage in the reach is measured over a period of time by measuring the rate of drop of water surface elevation in the canal reach. Alternatively, water may be added to maintain a constant water surface elevation. In this case, the volume of water added is measured along with the elapsed time to compute the rate of seepage loss. The ponding method provides an accurate means of measuring seepage losses and is especially suitable when they are small (e.g., in lined canals).

Seepage Meter Method. The seepage meter is a modified version of permeameter developed for use under water. Various types of seepage meters have been developed. The two most important are seepage meter with submerged flexible water bag and falling head seepage meter. Seepage meters are suitable for measuring local seepage rates in canals or ponds and used only in unlined or earth-lined canals. They are quickly and easily installed and give reasonably satisfactory results for the conditions at the test site, but it is difficult to obtain accurate results when seepage losses are low.

The total losses from the canal system generally consist of the evaporation losses (E_c) and the seepage losses (R_c). The evaporation losses are generally 10–15% of the total losses. Thus, the R_c value is 85–90% of the losses from the canal system.

Recharge from Field Irrigation (R_i)

Water requirements of crops are met, in parts, by rainfall, contribution of moisture from the soil profile, and applied

irrigation water. A part of the water applied to irrigated field crops is lost in consumptive use and the balance infiltrates to recharge the groundwater. The process of re-entry of a part of the water used for irrigation is called return flow. Percolation from applied irrigation water, derived both from surface water and groundwater sources, constitutes one of the major components of groundwater recharge. The irrigation return flow depends on the soil type, irrigation practice, and type of crop. Therefore, irrigation return flows are site specific and will vary from one region to another.

The recharge because of irrigation return flow may be estimated, based on the source of irrigation (groundwater or surface water), the type of crop (paddy, nonpaddy), and the depth of water table below ground surface. For surface water, the recharge is to be estimated based on water released at the outlet from the canal/distribution system. For groundwater, the recharge is to be estimated based on gross draft. Where continuous supply is used instead of rotational supply, an additional recharge of 5% of application may be used. Specific results from case studies may be used, if available.

For a correct assessment of the quantum of recharge by applied irrigation, studies are required to be carried out on experimental plots under different crops in different seasonal conditions. The method of estimation comprises application of the water balance equation involving input and output of water in experimental fields.

Recharge from Tanks (R_t)

Studies have indicated that seepage from tanks varies from 9–20% of their live storage capacity. However, as data on live storage capacity of large number of tanks may not be available, seepage from the tanks may be taken as 44–60 cm per year over the total water spread, taking into account the agroclimatic conditions in the area. The seepage from percolation tanks is higher and may be taken as 50% of its gross storage. In the case of seepage from ponds and lakes, the norms as applied to tanks may be taken. Groundwater Resource Estimation Committee (5) has recommended that, based on the average area of water spread, the recharge from storage tanks and ponds may be taken as 1.4 mm/day for the period in which the tank has water. If data on the average area of water spread is not available, 60% of the maximum water spread area may be used instead of the average area of water spread.

In the case of percolation tanks, recharge may be taken as 50% of gross storage, considering the number of fillings, with half of this recharge occurring in monsoon season and the balance in nonmonsoon season. Recharge because of check dams and nala bunds may be taken as 50% of gross storage (assuming annual desilting maintenance exists), with half of this recharge occurring in the monsoon season and the balance in the nonmonsoon season.

Influent and Effluent Seepage (S_i & S_e)

The river-aquifer interaction depends on the transmissivity of the aquifer system and the gradient of the water table in respect to the river stage. Depending on the water level in the river and in the aquifer (in the vicinity of river), the river may recharge the aquifer (influent) or the aquifer may contribute to the river flow (effluent). The effluent or influent character of the river may vary from season to season and from reach to reach. The seepage from/to the river can be determined by dividing the river reach into small sub-reaches and observing the discharges at the two ends of the sub-reach along with the discharges of its tributaries and diversions, if any. The discharge at the downstream end is expressed as:

$$Q_d.\Delta t = Q_u.\Delta t + Q_g.\Delta t + Q_t.\Delta t - Q_o.\Delta t - E.\Delta t \pm S_{rb} \quad (5)$$

where Q_d = discharge at the downstream section
Q_u = discharge at the upstream section
Q_g = groundwater contribution (unknown quantity; −ve computed value indicates influent conditions)
Q_t = discharge of tributaries
Q_o = discharge diverted from the river
E = rate of evaporation from river water surface and flood plain (for extensive bodies of surface water and for long time periods, evaporation from open water surfaces cannot be neglected)
S_{rb} = change in bank storage (+ for decrease and − for increase)
Δt = time period

The change in bank storage can be determined by monitoring the water table along the cross section normal to the river. Thus, using the above equation, seepage from/to the river over a certain period of time, Δt, can be computed. However, this would be the contribution from aquifers on both sides of the stream. The contribution from each side can be separated by the following method:

$$\textit{Contribution from left bank} = \frac{I_L T_L}{I_L T_L + I_R T_R} \cdot Q_g \quad (6a)$$

$$\textit{Contribution from right bank} = \frac{I_R T_R}{I_L T_L + I_R T_R} \cdot Q_g \quad (6b)$$

where I_L and T_L are gradient and transmissivity, respectively, on the left side and I_R and T_R are those on the right.

Inflow from and Outflow to Other Basins (I_g and O_g)

For the estimation of groundwater inflow/outflow from/to other basins, regional water table contour maps are drawn based on the observed water level data from wells located within and outside the study area. The flows into and out of a region are governed mainly by the hydraulic gradient and transmissivity of the aquifer. The gradient can be determined by taking the slope of the water table normal to water table contour. The length of the section, across which groundwater inflow/outflow occurs, is determined from contour maps, the length being measured parallel to the contour. The inflow/outflow is determined as follows:

$$I_g \textit{ or } O_g = \sum^{L} T\, I\, \Delta L \quad (7)$$

where T is the transmissivity and I is the hydraulic gradient averaged over a length, ΔL, of contour line.

Evapotranspiration from Groundwater (E_t)

Evapotranspiration is the combined process of transpiration from vegetation and evaporation from both soil and free water surfaces. Potential evapotranspiration is the maximum loss of water through evapotranspiration. Evapotranspiration from groundwater occurs in waterlogged areas or in forested areas with roots extending to the water table. From the land use data, area under forests is available whereas the waterlogged areas may be demarcated from depth to water table maps. The potential evapotranspiration from such areas can be computed using standard methods.

Depth to water table maps may be prepared based on well inventory data to bring into focus the extensiveness of shallow water table areas. During well inventory, investigation should be specifically oriented toward accurately delineating water table depth for depths less than 2 meters. The evapotranspiration can be estimated based on the following equations:

$$E_t = \mathrm{PE}_t * A \qquad \text{if } h > h_s \tag{8a}$$

$$E_t = 0 \qquad \text{if } h < (h_s - d) \tag{8b}$$

$$E_t = \mathrm{PE}_t * A(h - (h_s - d))/d \qquad \text{if } (h_s - d) \le h \le h_s \tag{8c}$$

where E_t = evapotranspiration in volume of water per unit time $[L^3T^{-1}]$
PE_t = maximum rate of evapotranspiration in volume of water per unit area per unit time $[L^3L^{-2}T^{-1}]$
A = surface area $[L^2]$
h = water table elevation $[L]$
h_s = water table elevation at which the evapotranspiration loss reaches the maximum value
d = extinction depth; when the distance between h_s and h exceeds d, evapotranspiration from groundwater ceases $[L]$

Draft from Groundwater (T_p)

Draft is the amount of water lifted from the aquifer by means of various lifting devices. To estimate groundwater draft, an inventory of wells and a sample survey of groundwater draft from various types of wells (state tubewells, private tubewells, and open wells) are required. For state tubewells, information about their number, running hours per day, discharge, and number of days of operation in a season is generally available in the concerned departments. To compute the draft from private tubewells, pumping sets, rahats, etc., sample surveys have to be conducted regarding their number, discharge, and withdrawals over the season.

In areas where wells are energized, the draft may be computed using power consumption data. By conducting tests on wells, the average draft per unit of electricity consumed can be determined for different ranges in depth to water levels. By noting the depth to water level at each distribution point and multiplying the average draft value with the number of units of electricity consumed, the draft at each point can be computed for every month.

Change in Groundwater Storage (ΔS)

To estimate the change in groundwater storage, the water levels are observed through a network of observation wells spread over the area. The water levels are highest immediately after monsoon, in the month of October or November, and lowest just before rainfall, in the month of May or June. During the monsoon season, the recharge is more than the extraction; therefore, the change in groundwater storage between the beginning and end of monsoon season indicates the total volume of water added to the groundwater reservoir, whereas the change in groundwater storage between the beginning and end of the nonmonsoon season indicates the total quantity of water withdrawn from groundwater storage. The change in storage (ΔS) is computed as follows:

$$\Delta S = \sum \Delta h \, A \, S_y \tag{9}$$

where Δh = change in water table elevation during the given time period
A = area influenced by the well
S_y = specific yield

Groundwater Resource Estimation Committee (5) recommended that the size of the watershed as a hydrological unit could be of about 100 to 300 sq. km area, and there should be at least three spatially well-distributed observation wells in the unit, or one observation well per 100 sq. km, whichever is more. However, as per IILRI (6), the following specification may serve as a rough guide:

Size of the Area (ha)	Number of Observation Points	Number of Observation Points per 100 Hectares
100	20	20
1,000	40	4
10,000	100	1
1,00,000	300	0.3

The specific yield may be computed from pumping tests. The values of specific yield in the zone of fluctuation of water table in different parts of the basin can also be approximately determined from the soil classification triangle showing relation between particle size and specific yield (7).

ESTABLISHMENT OF RECHARGE COEFFICIENT

Groundwater balance study is a convenient way of establishing the rainfall recharge coefficient, as well as to cross check the accuracy of the various prevalent methods for the estimation of groundwater losses and recharge from other sources. The steps to be followed are:

1. Divide the year into monsoon and nonmonsoon periods.
2. Estimate all the components of the water balance equation other than rainfall recharge for monsoon period using the available hydrological and meteorological information and employing the prevalent methods for estimation.
3. Substitute these estimates in the water balance equation and thus calculate the rainfall recharge and, hence, recharge coefficient (recharge/rainfall ratio). Compare this estimate with those given by various empirical relations valid for the area of study.
4. For nonmonsoon season, estimate all the components of water balance equation including the rainfall recharge, which is calculated using recharge coefficient value obtained through the water balance of monsoon period. The rainfall recharge (R_r) will be of very small order in this case. A close balance between the left and right sides of the equation will indicate that the net recharge from all the sources of recharge and discharge has been quantified with a good degree of accuracy.

By quantifying all the inflow/outflow components of a groundwater system, one can determine which particular component has the most significant effect on the groundwater flow regime. Alternatively, a groundwater balance study may be used to compute one unknown component (e.g., the rainfall recharge) of the groundwater balance equation when all other components are known. The balance study may also serve as a model of the area under study, whereby the effect of change in one component can be used to predict the effect of changes in other components of the groundwater system. In this manner, the study of groundwater balance has a significant role in planning a rational groundwater development of a region.

CONCLUDING REMARKS

- Water balance approach, essentially a lumped model study, is a viable method of establishing the rainfall recharge coefficient and for evaluating the methods adopted for the quantification of discharge and recharge from other sources. For proper assessment of potential, present use, and additional exploitability of water resources at optimal level, a water balance study is necessary.
- Groundwater exploitation should be such that protection from depletion is provided, protection from pollution is provided, negative ecological effects are reduced to a minimum, and economic efficiency of exploitation is attained. Determination of exploitable resources should be based on hydrological investigations. These investigations logically necessitate use of a mathematical model of groundwater system for analyzing and solving the problems. The study of water balance is a prerequisite for groundwater modeling.
- A need exists for studying unsaturated and saturated flow through weathered and fractured rocks for finding the recharge components from rainfall and from percolation tanks in hard rock groundwater basins. The irrigation return flow under different soils, crops, and irrigation practices needs to be quantified. Assessment of groundwater quality in many groundwater basins is a task yet to be performed. A hydrological database for groundwater assessment should be established. Also, user-friendly software should be developed for quick assessment of regional groundwater resources.
- Nonconventional methods for utilization of water, such as through interbasin transfers, artificial recharge of groundwater, and desalination of brackish or seawater as well as traditional water conservation practices like rainwater harvesting, including rooftop rainwater harvesting, need to be practiced to further increase the usable water resources.

BIBLIOGRAPHY

1. Kumar, C.P. and Seethapathi, P.V. (2002). Assessment of natural groundwater recharge in Upper Ganga Canal command area. *J. Appl. Hydrol. Assoc. Hydrologists of India* **XV**(4): 13–20.
2. Thornthwaite, C.W. (1948). An approach towards a rational classification of climate. *Geogr. Rev.* **38**(1): 55–94.
3. Thornthwaite, C.W. and Mather, J.W. (1955). The water balance. *Publ. Climatol. Lab. Climatol. Drexel Inst. Technol.* **8**(1): 1–104.
4. Johnson, A.I. (1963). *Application of Laboratory Permeability Data, Open File Report*. USGS, Water Resources Division, Denver, CO, p. 34.
5. Groundwater Resource Estimation Methodology. (1997). *Report of the Groundwater Resource Estimation Committee*. Ministry of Water Resources, Government of India, New Delhi, India.
6. IILRI. (1974). *Drainage Principles and Applications, Survey and Investigation*. Publication 16, **III**.
7. Johnson, A.I. (1967). *Specific Yield—Compilation of Specific Yields for Various Materials, Water Supply Paper, USGS*. Denver, CO, p. 74.

HYDRAULIC HEAD

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Hydraulic head is defined as the fluid energy per unit weight at a given point in a fluid system (like a pipe filled with flowing water or an aquifer). In simple, everyday terms, we can conceptualize (and measure) hydraulic head as an elevation—more specifically, the elevation to which water rises in a manometer, in a pressurized water pipe or in a piezometer.

Water elevations is a manifestation of the fluid energy in a groundwater system, and measuring a water elevation

in a piezometer is really a measurement of the energy in the fluid at a certain point in a groundwater system.

WHAT DO WE MEAN BY "ENERGY"?

Everything in the universe has some amount of energy associated with it, and that energy is present in various forms. Energy drives every natural process, and the key to understanding physical processes is understanding how energy is distributed in a system.

There are two basic types of energy:

Potential Energy: energy stored in a piece of matter or at a point in a system, generally associated with position or with the thermodynamics of the system (elevation, pressure, chemical, thermal).

Kinetic: energy of motion (velocity).

At every point in an aquifer, the fluid possesses some total amount of energy. That energy is the *sum* of all the potential and kinetic energy in the fluid associated with the velocity of the fluid, pressure of the fluid, temperature of the fluid, chemical bonds in the fluid, etc.

As previously stated, the fluid energy at a point in an aquifer manifests itself as the water level in a piezometer. So we could also say that the water level, or hydraulic head, represents the total energy in the aquifer at a given point, and we can use the various energy components of the hydraulic head (elevation, pressure, velocity, etc.) to understand the driving forces behind fluid motion in the subsurface.

THE BERNOULLI EQUATION

As previously stated, fluid energies (and, subsequently, water levels) vary from one point in an aquifer to the next (Figs. 1 and 2). Now, if we recall the first and second laws of thermodynamics:

First law of thermodynamics: Energy is conserved.

$$\text{Energy added} - \text{energy subtracted} = \text{change in total energy}$$

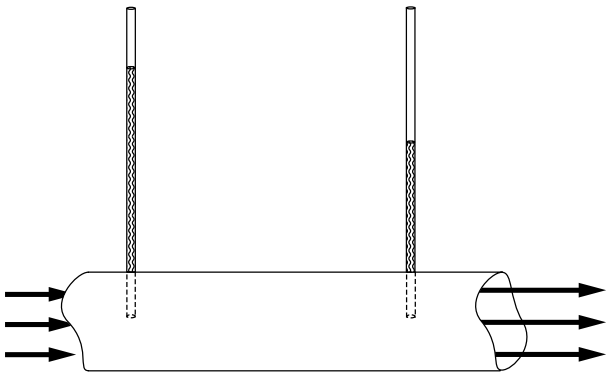


Figure 1. Pipe of flowing water with manometers showing the loss of head along the flow path.

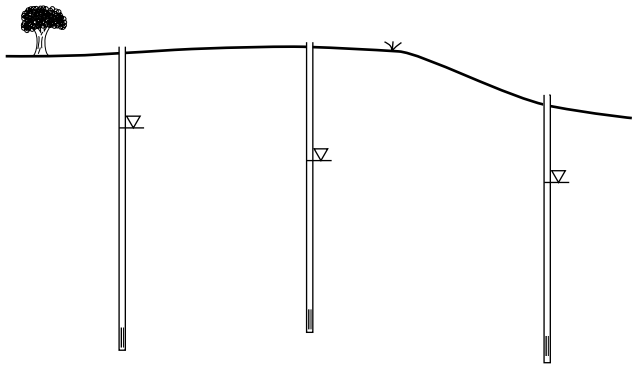


Figure 2. Cross section of aquifer showing hydraulic heads in three wells.

We could also express the first law in terms of the difference in energy at two points in a dynamic system:

$$\text{Total energy}_{(\text{atpoint1})} + \text{energy added/lost}_{(\text{betweenpoint1and2})} = \text{total energy}_{(\text{atpoint2})}$$

Second law of thermodynamics: Closed systems move toward increasing entropy.

- In a dynamic system like an aquifer, water will move from a point of higher energy (i.e., lower entropy) to a point of lower energy (higher entropy).
- In other words, groundwater moves in the direction of decreasing hydraulic head.

The *Bernoulli equation*, which describes the total energy of a fluid at all positions along a flow path in a closed system, is basically an expression of the first and second laws of thermodynamics:

$$z_1 + \frac{p_1}{\rho_w g} + \frac{v_1^2}{2g} + H_a = z_2 + \frac{p_2}{\rho_w g} + \frac{v_2^2}{2g} + H_L + H_E \qquad (1)$$

where z = elevation (L)
p = pressure ($\mathrm{M{\cdot}L^{-1}{\cdot}t^{-2}}$)
ρ_w = fluid density ($\mathrm{M{\cdot}L^{-3}}$)
g = gravitational acceleration ($\mathrm{L{\cdot}t^{-2}}$)
v = velocity ($\mathrm{L{\cdot}t^{-1}}$)
H_a = heat energy added (L)
H_L = mechanical energy lost (L)
H_E = heat energy extracted (L)

and the numerical subscripts represent two different positions along the flow path.

Let's assume that we don't add or subtract any heat energy from the system and the only change is the loss of mechanical energy from one point to the next; then we can rewrite the equation as

$$z_1 + \frac{p_1}{\rho_w g} + \frac{v_1^2}{2g} + I_1 = z_2 + \frac{p_2}{\rho_w g} + \frac{v_2^2}{2g} + I_2 \qquad (2)$$

where $\mathbf{I}$ is the internal energy at each point (i.e., the rest of the potential energy not described by the other terms) and $\mathbf{I}_2\mathbf{I}_1$ is equal to $\mathbf{H}_L$ in Eq. 1.

We can understand this equation by considering that each term in the equation represents a specific component

of energy with units of length. The terms of the equation represent, (respectively),

— elevation
— pressure
— kinetic (velocity)
— other internal energies (thermal, chemical)

This equation describes the change in energy from one point along a flow path to the next point. This equation expresses all the components of energy in the same units (i.e., length), so we can use it to compare the relative magnitude of the individual components. When we do that, we see that for most groundwater situations, the internal and kinetic components of the total energy are so small that we can ignore them. The result is that we can describe fluid energy in a groundwater system by only the elevation and pressure components.

HYDRAULIC HEAD AND HYDRAULIC POTENTIAL

If we assume that we can ignore velocity and internal energy components when dealing with groundwater, we can drop all that out of the equation and express the fluid energy as the sum of the elevation and pressure components. That sum is what we call *hydraulic head*; in physical terms, it is the fluid energy per unit weight, and in mathematical terms, it is

$$h = z + p/\rho_w g \tag{3}$$

where h = hydraulic head (L)
z = elevation (L)
p = pressure ($M{\cdot}L^{-1}{\cdot}t^{-2}$)
ρw = fluid density ($M{\cdot}L^{-3}$)
g = gravitational acceleration ($L{\cdot}t^{-2}$)

If we multiply both sides of the equation by the gravitational constant, g, we get a quantity called *hydraulic potential* (Φ), which is the fluid energy per unit *mass*, or

$$\Phi = gz + p/\rho_w \tag{4}$$

such that

$$\Phi = gh \tag{5}$$

The hydraulic potential is simply a way of expressing the same fluid energy, so that it is independent of gravity.

PHYSICAL DESCRIPTION OF THE COMPONENTS OF HEAD

From Eq. 3, we can see that hydraulic head is the sum of the elevation component (or *elevation head*) and the pressure component (or *pressure head*). The physical meaning of pressure head and elevation head are defined and described in Fig. 3a–c. These figures show an idealized cross section of a piezometer that has a screened interval at the bottom. Figure 3a shows the depths and elevations measured in the field (relative to some datum, like mean sea level). Figure 3b shows the pressure, elevation, and total heads, and Fig. 3c is a combination of the other two figures.

From Fig. 3b, we see that the elevation head is the height of the screened interval above the datum. Keep in mind that the datum is arbitrarily chosen—if we wanted, we could choose the bottom of the well as the datum, and the elevation head would be zero. However, it is important to realize that the head is really only important to us when we are looking at multiple wells in the same aquifer, and we need to have a constant datum for all those wells make the comparison meaningful. Sea level is usually chosen, but it is not the necessary datum.

We also see that the pressure head is the length of the column of water in the well above the screened interval. Keep in mind that *pressure* and *pressure head* are two different things; the *pressure* at the screened interval is the force per unit area of the column of fluid above that point; the *pressure head* is the pressure divided by the product of the density of the fluid and gravitational acceleration and is manifest as the length of the column of water above the screen. If we know the density of the fluid and the length of the column of water in the well, we can calculate the pressure at the well screen.

Finally, we see that the total head is just the sum of the other two heads, or more generally, the height of the water level in the well above the datum, this brings us full circle to the concept of water levels reflecting fluid energy.

DISTRIBUTION OF HEADS (I.E., FLUID ENERGY) IN A 3-D AQUIFER

An aquifer is a dynamic system of flowing water. The fluid energy varies throughout the system and is different from one point to the next. The result is

— different water levels throughout the aquifer
— hydraulic gradients
— movement of water driven by those gradients

Head is a scalar quantity; it is measured at a point, and it has a single magnitude that doesn't vary with respect to direction. So, when we talk about heads, from a theoretical standpoint, we are talking about the energy at an infinitesimal point in an aquifer. However, that aquifer exists in three dimensions, contains an infinite number of points, and the head varies from point to point.

The trends in that variation control the directions and magnitudes of flow. We call this variation the *hydraulic gradient*. The hydraulic gradient is defined as the change in hydraulic head over the change in length, and it is directly analogous to other physical gradients (topographic slope, thermal gradient, concentration gradients, etc.)

Hydraulic heads exist in three dimensions, so hydraulic gradients are not necessarily horizontal. In reality, most groundwater flow is generally in a horizontal direction, and it is often a realistic assumption to ignore fluid movement in a vertical dimension. However, there are many situations where vertical gradients (and, subsequently, vertical flow) are significant.

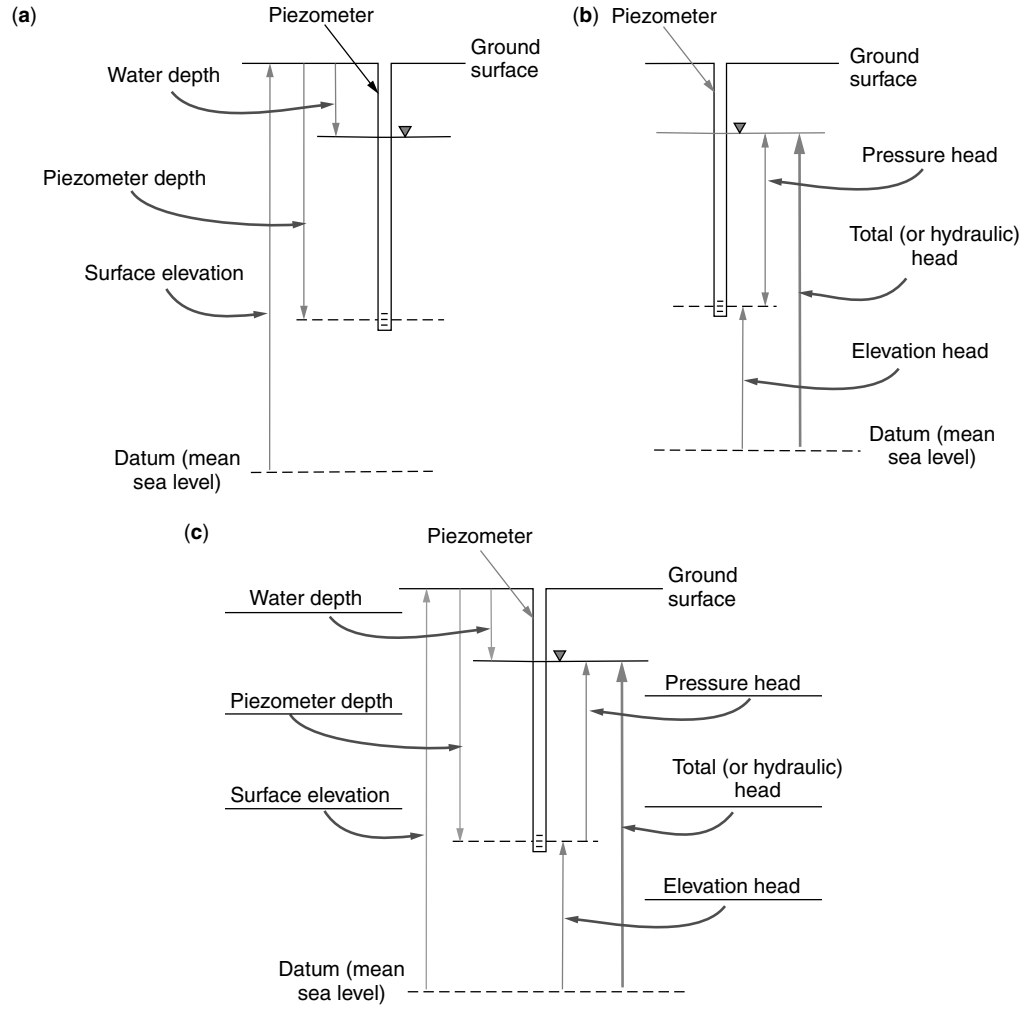


Figure 3. Hypothetical well showing depths, elevations, and heads.

THE ROLE OF HEAT IN GROUNDWATER SYSTEMS

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The role of heat in the subsurface includes the study of the overall transport of heat in saturated groundwater systems. Once site specific dynamics of heat transport are understood the effects of temperature on physical, chemical, and biological processes that govern the transport and degradation of contaminants in an aquifer can be evaluated.

FUNDAMENTALS

Of the many parameters that are monitored in association with the assessment and remediation of contaminated groundwater, temperature is typically regarded as a background condition that must be accepted for a given site. In the northern tier of states, it is customary that in the winter months remediation processes will be slowed or stopped depending on the depth of groundwater.

DEFINITIONS

Heat is an added or external energy that causes a rise in temperature, physical expansion, evaporation or other physical change. The rise or drop of temperature in an aquifer is the result of the transport of heat into or away from the aquifer. The key measure of the relationship between heat flow and resulting temperature is heat capacity, Cp. Heat capacity is used as specific heat in English units, which is the number of BTUs required to raise one pound of aquifer matrix by one degree Fahrenheit.

There are two primary materials through which heat is transported in an aquifer, the mineral matrix and the entrained groundwater. Density of the mineral matrix and water, porosity, and heat capacity combine to govern

the temperature response of an aquifer to heat flow. The specific heat Cp (as BTU/lb °F), dry density (rho, as lbs/ft^3) and percent porosity (phi) of some soils and minerals are as follows:

	Specific Heat	CpDensity (rho) lbs/ft^3	% Porosity (phi)
Water	1.00	62.4	NA
Clay	0.27	65.0	75
Sand	0.19	110.0	35
Granite	0.20	165.0	1
Limestone	0.22	155	4
Organic Fraction	0.30	55	65

The thermal energy capacity per unit volume per degree of temperature change is called the aquifer thermal capacity (q). With the above information, it is possible to calculate the thermal capacity (q) of an aquifer:

$$\mathbf{q} = (\mathrm{Cp} \times \mathrm{rho})_{\mathrm{rock}}(1 - \mathrm{phi}) + (\mathrm{Cp} \times \mathrm{rho})_{\mathrm{water}} \times \mathrm{phi}$$

Assuming a sandy aquifer with a specific heat of 0.19 for the mineral matrix, a density of 110 lb/ft^3, and a porosity of 0.35, the specific thermal capacity per cubic foot of aquifer is

$$\mathbf{q} = (0.19 \times 110)_{\mathrm{rock}} \times (1 - 0.35) + (1.0 \times 62.4)_{\mathrm{water}} \times 0.35$$

$$\mathbf{q} = 13.59_{\mathrm{rock}} + 21.84_{\mathrm{water}}$$

$$= 35.4 \text{ BTU per cubic foot per 1 degree Fahrenheit}$$

EXAMPLE

Given a volume in an aquifer 100 feet by 100 feet by 20 feet in depth, it would require 7,080,000 Btu to raise the temperature 1 °F. Converting Btu to kilowatt hours gives 2073 KW hours. At 6 cents per Kilowatt, that is equal to $125 in electrical cost. That estimate does not take into account the efficiency of the heat generation system, transfer of that heat into the aquifer, and effects of heat transport away from the zone undergoing heating.

Three physical processes are responsible for heat transfer in groundwater systems:

1. Conduction—heat flows from hotter regions to cooler regions through the molecular transfer of kinetic energy.
2. Convection—heat is transported along with overall mass transport of groundwater.
3. Radiation—the transference of heat through space via electromagnetic radiation.

The dominant mechanisms in groundwater systems are convection and conduction.

Thermal conductivity (k) is the amount of heat that will flow through a unit area in a unit time with a unit temperature difference. Under saturated conditions, the value of thermal conductivity is primarily governed by the texture, degree of compaction, and mineralogical composition of the aquifer matrix. Thermal conductivity decreases with the reduction of particle size. The units of thermal conductivity are Btu per hour per foot per degree Fahrenheit. Typical values are as follows:

Water	0.346
Air	0.0145
Wet Sand	0.95
Dry Sand	0.157
Wet Clay	0.87
Dry Clay	0.138

Notice that the thermal conductivity of water is about 23 times that of air. In the past, the use of heat as an augmentation to remediation has been applied to the vadose zone through the application of steam. For heat transport efficiency, that is probably not the most efficient application of a subsurface heating process.

Heat flow through a mass (qx) is calculated by the equation:

$$\mathrm{qx} = Ak(dT/dX)$$

where A is the cross-sectional area normal to the heat flow,
k is the thermal conductivity,
T is temperature in Fahrenheit,
X is the distance over which the heat must flow.

The solution to the above function requires substitution of an equation describing the system geometry for the dX term followed by integration. That is beyond the scope of this article.

Thermal diffusivity (in units of square feet per hour) is equal to the thermal conductivity (k) divided by the thermal capacity (q) of the aquifer; it measures the rate at which temperature changes occur in the soil mass. Higher values of thermal diffusivity result in more rapid changes in temperature and deeper penetration of heat into the soil.

Ratio of Thermal Velocity to Groundwater Velocity Versus Porosity

Lastly, as heated groundwater moves through an aquifer, thermal energy is transferred to the mineral matrix. As a consequence the thermal front associated with the advective flow of heated groundwater will move at a lower velocity than the groundwater. Aquifer porosity is the dominant element in this dynamic. The ratio of the velocity of the migration of the thermal front versus the groundwater velocity is affected by aquifer porosity. The smaller the ratio, the slower the thermal front velocity compared with the overall groundwater velocity.

EFFECT ON PHYSICAL PROPERTIES AND REACTION KINETICS

The two dominant physical characteristics of groundwater that change with temperature are viscosity and density. Their relationship is not linear. In the temperature range

of 0 °C to 30 °C, the viscosity decreases by over 50%. This change improves the efficiency of both advective fluid flow and diffusional transport. In contrast, water density decreases significantly at temperatures over 60 °C.

Next, chemical reactions should be considered. Most salts increase in solubility as the temperature increases, the common exception to this general rule being carbonates in which solubility decreases as temperature increases. As temperature increases, the solubility of gases in groundwater decreases. The solubility (in milligrams/liter) of environmentally important gases over the temperature range of 5 °C to 35 °C is as follows:

Oxygen with air as the source	12.7 to 7.1
Carbon Dioxide	2774 to 1105
Methane	34.1 to 17.3

The relationship between temperature and the kinetics of chemical reactions is expressed by the Arrhenius equation:

$$\ln k = \ln A - E_a/RT$$

where k is the rate constant,
A is an integration constant,
E_a is the energy of activation,
R is the universal gas constant, and
T is the temperature in Kelvin.

Commonly, this relationship is graphed as ln k versus $1/T$, which results in a straight line in which k increases exponentially as T increases. Under proper circumstances, small increases in temperature can have large effects on kinetic rates.

In addition to reaction rates, temperature also affects equilibrium constants, particularly those that involve reactions with noncovalent bonds. Covalent bonds are relatively resistant to thermal perturbation. However, van der Waals interactions, hydrogen bonds, weak ionic bonds, and hydrophobic interactions are disrupted by relatively small temperature changes.

Hydrogen bonds, ionic bonds, and van der Waals interactions all form with the release of heat, and hydrophobic interactions form with heat consumption.

Increases in temperature will destabilize the first three, whereas it will stabilize the hydrophobic interactions.

As temperature increases, the solubility of hydrocarbons increases, not uncommonly two to three times in the temperature range of 5 °C to 30 °C. Through this and the bonding reactions mentioned above, the forces responsible for the retardation of hydrocarbons within the soil matrix are reduced as temperature increases, improving the flushing action of groundwater flow induced by pump and treat recovery systems.

Vapor pressure also increases with temperature, and increased vapor pressure results in increased mass transport rates in soil vapor extraction systems, which is where many of the prior applications of external heat to subsurface remediation have been used. Examples of the percent increase in vapor pressure as a result of a temperature increase from 5 °C to 35 °C are as follows:

Benzene	417%
Ethylbenzene	638%
Toluene	513%
TCE	476%
Tetrachloroethylene	545%

With regard to free product recovery, an increase in temperature will reduce the hydrocarbon viscosity and increase the recovery of free product from the surface of a water table. A temperature increase from 10 °C to 50 °C can increase the recoverable amount of middle distillates by 10%.

Molecular diffusion is driven by the presence of a chemical concentration gradient between adjacent zones in the subsurface. The presence of a temperature gradient will also set up the diffusion of dissolved components in a fluid. The phenomena is called the Soret Effect and is known generally as thermal diffusion. Mass transport rates under thermal diffusion are described by the equation:

$$N_{AT} = D_T(\text{Rho})d \ln (T/dz)$$

where N_{AT} is the mass transport rate as number of moles/cm2/second, D_T is the coefficient of thermal diffusion in centimeters squared/second, T is temperature in kelvins, z is the distance in the direction of diffusion in centimeters, and Rho is the fluid density in g-moles/centimeters cubed.

The magnitude of thermal diffusion is dependent on the size and chemistry of the molecules involved as well as on the temperature. At maximum, it may reach a diffusional mass transport rate of 30% that is seen for molecular diffusion driven by chemical concentration gradients, and it is typically significantly less than that.

Lastly, a brief discussion on temperature and biological systems. Bacteria typically have a relatively narrow temperature range (about 10 °C) in which they experience maximum growth and metabolic activity. As groundwater temperatures increase, the dominant bacterial consortia will change in response. This is true with increases of temperature up to about 35 °C; temperatures of 50 °C or above will cause traumatization and partially kill many bacterial species indigenous to the subsurface. It is common for the rates of physiological and biochemical processes to undergo a two-fold increase because of a temperature change of only about 10 °C. This change is caused by the nature of the Arrhenius equation previously discussed as applied to biological systems.

A practical note with regard to bench scale studies of soil bacteria: Incubation of bacteria in the laboratory ideally should be conducted in a temperature range that is from 5 °C below the in situ groundwater temperature to 10 °C above. On average, the groundwater temperature in the United States is approximately 10 °C. Most bench scale laboratory testing is done at room temperature (about 25 °C).

In conclusion, many of the processes exploited in aid of subsurface remediation are impacted by temperature. The overall compounded physical/chemical/biological effects that can be anticipated within a relatively normal temperature range (5 °C to 35 °C) could on an additive basis make a three- to five-fold increase in remediation rates, which is not insignificant. The issue is then site specific, i.e., shallow versus deep contamination. Passive heating systems using modification of the ground surface to improve heat adsorption or low-intensity intrusive systems such as those associated with heat pump systems could offer remediation actions with possible economic benefits.

GROUNDWATER FLOW IN HETEROGENETIC SEDIMENTS AND FRACTURED ROCK SYSTEMS

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Groundwater flow in heterogenetic sediments and fractured rock systems is highly complex. Contaminants within these types of subsurface conditions are relatively common. Similarities and differences exist in flow characteristics of heterogenetic sediments and fractured rock systems, which influence contaminant fate and transport and subsequent remediation efforts at environmentally impacted properties.

FLOW IN HETEROGENETIC SEDIMENTS

Heterogeneity in granular aquifers is common and is caused by the large variability in water flow regimes in various depositional environments. The vertical and lateral variability in granular aquifers can occur on a scale of centimeters or less.

Anisotropic advective flow, dispersion, diffusional transport, contaminant adsorption, and other physical/chemical processes taking place in these systems is complicated. Complete evaluation and understanding of these processes at any given site is impractical, and attempting to gather comprehensive data in support of that understanding is prohibitively expensive. Anisotropic advective groundwater flow dominates the heterogenetic sedimentary systems.

Heterogeneity and subsequent anisotropic groundwater flow conditions are considered normal at most contaminated sites. Near-surface granular aquifers that are impacted by the release of contaminants are usually poorly indurated and can be classified according to the depositional regime as follows:

- Fluvial that includes rivers, streams, and alluvial fans
- Glacial such as tills
- Lacustrine lake deposits
- Eolian sand dune systems

In these depositional systems (particularly fluvial and glacial), it is common to have granular deposits of high permeability contrast juxtaposed to each other, and therein lies the source of great complexity.

Granular media advective flow regimes can be classified into three broad types:

- Uniform, medium-to-coarse granular soils capable of supporting significant intergranular advective flow
- Low permeability silts, clays, and tills in which any advective flow actually occurs in secondary permeable channels such as fractures or joints
- Complex interbedded soils with zones of high permeability contrast resulting in anisotropic advective flow

Sediment source and energy of transport are the primary controllers of the characteristics of water-deposited materials. A rain storm, rising tide, or flood waters carry an initial high-energy load of coarser material (that may be mixed with finer grained silts and clays). As a given deposition event begins to subside, the denser and typically larger size grains settle first, followed by granular materials of decreasingly less dense and smaller sizes. The last stage may involve quiescent waters from which the finest clay and silt particles will settle over a significant period of time. The result of a given episode is a layer stratified by size within the overall soil mass.

Scale is important when evaluating water flow characteristics. The smallest scale heterogeneity is expressed by variations in pore size and shape. Slightly larger, bench scale heterogeneity is expressed by variance in the particle size; on the larger scale of a road cut, heterogeneity is seen as the layering of individual bedding planes; and on larger scales, as changes in size of the layers occurs, pinch outs and facies change. In layered sediments of this type, horizontal flow is dominated by the most permeable units in the sequence and vertical flow by the least permeable. Mega scale depositional heterogeneity can also be created by processes such as braided stream sediments or glacial till systems, where lenticular pods of sand may be deposited in a matrix of lower permeability silts and clays.

Material that is two or three orders of magnitude higher in permeability than the bulk soil matrix will totally govern the groundwater flow system. For example, 1 in. of sand can dominate the flow through tens of feet of silt or clay. The practical problem this presents is the determination of the spatial configuration of the physically small but hydraulically dominant units in the soil matrix. Because of this significant problem, continuous soil coring is recommended during subsurface investigations of soils with mixed sands and clay or silts, where practical.

One potentially most damaging situation includes conditions in which the permeable channels or layers are preferentially exposed to the surface. These zones are susceptible to contaminant impact followed by surface recharge, which can act as a hydraulic driver of contaminants within a matrix that overall does not support high rates of advective groundwater flow, even

in the more permeable (but unexposed) portions of the coarser soil units.

The testing and analysis of these anisotropic heterogenetic flow systems is potentially extremely complex. As a matter of practicality, a significant number of assumptions must be made in the analysis of these aquifers. As readily available computing power has increased over the past decades, the number and degree of required assumptions have declined in the more sophisticated applications. Irrespective, two prime assumptions are that at some scale the heterogenetic soil can be treated as a homogenous block and that the spatial configuration of the heterogeneity has been defined. Increasing computational power typically allows for a finer mesh of blocks, but it has not addressed the issue of spatial configuration.

A significant new tool that is beginning to be put to use is the employment of fractal concepts to study the hydrology of heterogenetic soils. This approach points to a serious flaw in the value of using finer blocks in the modeling matrix. If the geometry of the heterogeneity is fractal in the soil matrix (which evidence increasingly indicates it often is), the assumption that the matrix can be represented by averaging is false. A fractal matrix will not become homogenous with averaging irrespective of block size. With further use of the concepts of fractal analysis, it is possible to model general features and hydraulic behavior and interpolate hydraulic dynamics from sparse data, an ability of potentially great value in these complex groundwater flow systems. With this approach, water level, flow, and soil data can be used from an operating groundwater recovery system to fine tune understanding of the site. Through an iterative process, the fractal model resolves hydrogeological attractors in the flow system. Known hydraulic properties model drawdown in the forward iteration, and observed drawdown and flow rates model hydraulic properties in the inverse iteration. This process has the potential to be a powerful tool for defining heterogenetic anisotropic groundwater systems.

At this juncture, computer capacity allows for primitive two-dimensional modeling in this manner. With improvements, it will soon be possible to robustly model three-dimensional systems. This technology will spatially identify which portions of the soil matrix have the greatest impact on the groundwater flow regime. It can also subtly determine areas where data gaps of high impact exist and that require additional testing wells.

FLOW IN FRACTURED ROCK SYSTEMS

Usually shallow water-bearing zones underlying a site are in shallow unconsolidated sediments. However, in some cases where bedrock outcrops or lies just meters below the surface, fractured rock hydrogeologic systems occur. In the latter case, any significant groundwater flow occurs in fracture systems within the bedrock. If soils are fine grained (i.e., tills or clays), fractures may also play a dominant role in advective flow.

The study of fluid flow through porous media was first established by Henri Darcy in 1857. Much of the science of hydrogeology was developed with and was designed for use in granular porous media because of the incentive to find and produce aquifers for large-scale groundwater consumption. It took almost 100 years before fractured flow was studied in great detail. The study of fluid flow through fractured rock was first developed by the petroleum industry in the 1950s (1). These petroleum studies resulted from observations that oil and gas production could be significantly increased by fracturing the oil-producing formations near the well bore (2). Fractured media in most instances will not produce groundwater on the same scale as homogeneous granular aquifers. Fracture flow systems are also more complex to analyze and hydraulically respond differently than do those in porous granular matrices. A good overview of contaminant transport in fractured media is presented in Schmelling and Ross (3).

To compare groundwater flow in fractured rock systems with granular media, under identical hydraulic gradients, one square meter of granular material with a hydraulic conductivity of 8.1×10^{-2} cm/s has the equivalent water-conducting capacity of one fracture in one square meter of rock with an aperture of 1 mm. In granular media, grain size, shape, and degree of sorting are the prime microscale parameters that determine hydraulic character. Fracture density, orientation, aperture, and type of rock matrix are the major parameters affecting groundwater flow in fractured media. The typical range for fracture aperture is from 0.2 to 25 mm, and fracture spacing is from 2 mm to 3 m.

Individual fractures are not infinite in extent. Therefore, where flow is supported, fracture density must be high enough to ensure connectivity through the system. The fracture density required to sustain advective flow is termed the "percolation threshold." Below that threshold, fractures may be connected, but only in small localized regions. Above, localized regions become interconnected, and flow over significant distances can take place. With an increase in fracture density, the system becomes increasingly previous.

An expression of the parameter that determines the percolation through fracture is $N(L_F)^2$, where N is fracture density and L_F is equal to fracture length times pi/2. The percolation threshold has been found to fall around 0.3.

As an example, in an area underlain by metamorphic rocks with discrete water-producing fracture systems:

- Fractures were approximately 0.5 m in length
- Rocks with a fracture density of 50 to 200 per 0.5 m

This process gave values of NL_F^2 of 30 to 120, well above the percolation threshold of 0.3.

Given adequate connectivity, the flow an individual fracture can support is proportional to the cube of the fracture aperture. This cube rule means that a few fractures with preferentially higher apertures can dominate the flow system, and those are the ones most important to delineate. Typically, fracture aperture will decrease with depth. Usually the highest flow rates occur in the upper 9 m of a fracture system, with flow decreasing to near zero below depths of 30 m.

To some degree, all rocks or soils are reactive. In most igneous, metamorphic, or fine-grained sedimentary

rocks, geochemical reactions tend to seal a given fracture over time. In carbonates, the opposite can be true, with the fracture aperture increasing with time (and the potential flow rate increasing with the cube of that aperture). The hydrodynamics of fracture flow systems will approach those in porous media in systems where fractures are randomly oriented and density is high. These systems can be analyzed with conventional granular media methodologies. To use those methods on other fracture systems is an error with potentially significant consequences.

Characterization of a fracture flow system is potentially an expensive process. Ideally, data should be gathered on fracture length, orientation, aperture, and density. Additionally, information on hydraulic head, the porosity and hydraulic characteristics of the bulk matrix, the type of contaminants, and the potential interactions between contaminants and the matrix are also important. Hydrogeologic characterization of fracture systems can be accomplished through coring, complex pumping tests, tracer tests, geophysical evaluation, or bore hole flow meters. In addition, evaluation of the hydrodynamics of a fracture system that has been defined with multiple orientations is mathematically extremely complex.

However, some level of useful knowledge can be inferred based on the structural setting of a site. The tectonic and depositional history of a given site is generally available in the geologic literature. The removal of overburden introduces stresses caused by reduction of overburden pressure, uplift of the region, and thermal stresses caused by cooling; the net stress is extensional.

Fractures that form in the tensile stress field can be placed into two classes:

- Unloading fractures, which include vertical fractures, indicating response to tensile stress in the horizontal plane and fractures horizontal or parallel to the topographic surface
- Release fractures that are fabric controlled in their orientation.

If a site has undergone even a mild degree of tectonic deformation, structural analysis can be a powerful predictive tool for the orientation of the dominant fracture sets at a site. Several points are important to use this concept:

- The deformational pattern observed in the large scale is replicated at medium, small, and microscopic scales. For example, the NE trend of the Appalachians is generally reflected as an NE-oriented fabric at all scales.
- Deformation imparts a fabric to the impacted rocks. This fabric imparts anisotropicity, which in turn will control subsequent fracture generation. For example, fractures will tend to propagate perpendicular to a strong linear fabric element.
- The stronger the degree of imprinted fabric, the greater the density of fractures in the controlled orientations.
- Depositional features such as bedding planes also impart anisotropic fabric.

Important differences exist between fractured and porous media with regard to contaminant fate and transport. Rapid transport in preferred directions can occur through rocks that normally would be thought impervious, such as bedrock fractured flow systems. Because of the general lack of organics in fractured rock systems, the flow of organic chemicals traveling through fractured rock systems is generally not retarded as much as in organic-rich granular sediments. Retardation is a function of matrix and contaminant chemistry and surface area. As an estimate, a block of granular media, such as well-sorted sand or gravel, will have a surface area 1000 to 100,000 times greater than a similar block of fractured media, such as fractured limestones or granites. Contaminant retardation will be roughly proportional. Contaminants in fractures can be mobile over long distances or until they are transported into a granular media.

Fractured rock systems create interesting challenges as well as opportunities. When drilling contaminant recovery wells in fractured terrain, it is suggested to orient the well bore such that it is perpendicular to the major water-bearing fracture set. The resulting well may not necessarily be vertical, but it will maximize the potential to intersect flow-bearing fractures, which allows for more complete contaminant removal.

BIBLIOGRAPHY

1. Gale, J.E. (1982). *Assessing the Permeability Characteristics of Fractured Rock*. Geological Society of America, Special Paper 189, pp. 163–181.
2. Duguid, J.O. and Lee, P.C.Y. (1977). Flow in fractured porous media. *Water Resources Res.* **13**: 558–566.
3. Schmelling, S.G. and Ross, R.R. (1989). *Contaminant Transport in Fractured Media: Models for Decision Makers*. United States Environmental Protection Agency Superfund Ground Water Issue, EPA/504/4-89/004, Washington, DC.

HORIZONTAL WELLS

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Horizontal wells are a new technology for solving problems in the environmental industry. Due to interest in horizontal wells for oil production, a large number of technical papers have been published regarding the reservoir engineering aspects of horizontal drilling and reservoir simulation. In the groundwater supply industry, the first theoretical analysis of groundwater flow to horizontal drains (collector wells) can be traced back to the early 1960s. In recent years, however, there has been renewed interest in horizontal wells for subsurface remediation. Horizontal wells offer significant advantages over vertical wells in environmental remediation and protection

in many hydrogeologic scenarios. Horizontal well-screen orientation complements common site logistics, typical aquifer geometry, and groundwater flow patterns. A single horizontal well can replace many closely spaced vertical wells.

The logistical advantages of horizontal wells are obvious. Horizontal wells avoid the need for installing wellheads inside buildings or in the midst of complex manufacturing or process facilities. Landfills, spoil mounds, and landfill liners need not be penetrated to extract leachate or other underlying contaminants. In addition, contaminant concentrations are often highest directly beneath buildings, landfills, and other obstacles to remedial operations, so that treatment facilities are constructed tens or hundreds of feet away from the target zone of remediation.

Soils are naturally stratified and individual aquifers or water-bearing zones are much wider than they are thick. Despite the dominance of the horizontal direction in aquifer shapes and groundwater flow, the dominant tool for extracting contamination from subsurface sources is a vertical well. However, in many environmental remediation scenarios, a horizontal well offers a better match of form and function than a vertical well. The tabular geometry of many aquifer zones renders horizontal wells more productive than vertical wells. The flow characteristics of many aquifers create elongate contaminant plumes, and extracting contaminated groundwater is often more efficient using horizontal wells. A horizontal well placed through the core of a plume can recover higher concentrations of contaminants at a given flow rate than a vertical well.

Horizontal wells also offer many advantageous over vertical wells in fractured aquifers. Fractures in an aquifer are commonly vertical. Because fluid or vapor recovery from fractured zones requires penetration of numerous fractures, a horizontal well oriented normally to vertical fractures is the optimal tool for pump-and-treat or soil vapor extraction systems in vertically fractured zones. By analogy, vertical wells are efficient in highly stratified soils that have little vertical communication between strata, where fluid or vapor recovery from many thin layers through a single wellbore is required.

Injection of groundwater is part of some remediation systems, either to create a water table mound or to reinject treated effluent from a manufacturing plant into the subsurface. Water table mounds can help control flow of contaminants toward recovery wells or trenches, or they can serve as hydraulic barriers. Manufacturing plants can avoid high sewer discharge costs if their treated plant effluent can be reinjected into a nondrinking water aquifer. Reinjection can cause mounding, but the mounding can be minimized by using horizontal wells. Hydraulic barriers are most efficiently created using horizontal wells oriented perpendicularly to the groundwater flow direction.

Various drilling technologies are capable of installing horizontal wells for subsurface pollution control. Such wells are typically installed in unconsolidated soils, 10 to 200 feet deep. Selection of drilling technique depends on surface access, well placement and completion requirements, and subsurface hydrogeology. During drilling of a well, drilling mud can invade the aquifer and change its permeability in the vicinity of the well and cause formation damage or a "skin effect." The thickness of the skin zone depends on drilling technology and also on the permeability of the aquifer. The additional drawdown due to the change in permeability and the turbulent flow around the well is called "well losses." Because of lower flow rate per unit screen length, horizontal wells show smaller well losses due to drilling mud invasion than vertical wells.

The current high installation cost of a horizontal well compared to that of a vertical well is offset by operating and maintenance cost savings. New developments in horizontal drilling technology will further reduce the cost of installing horizontal wells, and subsurface pollution control using horizontal wells should become as common as using vertical wells.

HORIZONTAL WELLS IN GROUNDWATER REMEDIATION

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Horizontal wells have been used in an increasing number of remediation projects. In addition to chemical and biological reactive barriers, horizontal borings can be used for groundwater extraction and control, air sparging, bioremediation, groundwater injection, for vadose zone soil vapor extraction or bioventing systems, and free product recovery. Although, in areas where there is a great deal of fluctuation in the groundwater table, use for free product recovery can be problematic.

Horizontal well technology was first used in the late 1920s by the petroleum industry to increase oil reservoir thickness per well and greatly increase oil production. In the 1970s, the technology was applied by utility companies to cross rivers and other natural or manmade barriers such as highways. The use of horizontal drilling technology for environmental applications began in the late 1980s and has escalated ever since.

Horizontal wells offer distinct advantages over trenching or vertical wells. Trenching produces massive quantities of excavation spoils and is economically limited in depth of application. In addition, horizontal wells can be installed beneath structures and other surface obstructions that would be impossible to access using trenches or vertical wells.

Horizontal wells have a unique advantage that originates in the geometry of the typical contaminated groundwater system. Horizontal permeability is on the order of ten times greater than vertical, because of the stratigraphic layering of near-surface soil horizons. The effect of increased horizontal permeability enhances the spread of contaminant plumes horizontally. Horizontal wells can be installed through contaminated zones, along their leading edges, or along a property line. All active groundwater remediation systems rely on the mass

transport of water, air, or other chemicals. Mass transport is induced through the interface offered by the screened sections of a well that are exposed to the contaminated strata. Compared with vertical wells, horizontal wells can increase well screen interface by an order of magnitude or more.

Various drilling heads and cutting removal technologies have been applied to horizontal drilling. Fluid-cutting systems, mechanical cutting, augers, percussion drilling, and sonic methods are all available. The selection of which is dependent on the geology and competency of the subsurface (and the selected technology vendor). With appropriate techniques, bore holes may be extended through difficult conditions such as gravel formations, coral reefs, and even boulders or bedrock.

The removal of cuttings is usually based on mud slurry systems for installation beneath the groundwater table and air systems for installation in the vadose zone. The formulation and engineering of a mud slurry system takes great care; historically this has been one of the most common points for the failure of an installation. The mixture must be capable of holding the hole open, removing the cuttings without erosion of the walls of the well bore, and it must be capable of decomposing with time to restore the well bore to permeable operation.

Inherent with the horizontal drilling process is the ability to accurately direct the placement of the horizontal well bore. Two dominant methods of achieving directional control of the drill head are available: magnetometer/accelerometer and radio beacon. A magnetometer/accelerometer array is expensive, and the long configuration of an array makes it prohibitive for short radius bends. It is also subject to magnetic interference, which can be a serious issue around tanks or other surface or near-surface structures (i.e., buildings, piers and piles, pipelines, or utility runs). Radio beacons previously have been limited to a depth of 25 feet or less, although there have been instances where down hole wirelines have increased accessible depth. Well casings for horizontal wells must be more highly engineered than for vertical wells. They must have great tensile strength to withstand the significant forces associated with installation. Compressive strength is required to resist the overburden load as the horizontal well bore collapses with time. The screen pack is also a critical issue with regard to installation and subsequent operational efficiency. Conventional sand packs can be installed, but they require great care. Many vendors now use prepacked screens. These are nested screens, an exterior screen (typically HDPE), a packing system (sand, filter cloth, or other filter media or mixtures of media), and an internal screen typically constructed of stainless steel. These prepacked screens are stiffer and subject to larger turn radii, but they obviate the difficulties associated with installing a conventional sand pack in a horizontal boring.

Horizontal drilling is a relatively costly process to use. It is driven by necessity, or the economic advantages of scale. Necessity drivers are generally the need for the installation of a remediation system underneath a structure or facility that cannot be disturbed. Economics of scale come in to play with regard to large contaminant plumes. A single horizontal boring can replace 10 to 30 vertical wells in a plume of large aerial extent. The break-even point for the choice between horizontal or vertical wells occurs around the need for four to five vertical wells. Installations requiring more than five vertical wells along a linear trend can often be more cost effectively addressed with horizontal wells.

Two basic methods of horizontal well installation are available. The simplest involves two ends, boring downward to near the desired depth at one end, curving the boring to the horizontal, traversing the required path and distance horizontally, and then recurving to the surface at the other end. The casing is then pulled back through the boring from the distal end. A more sophisticated approach is to use a single end, through which the boring is advanced, followed by the casing being pushed through the boring, a more difficult, risky, and time-consuming process. Horizontal drilling using the two-end approach can cost as little as $30 to $40 per linear foot; the cost for single-ended systems start at $80 to $90 per linear foot.

As with many other technologies applied to the environmental industry, developers over the last decade have focused on the creation of a "just good enough" technology. Placement accuracy is sufficient, boring sizes are minimal, and construction materials are designed for the limited life of the project. Successful installation of horizontal wells depend on the selection of a vendor who is flexible enough to use an approach that is appropriate for the subsurface condition of your site; who is experienced in the use of the specialized drilling equipment and screens; who can engineer the application as well as the installation procedures; and who is experienced enough to be quick. Aside from failure caused by inadequate mud engineering, taking too long is another key source of failure; the well bores simply cave in before installation is complete.

Horizontal wells have been adapted for use in many soil and groundwater projects. The use includes groundwater extraction, air sparging, free product recovery, in situ bioremediation and bioenhancement, soil vapor extraction, in situ soil flushing, in situ radio-frequency heating, treatment walls, hydraulic and pneumatic fracturing, and leachate containment and collection (1). The overall performance of horizontal wells used for air sparging and vacuum extraction at the Savannah River Site in South Carolina (2) shows the following:

- A five-time increase in chlorinated solvent removal as compared with conventional vertical wells.
- Eight tons of chlorinated solvents were removed over a 20-week period. The equivalent would have been 11 vertical wells at a pump and treat system, each extracting at a rate of 500 gallons per minute;

The Savannah River Site project managers estimate that a 40% cost savings was predicted when compared with the use of conventional pump and treat technologies.

In the six years between 1987 and 1993, over 100 horizontal wells were drilled in the United States as part of environmental remediation projects. One quarter of them were used for groundwater extraction, one quarter of them were used for soil vapor extraction, and one half

of them were used for other technologies (air injection, bioventing, and free product recovery). Eighty percent of the horizontal wells were installed at depths of 25 feet or less (2).

The advantages of horizontal wells are well known: Horizontal well screens contact a larger surface area of contaminated aquifer than do conventional vertical wells; the cost of horizontal wells, although more than vertical wells, is less expensive when comparing the fewer number of wells required for a particular remediation project; and finally because horizontal transmissivity generally exceeds vertical transmissivity in most aquifers, horizontal wells can deliver and recover more fluids, gases, and groundwater than can vertical wells (1). With these advantages and the improvements in directional drilling and global positioning systems (GPS), it is likely that horizontal wells will become more common in future remediation projects.

BIBLIOGRAPHY

1. Miller, R.R. (1996) *Horizontal Wells, Ground-Water Remediation Technologies Analysis Center (GWRTAC)*. Technology Overview Report TO-96-02.
2. Hazardous Waste Remedial Actions Program (HAZWRAP). (1995). *In situ Bioremediation Using Horizontal Wells*. Innovative Technology Summary Report, prepared for U.S. Department of Energy. Available: http://www.gnet.org/gnet/tech/reports/sbu.htm.

HEAD

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Water moves from zones of higher energy to zones of lower energy. For example, gravity causes water to move from higher to lower elevations. Water also moves from higher to lower pressures. The total energy is the sum of the all forces acting on water. This total energy is referred to as the *head*, which can determine the direction and rate of water movement.

Bernoulli's equation commonly combines the dominant forces that cause water to move:

$$H = z + \frac{P}{\gamma} + \frac{v^2}{2g} \tag{1}$$

where H is the total head, z is the elevation of the point where the head is measured, P is the fluid pressure at the point of measurement, $\gamma = \rho g$ is the fluid specific weight, ρ is the fluid density, g is the gravitational constant, and v is the fluid velocity.

The velocity component can be omitted if the flow is slow, $v \approx 0$, which is generally true in groundwater systems. When the velocity is neglected, the total head is

$$H = z + p \tag{2}$$

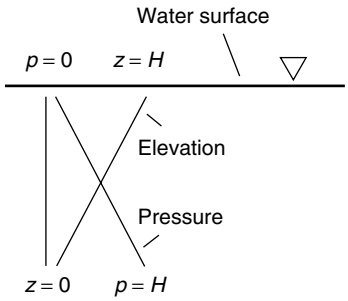


Figure 1. Total head is the sum of the elevation and pressure heads. For example, the elevation decreases and the pressure increases when moving downward from the water surface in a column of still water.

where $p = P/\gamma$ is the fluid pressure head. Figure 1 shows how the pressure head and elevation head compensate in a column of still water.

The pressure term is omitted when the water surface elevation is measured, because the fluid pressure is zero, $p = 0$, at this point. This simplification yields the equation, $H = z$, where z is the elevation of the water surface.

Important assumptions required for the use of water levels to determine the head include (1) hydrostatic conditions exist with no vertical water movement; (2) the water velocity within the aquifer is sufficiently small; (3) water within the monitoring borehole or piezometer is pure water at a standard temperature and density; and (4) the air pressure on the water surface equals the mean barometric pressure.

CAPILLARY AND OSMOTIC FORCES

Capillary and osmotic forces also affect the total head. Failure to account for these forces may result in incorrect predictions of water flow and transport.

Capillary forces develop because of the tendency of soil surfaces to attract water. Water held on soil surfaces resists the downward force of gravity, and it does not readily drain from the soil. The head must consider the negative fluid pressure that develops because of capillary forces. A measure of the force by which water is held is the *matric tension*, which can be measured with *tensiometers*.

Water may move upward above the regional water table because of capillary forces. The height of the saturated zone formed above the water table (i.e., the capillary fringe) is largely determined by the magnitude of capillary forces, which is a function of the pore surface area. Finer grained media have greater capillary forces, which result in higher capillary fringes.

Capillary forces generally increase with decreasing pore size, as shown in Fig. 2. The *capillary rise equation* relates the pore size to the height of rise:

$$\psi = \frac{2\sigma \cos\alpha}{\gamma r} \tag{3}$$

where ψ is the capillary height of rise, σ is the surface tension of water, α is the solid–liquid contact angle, and r is the pore radius (1).

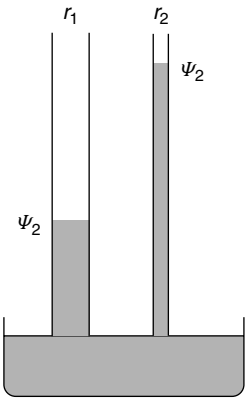


Figure 2. Height of rise of water in capillary tubes. Note that the height of rise increases as the radius of the tube decreases. Equivalently, small pores hold water to greater tensions than do large pores.

An additional force that induces fluid movement is a change in solute concentration. The *osmotic potential* decreases the head of water, which causes water to flow from areas of low solute concentrations to areas where solute concentrations are higher. In arid areas with high soil solute concentrations, salts may become concentrated as water evaporates at the soil surface, which causes an increase in the salt concentration. This increase in salt concentration induces an additional force that causes water to move upward from less saline groundwater to the surface.

Thus, evaporation can increase the height of the capillary fringe by augmenting the capillary force with osmotic forces. The osmotic height of rise in dilute solutions is

$$\phi = \frac{kTC}{\gamma} \tag{4}$$

where ϕ is the osmotic height of rise, k is the Boltzmann constant, T is the absolute temperature, and C is the solute concentration (2).

FLUID DENSITY

Water levels can be affected by the density of the fluid within the borehole. For example, water levels in a well monitoring a deep aquifer may be affected by the temperature of the water in the borehole.

Warmer water is less dense than is colder water (except below 4 °C) and so a column of warm water will display a higher water level than will a column of colder water for the same pressure at the bottom of the borehole. Because of the *geothermal gradient* (the tendency of temperature to increase with depth below the surface), deeper water within the borehole is warmer and slightly less dense than is water near the surface.

Other factors besides temperature affect the water density in a well. The dissolved solids concentration (salinity) causes the water density to increase. Suspended sediments also increase the weight of the fluid, whereas air bubbles rising to the surface lower the density of the water column. Small changes in density over a long water column cause an appreciable difference in observed water levels.

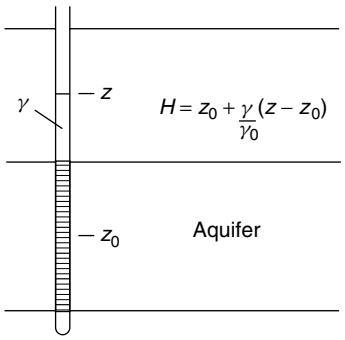


Figure 3. Total head, H, adjustment for conditions when the borehole specific weight, γ, is different from the freshwater weight, γ_o. The effect is greater for larger differences in elevation between the water level, z, and the screened zone, z_o.

To account for the variation in fluid density, observed water levels should be adjusted with a standard water density, called the *freshwater density*. The corrected head is called the *freshwater head*, which accounts for the fluid density within the borehole:

$$H = z_o + \frac{\gamma}{\gamma_o}(z - z_o) \tag{5}$$

where H is the freshwater head, z_o is the elevation of the screened interval, z is the observed water level elevation in the well, $\gamma = \rho g$ is the average fluid specific weight in the well, and $\gamma_o = \rho_o g$ is the standard freshwater specific weight. Figure 3 illustrates the geometry of this problem.

The freshwater head equation can also be written as

$$H = z_o + \varrho\, \Delta z \tag{6}$$

where $\varrho = \gamma/\gamma_o$ is the specific gravity of the fluid within the well and $\Delta z = z - z_o$ is the height of the column of water within the monitoring well above the screened zone.

These equations show that the freshwater head correction is larger for longer water columns and for water with a density that is substantially different from the freshwater density.

SPATIAL AND TEMPORAL VARIATION

Head is often observed to vary over both space and time. These variations are particularly important when mapping the regional potentiometric surface, because long-term averages may not accurately reflect the surface dynamics over time.

Temporal variations result from barometric (atmospheric pressure) influences, tidal effects, fluid density (sediment, salinity) changes, and vertical flow (nonhydrostatic conditions) within the water column (2). Spatial variations are a function of aquifer properties as well as of the regional hydrogeologic flow environment.

Heads within a specific hydrogeologic unit generally vary smoothly over space, unless some kind of intervening boundary causes a jump in the head within the formation. For example, water levels may decline smoothly, only to change abruptly when a fault displaces one side of an

aquifer relative to the other, which causes a sharp change in the head across the boundary.

Also, heads in different hydrogeologic units may be different because the recharge and discharge patterns for each aquifer are different. A unit that outcrops in one area may have a different head than one that outcrops at a higher elevation. Wells that tap different aquifers are commonly observed by scientists to have different water levels, even when the wells are situated next to each other. This variation of head by aquifer is a result of the regional hydrogeologic setting, which must be considered when trying to evaluate water head data.

Spatial variations are plotted on maps with *equipotentials*, which are lines of constant head within a hydrogeologic unit. Each aquifer generally has a unique set of equipotentials that can also vary over time. In *isotropic* media (i.e., aquifers with no preferential flow direction), the direction of fluid flow is shown by placing lines, called *streamlines*, on the map that are perpendicular to the equipotentials.

Water levels in wells can also vary over time. Water levels in wells are commonly affected by barometric pressure—they fall as barometric pressure rises, and they rise as the pressure falls—because the total head in the aquifer is the sum of the water level elevation plus the atmospheric pressure on the water surface in the borehole.

Although the influence of barometric pressure is commonly neglected when monitoring water levels in wells, large changes in barometric pressure (such as when large storms pass overhead) can occasionally cause large errors in the determination of the total head.

To correct for the effects of barometric pressure, observed water levels, W, can be adjusted by the variation in pressure about the mean, $\Delta B = B - \overline{B}$:

$$H = W + \Delta B \tag{7}$$

The mean pressure, $\overline{B}$, can be taken as the average global sea-level barometric pressure, $\overline{B} = 1013.25\ hPa \approx 33.9$ ft, or, alternatively, equal to the local average barometric pressure, which varies with elevation and local weather conditions. Air pressure variations can be neglected by sealing the well, or by measuring absolute pressure instead of the gauge pressure within the monitored interval.

Barometric pressure changes cause many wells to fluctuate over short time periods (e.g., from day to day), whereas precipitation, evapotranspiration, and pumping patterns often cause longer term variations. Climatic variation over time also can have a large influence on observed head. In trying to establish a long-term average head for a well, one must consider all possible sources of short- and long-term variation.

BIBLIOGRAPHY

1. Hillel, D. (1971). *Soil and Water: Physical Principles and Processes*. Academic Press, New York.
2. Spane, F.A., Jr. and Mercer, R.B. (1985). HEADCO: A program for converting observed water levels and pressure measurements to formation pressure and standard hydraulic head. Pacific Northwest National Laboratory, Rockwell Hanford Operations, Richland, WA, Report PNL-10835.

WELL HYDRAULICS AND AQUIFER TESTS

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The objectives of an aquifer test are to identify the performance of a well (to estimate the yield capability) and to estimate aquifer properties. Accurate estimates of the hydraulic characteristics of aquifers depend on reliable aquifer test data. The tests are done on existing wells or a well drilled specifically for that purpose. An aquifer test is a controlled, field site experiment to determine hydraulic conductivity and aquifer storage. The test consists of measuring groundwater discharge and observing water level changes in the pumped well.

These are the hydrologic and geologic conditions needed for a successful aquifer test:

- Hydrogeologic conditions should not change over short distances.
- No discharging well or stream nearby.
- Discharge water should not return to the aquifer.
- The pumped well should be completed to the bottom of the aquifer and should be screened or perforated through the entire thickness of the aquifer.
- Observation wells (at least three) should be screened at the middle point in the aquifer. One observation should be located outside the area of influence of the pumping well drawdown.
- Location of observation wells should be based on the aquifer character.
- Determination of prepumping water-level trend.

The following conditions and field measurements are needed for an aquifer test:

- Accurate water-level measurements during pumping and recovery
- Pumped well developed prior to test (several hours of pumping and surging)
- Dependable power source to provide a constant pumping rate
- A flow meter that can read instantaneous and cumulative discharge
- Electrical conductance, Eh, pH, DO, and temperature measurements
- Water levels measured several hours before the test begins
- Pumping rate maintained at 5% tolerance. An optimal rate is 50% of maximum yield
- Water level is measured with an electric sounder or pressure transducer
- Remove the discharge water from the site

- Observation wells should be tested by injecting a known volume of water and measuring the recovery response
- Establish baseline trends of regional water level changes and barometric pressure changes
- Pumping well lithology and construction data

TYPES OF TESTS

Specific Capacity Test

The amount of water that a well will yield can be determined by a specific-capacity test, in which the pumping rate and water-level changes are monitored for a set period of time. The first step is to measure the initial water level in the well. Commonly, a well is pumped at several successively increasing rates for uniform periods (typically 1 hour) to establish a rate that can be maintained for long-term pumping. The well is then pumped at a steady rate and the water-level changes are monitored at the pumped well. Water levels should also be monitored in at least one observation well 2 to 20 meters (6 to 65 feet) from the pumped well. The water level will decline quickly at first, as water is removed from the well, then more slowly as the rate of flow into the well approaches the pumping rate. The ratio of the discharge rate (Q) to water-level change (drawdown, dd) gives the well's specific capacity, or $\mathrm{Sc} = Q/\mathrm{dd}$. For example, if the discharge rate is 6 liters per second (L/s) (100 gallons per minute) and the drawdown is 3 meters (10 feet), the specific capacity of the well is 2 L/s per meter (10 gpm/ft) of drawdown. Once the specific capacity and the available amount of drawdown are known, the yield of the well can be determined from the formula $Q = \mathrm{Sc} \times \mathrm{dd}$. The pump should be deep enough that the water level does not go below the pump intake. The pump depth should also be sufficient to allow drawdown caused by pumping and natural declines in water level during periods of drought

Step-Drawdown Test

The step-drawdown test evaluates the performance of a well. Well performance can be affected by resistance to flow in the aquifer itself; partial penetration of the well screen, incomplete removal of mud from the gravel envelope, or invasion of fines into the envelope; and blockage of part of the screen area. The well should be developed prior to the test using a surge block and/or pumping until the well discharge is clear In this test, the well is pumped at several (three or more) successively higher pumping rates, and the drawdown for each rate is recorded. The test is usually conducted for 1 day. The discharge is kept constant through each step. The test measures the change in specific capacity. The data provide a basis to choose the pump size and discharge rate for the aquifer test and for long-term production.

Slug Test

In this test, a small volume of water is removed from a well, or a small volume is added and the recovery of the water level is measured. The aquifer transmissivity can be determined from the time–drawdown or recovery data. The disadvantages of the test are that a data logger is needed to measure water-level changes and water removed represents only a small volume of the aquifer. Slug test data are evaluated by the Bower and Rice (1) method for unconfined aquifers and the Cooper, Bredehoeft, and Papadopulos (2) method for confined conditions. The advantages of these tests, compared to those of full aquifer tests with observation wells, are reduced cost and time. The disadvantage is that a storage coefficient is not determined and only a small volume of the aquifer is sampled. Many factors contribute to error in slug tests as follows: entrapped air, partial penetration, leaky joints, and the radius of influence of the test.

ANALYSIS OF AQUIFER TEST DATA USING THE THEIS EQUATION

The Theis equation (3) is used to determine the hydraulic characteristics of an aquifer. In this test, a well is pumped, and the rate of decline of the water level in nearby observation wells (two or more) is noted. The time drawdown is then interpreted to yield the aquifer parameters. In 1935, C.V. Theis (3) developed the first equation to include pumping time as a factor (4). The following are assumed:

1. The pumping well is screened only in the aquifer being tested.
2. The transmissibility of the aquifer is constant during the test to the limits of the cone of depression.
3. The discharging well penetrates the entire thickness of the aquifer, and its diameter is small compared to the pumping rate.

These assumptions are most nearly met by confined aquifers at sites far from the aquifer boundaries. However, if certain precautions are observed, this equation can also be used to analyze tests of unconfined aquifers (5).

BIBLIOGRAPHY

1. Bower, H. and Rice, R.C. (1976). A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. *Water Resources Research* **12**: 423–438.
2. Cooper, H.H. et al. (1996). Response of a finite-diameter well to an instantaneous charge of water. *Water Resources Research* **3**: 263–269.
3. Theis, C.V. (1935). The significance of the cone of depression in groundwater bodies. *Economic Geology* **33**(8): 880–902.
4. Heath, R.C. (1989). *Basic ground-water hydrology*. USGS Water Supply Paper 2220, p. 84.
5. Lohman, S.W. (1972). *Ground-water hydraulics*. USGS Professional Paper 708, p. 70.

HYDRAULIC PROPERTIES CHARACTERIZATION

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Groundwater is becoming an important issue as a source of fresh water. The groundwater that exists at the subsurface is called an aquifer. An aquifer is a geologic unit that can store and transmit water at rates fast enough to supply reasonable amounts to wells. Thus, understanding a groundwater body is an essential factor in groundwater development and protection.

The geohydrologic properties of a groundwater body consist of physical, chemical, and biological parameters of the solid matrix and liquid within its pore space. These parameters determine the quantitative, qualitative, and interpretive aspects of the groundwater body. The solid matrix may consist of various sedimentary deposits or rock types. The liquid within the pore space of the groundwater body consists of water, dissolved minerals and gases, microorganisms, and colloidal material.

INTRODUCTION

Many groundwater professionals define a groundwater body by its flow property, such as aquifer, aquitard, and aquiclude (1), which is only good in defining the rate of water yield from a groundwater body. When dealing with water quality and environmental issues, we need better definition of the other properties and characteristics, not just dissolved chemicals, hydraulic conductivity, and effective porosity.

The following parameters characterize groundwater body properties:

- *Geophysical parameters*: electrical conductivity, hydraulic conductivity, storativity, effective porosity, temperature, media thickness, pressure or hydrostatic level, adsorption, absorption, radioactivity, electrical charge, electrokinetic flow, porous or fracture media, recharge, discharge
- *Biochemical parameters*: pH, bacteria counts, inorganic chemicals, organic chemicals, oxidation/reduction, ion exchange potential

Most of these parameters are not required for site characterization by natural resources agencies and the U.S. EPA (2,3). It is very clear that most groundwater bodies are poorly characterized because there is no incentive or pressure to understand these parameters, as long as the groundwater is fit for use. Most textbooks define only some of the parameters but without standardized procedures. The following sections provide typical definitions of the parameters, analytical methods, use, interpretation, limitations, and the necessity for future improvement in characterization.

PARAMETER DEFINITIONS

The definitions of the following parameters are provided in Driscoll (4), Freeze and Cherry (1), Todd (5), Lohman (6), and Batu (7), Ferris et al. (8) Loo et al. (9) unless otherwise noted.

Geophysical Parameters

Electrical conductivity is the ability of a medium to conduct electricity measured in μmho/cm. Resistivity is the inverse of electrical conductivity measured in ohm-meters.

Hydraulic conductivity is the measurement of the ease of water flowing through a medium or water permeability. It is often expressed as cm/s or gpd/ft^2.

Storativity of a saturated aquifer is the volume of water release from storage per unit surface area per unit decline of hydraulic head.

Effective porosity or flow porosity is the interconnected pore space available for water to flow through (10).

Media thickness is defined as the aquifer thickness or productive water-bearing zone.

Potentiometric surface is expressed as the pressure in the water head in a confined aquifer. It is called the groundwater table when the aquifer is unconfined.

Adsorption/Absorption is the process by which molecules of dissolved chemicals in a fluid attach to solid surfaces (11–13).

Radioactivity is the radiation emitted by natural elements or radioactive wastes. Radon and tritium are commonly occurring radioisotopes of uranium or other radioactive elements (14).

Electrical charge is measured as the electrical potential difference (in millivolts) between layers of different materials. Fine-grain material such as clay and silt are slightly positively charged whereas sand and gravel are slightly negatively charged.

An **electrokinetic gradient** occurs when a flow of water is created by dc electricity flow from an anode to a cathode (1,15). It is common to create several feet of water head at the cathode when the applied direct current potential difference is 50 volts over a short distance of 40 to 50 feet between electrodes.

Recharge/Discharge Boundaries can be detected during a pump test when the drawdown curve becomes flat, recharge condition and change (steepened) slope, negative or discharge condition (16). Pumping near a surface stream can often detect a recharge condition. Pumping near a fault or lithologic discontinuity can often detect a negative boundary condition.

Biochemical Parameters

pH is an indication of the acidity or alkalinity of soil or water.

Bacteria count is the enumeration of the population of indigenous bacteria in soil or water which often is expressed in colony forming units, CFU (17).

Inorganic Chemicals are any chemicals not based on carbon such as any salts of major cations and anions and trace metals.

Organic Chemicals are carbon based compounds and can be naturally occurring or occurring as spilled chemicals.

Oxidation/Reduction Potential redox potential in short as is the state of electrochemical reaction which is measured in millivolts.

Ion exchange potential is related to the electrical charge measured in millivolts of colloidal particles which carry relatively large surface area. Colloidal particles have diameters in the range of 10^{-3} to 10^{-6} millimeters. Clayey material has very high cation exchange potential.

FIELD TESTING AND ANALYSIS OF PARAMETERS

Geophysical Parameters

Many of the following physical parameters can be defined by field pump tests:

electrical conductivity
hydraulic conductivity
storativity
effective porosity or flow porosity
temperature
radioactivity
media thickness
pressure or hydrostatic level or potentiometric surface
porous or fracture media
recharge/discharge boundaries

Pumping Test. Before a pumping test is conducted, geological and hydrological information such as the geological characteristics of the subsurface, the type of aquifer and confining bed; the thickness and lateral extent of the aquifer and confining beds, including boundary conditions, is obtained, preferably by surface resistivity and electric logs. Also, data on the groundwater flow system, including the hydraulic gradient and regional groundwater flow and existing wells in the area, should be collected. Then, the site for the well is selected considering the area representative of hydrological conditions, not near railroads and motorways, not in the vicinity of an existing discharge well, or a low water level gradient. After the well site has been chosen, the drilling operation can begin. The pumping well should be drilled to the bottom of the aquifer. Then the pump size and pump type are planned. Besides the well diameter and well depth, the location of the well screen is to be determined. The length of the well screen will largely be decided by the depth at which coarse materials are found. A general rule is to screen the well 100% of the aquifer thickness or full penetration. Partially penetrated observation wells can be used if the distance of the observation is more than 2.5 times the thickness of the aquifer tested, which is true for isotropic and anisotropic aquifer pump tests.

With regard to a pumping rate, too low or too high a pumping rate is not desirable. Too high a rate can produce water loss, and too low a rate may make too gentle a drawdown curve. The water levels measured in observation wells represent the average head at the screen of the observation wells. The measured drawdown responses to be taken during a pumping test are of two kinds, measurements of the water levels in the well and the observation wells and measurements of the discharge rate of the well.

To be practical, each pump test should last no more than one day (1440 minutes), which is enough to cover more than three time log cycles; 10, 100 and 1000 minutes, respectively. Measurements should also be made of the atmospheric pressure, temperature, the levels of nearby surface water, if present, and any precipitation. A longer duration pump test is good only for the analysis of boundary conditions (16). Drawdown data for the time period to overcome well bore storage should not be plotted for analysis.

A step drawdown test should not be conducted because it is a test for well yield and well efficiency for well drillers' use and not for the analysis of geohydrologic parameters (18).

Single Dimensional Pump Test Analysis. The data analysis for the result of the pumping test is dependent on the aquifer conditions such as isotropic or anisotropic aquifer, homogeneous or non-homogenous aquifer, non-leaky or leaky aquifer, confined or unconfined aquifer, confining aquitard, etc. Data analysis also depends on the drawdown condition such as steady state or transient conditions. Before interpreting the pumping test result, conversion of the data into appropriate units and correction of the data for external influences are necessary. The interpretation of the pumping test data is primarily a matter of identifying an unknown system. Theoretical models comprise the type of aquifer and the initial and boundary conditions, which, in a pumping test, affect the drawdown behavior of the system in their own individual ways.

Old fashioned curve matching techniques and computer fitting analysis all have inherent errors such as matching inaccuracy and oversimplified statistical assumptions. Therefore, curve matched analysis results may not be very accurate.

It is more practical to do a pump test analysis on semilog paper using the straight line plot interpretations established by Cooper and Jacob (19) for hydraulic conductivity, storativity, and radius of influence from drawdown versus time and drawdown versus distance semilog plots. The scatter of the data points is also an indication of whether anisotropic or heterogeneous conditions are encountered. An isotropic and homogeneous aquifer will be reflected by subparallel slopes on the drawdown versus time plots for observation wells, and all points on the drawdown versus distance plot will fall on a straight line (only isotropic). If the slopes of the drawdown versus time plots are not subparallel, the aquifer is heterogeneous. If the points on the drawdown versus distance do not fall or fit onto a straight line (scattered), the aquifer is anisotropic or shows a potential

preferential flow direction such as channel flow, fracture media, or artificial conduits of migration (20,21).

For aquifer test analysis in unconfined aquifers, the Boulton analytical method will apply for determining hydraulic conductivity and specific yield or storativity (22). New analytical solutions for evaluating the drawdown near horizontal and slanted wells with finite length screens in water table aquifers are presented in Zhan et al. (23). These fully three-dimensional solutions consider instantaneous drainage or delayed yield and aquifer anisotropy.

For the analysis of the leakage property of the confining layers of the aquifer, Hantush (24) developed a semilog straight line analytical method, known as the 'inflection point' method.

Multidimensional Pump Test and Analysis. Two-dimensional horizontal hydraulic conductivity anisotropic tests (major and minor tensor) require three or more observation wells at different distances and orientations from the fully penetrating pumping well (25,26). The Hantush and Thomas analytical method is a hand contouring method which is not very accurate and may require many observation wells. The Papadopulos method requires drawdown data from three or more observation wells at the same elapsed time and a least squares or equivalent numerical fitting technique for an elliptical fit. The fitted ellipse orientation and axes thus define the horizontal anisotropic hydraulic conductivity tensors (20,21) Loo (27).

For the analysis of vertical hydraulic conductivity (not leakage from confining layers), the pump test requires nonoverlapping partially penetrated wells, one pumping well and one or more observation well, located within 2.5 times the aquifer's thickness from the pumping well (28). The pump test procedure for multi dimensional hydraulic conductivity tensors was first conducted in an alluvial deposit at Christensen Ranch in Powder River Basin, Wyoming, at an *in situ* uranium mining test site. Loo et al. (29) conducted a similar test at the Equity/DOE BX *in situ* oil shale project.

All pump test and analysis procedures described were documented in the manual written by Loo (20), Loo (30) and Loo (27).

Effective Porosity Testing and Analysis. No pump test can analyze effective porosity. The specific yield value from pump test analysis provides only a partial characterization because the specific retention is not defined.

Freeze and Cherry (1) described the tracer test analysis for dispersivity and effective porosity. However, the tracer test procedures have not considered retardation of the sorption properties of the solid matrix. The selection of different tracers for different media is an art more than a science because there is no perfect tracer. Therefore, a tracer test for determining effective porosity is not very practical.

The analysis of effective porosity can actually be easily determined (though seldom used) from stressing or loading an aquifer. This can be done by tidal efficiency or barometric efficiency tests or simply by sucking a vacuum on the pump test well. The effective porosity can then be calculated once the storativity is defined by the pump test analysis. Jacob (31) provides an analytical solution for a confined aquifer. Hantush (32) provides an analytical solution for an unconfined aquifer.

Radioactivity can be mapped by a natural gamma ray borehole geophysical log. If an abnormal level of radiation is mapped, then it may be necessary to test for radioisotopes of uranium, radon, and tritium and the level of their radioactivity (14).

Electrokinetic Parameter Testing and Analysis. A resistivity survey can be conducted in boreholes to distinguish the lithologic layering sequence. A surface resistivity survey can define lateral continuity or discontinuity or boundaries (33,34). These geophysical surveying methods provide large areal extent and vertical definition or three-dimensional mapping of the groundwater body.

The electrokinetic gradient was mentioned in only one paragraph in Freeze and Cherry (1). The electrokinetic gradient can be tested between monitoring wells by impressing a dc voltage across the wells (15). The response of the water level rise in the cathode well can be quite large (some times more than 10 feet) between wells 50 feet apart at a modest 50 volts potential difference and 10 amperes of dc flow. However, there is no standard test procedure at this time. This is an evolving field testing technology which may ultimately partly replace the standard pumping test. It may also provide artificially induced desorption and oxidation/reduction environments for contaminant treatment.

Elemental adsorption can be tested for cation and anion exchange capacity on soil samples in the laboratory (35). The amount of adsorbed chemical can be estimated from the Freundlich and Langmuir approximations (11). There is no standardized laboratory test for adsorption/absorption parameters of on organic compounds a fine-grain solid matrix at this time. But these are important properties because for most contaminant mass migration (mostly not very soluble), more than 90% by weight is adsorbed/absorbed by the solid matrix.

Biochemical Parameters

pH
bacteria count (17)
inorganic chemicals
organic chemicals
oxidation/reduction
ion exchange potential

All these parameters can be determined by standardized U.S. EPA laboratory analytical methods for water and wastewater. The redox potential of groundwater was required only recently for evaluating natural attenuation or intrinsic bioremediation.

However, there is very little emphasis on the test procedures for a solid matrix below the groundwater level. Most people treat soil as soil in the vadose zone. There is no requirement for characterizing soil or rock properties underneath the water table (2,3). It is important to understand that the weight of solid matrix underneath the groundwater table represents more than 90% of the total

weight. The laboratory procedures can easily be changed to accommodate the characterization of these properties in a solid matrix submerged under groundwater.

USE, INTERPRETATION, AND LIMITATIONS

After the aquifer system's properties are properly characterized, then groundwater use planning and management can be implemented.

Groundwater Resources Use

Groundwater is a limited resource, and it is very easy to overdraw a groundwater system. The result is water shortages, coastal saline water intrusion, and land subsidence. The remedy for the situation is to ensure that the design of the groundwater withdrawal system is within safe yield limits that is, using groundwater at less than the natural recharge rate. Groundwater recharge usually can be expressed as 1 to 10% of natural precipitation. The rate of recharge is dependent on the evapotranspiration rate of the area.

The remedy for saline water intrusion or upwelling is either to pump less or design a water mound or recharge mound near the coastal area (5). It is most unfortunate that, once the aquifer is intruded by saline water, the aquifer will be difficult to clean up by natural dilution.

The remedy for land subsidence is to use surface water to recharge the groundwater during the wet season. This is cyclic recharge and pumping management of a groundwater basin.

Groundwater Pollution, Prevention, and Remediation

Since the U.S. EPA was formed about 30 years ago, groundwater pollution has not stopped. Nitrate pollution due to overfertilization and from feed lots, dairy farms, pig farms, and chicken farms continues unabated. This has resulted in the 'dead zone' at the estuary of the Mississippi River in the Gulf of Mexico. Inland, the Salton Sea and the Kesterson Reservoir in California here become irrigation drainage wastewater catch basins. Farmers and agricultural business are often exempted from environmental protection regulations. Most shallow groundwater in these areas is heavily polluted.

Organic solvents such as PCE and TCE exist at almost all Superfund sites, electroplating shops, dry cleaners, and electronic manufacturing sites. Fuel hydrocarbons containing benzene, MTBE, and PAHs (such as naphthalene in diesel) have reached the groundwater at many groundwater supply sources. Chromium and naturally occurring arsenic are also reaching groundwater supplies. Fortunately, there are cost-effective technologies for cleanup at the source (15).

FUTURE IMPROVEMENTS

As mentioned in the previous sections, there is much room for improvement in geohydrologic characterization. Characterization efforts need large-scale representation area. This will lead to large-scale geohydraulic tests, geophysical surveys, and more in-depth characterization of the solid matrix submerged under groundwater.

New Test Methods

Future geohydraulic tests will most likely replace the aquifer pump test by stressing the aquifer by seismic or electrokinetic methods, so that it is more cost-effective. The mapping of anisotropic flow can be done better by horizontal and vertical resistivity profiling to map these geohydrologic anomalies. Electrokinetic surveys may in the future characterize adsorption, ion exchange, electrical charge properties in situ and have a large areal representation.

Interpretive Techniques

When all is said and done, then it's time to do some real groundwater modeling using real data. There is no doubt that the theory and modeling effort have advanced much further than parameter characterization methods.

After trying for more than 20 years, leaders in geohydrology admitted in the early 1990s that groundwater modeling does not work because of the general lack of real geohydrologic data. Hopefully, groundwater modeling will work in the next decade with real data on hand.

BIBLIOGRAPHY

1. Freeze, A.R. and Cherry, J.A. (1979). *Groundwater*. Chapter 2, 9, Prentice Hall, New York, 384–462, pp. 1579.
2. RCRA Groundwater Monitoring Technical Enforcement Guidance Document. (1986). National Water Well Association.
3. Mercer, J.W. and Spalding, C.S. (1991). Site Characterization for Subsurface Remediation, EPA/625/4-91/026.
4. Driscoll, F.G. (1986). *Groundwater and Wells*. Glossary, Johnson Filtration Systems Inc., St. Paul, MN, pp. 885–892.
5. Todd, D.K. (1980). Groundwater Hydrology. In: *Groundwater and Well Hydraulics*. John Wiley & Sons, New York, pp. 111–163, Chapter 4.
6. Lohman, S.W. (1979). *Ground-water Hydraulics*. USGS Prof. Paper 708, p. 72.
7. Batu, V. (1998). Aquifer hydraulics. *A Comprehensive Guide to Hydrogeologic Data Analysis*. John Wiley & Sons, New York.
8. Ferris, Knowles, and Stallman. (1965). *Theory of Aquifer Tests*. USGS Water Supply Paper 1536-E, p. 174.
9. Loo, W.W., Wang, I.S., and McSpadden, W.R. (1984). *Effective Porosity, Basalt Waste Isolation Project (BWIP)*. Richland, WA, Report no. SD-BWI-TI-254.
10. Loo, W.W. (1984). Practical Groundwater Modelling and Effective Porosity. *Proceedings of Groundwater Modelling Conference*, National Water Well Association.
11. Devinny, J.S. et al. (1990). Subsurface migration of hazardous wastes. In: *Chemical and Physical Alteration of Wastes and Leachates*. Van Nostrand Reinhold, New York, pp. 142–168, Chapter 5.
12. Myers, D. (1991). *Principles and Applications of Surfaces, Interfaces and Colloids*. VCH Publishers, New York.
13. Rosen, M.J. (1989). *Surfactants and Interfacial Phenomena*. John Wiley & Sons, New York.

14. Murray, R.L. (1994). *Understanding Radioactive Wastes*. Battelle Press, Colombus, OH, pp. 11–22.
15. Lehr, J.H. (Ed.). (2001). *Standard Handbook of Environmental Health, Science and Technology*. Chapters 14.4 & 14.6 on Bioremediation & Electrokinetic Treatment of Hazardous Wastes by Walter W. Loo, McGraw-Hill, New York.
16. Heath, R.C. and Trainer, F.W. (1981). *Introduction to Groundwater Hydrology*. Chapter 2, 12, Water Well Journal Publishing Co., pp. 13–17, 157–170.
17. Gaudy, A.F. and Gaudy, E.T. (1980). *Microbiology for Environmental Scientists and Engineers*. McGraw-Hill, New York.
18. Walton, W.C. (1987). *Groundwater Pump Tests Design and Analysis, Step Drawdown Test Analysis*. Lewis Publishers, Boca Raton, FL, pp. 77–79.
19. Cooper, C.C. and Jacob, C.E. (1946). A generalized graphical method for evaluating formation constants and summarizing well field history. *Trans. Amer. Geophysical Union* **27**: pp. 526–534.
20. Loo, W.W. (1987). *Standard Operational Procedures of Pump Tests and Analysis*. Certificate Seminar Manual for SUPERFUND and HAZMAT Conferences.
21. Loo, W.W. (1989–1995). *Groundwater Hydrology for Beginners Certificate Seminar*. HAZMAT & SUPERFUND Conferences.
22. Boulton, N.S. (1954). *Unsteady State Radial Flow to a Pumped Well Allowing for Delayed Yield from Storage*. International Assoc. Sci. Hydrology, General Assembly, Rome, vol. 2, Publ. 37.
23. Zhan, H., Zlotnik, V.A., and Park, E. (2001). Hydraulics Of Horizontal And Slanted Wells. In: *Water Table Aquifers*, GSA Annual Meeting, November 5–8, 2001 Proceedings, Session No. 117.
24. Hantush, M.S. (1956). Analysis of Data from Pumping Test in Leaky Aquifer. *Trans. Amer. Geophysical Union* **37**: pp. 702–714.
25. Hantush and Thomas. (1966). Analysis of Data From Pumping Tests in Anisotropic Aquifers. *Journal of Geophysical Research* **71**: No. 2
26. Papadopulos, I.S. (1965). Nonsteady flow to a well in an infinite anisotropic aquifer. *Symp. Intern. Assoc. Sci. Hydrology, Dubrovinik Symposium* **1**: pp. 21–31.
27. Loo, W.W. (1989–1995). *Groundwater Plume Management Certificate Seminar*. SUPERFUND Conferences, and HAZMAT Conferences, Washington, DC.
28. Weeks, E.P. (1969). Determining the ratio of horizontal to vertical permeability by aquifer test analysis. *Water Resources Research* **5**: 1.
29. Loo, W.W., Markley, D.E., and Dougan, P. (1979). *Three Dimensional Multiple Well Testing and Reservoir Analysis of the Leached Zone of the Green River Formation*. Equity/DOE BX In-situ Oil Shale Project, Proceedings of the Ninth Annual Rocky Mountain Groundwater Conference, Reno, NV, October 22, 1979.
30. Loo, W.W. (1989–1995). *Principles of Groundwater Hydrology Certificate Seminar*. HAZMAT Conferences.
31. Jacob, C.E. (1950). Flow of groundwater. In: *Engineering Hydraulics*. John Wiley & Sons, New York, Chapter 5.
32. Hantush, M.S. (1964). Hydraulics of Well. In: *Advances in Hydroscience*. Academic Press, New York.
33. Milsom, J. (1989). Field Geophysics, Electrical Methods. *Geological Society of London Handbook Series*. Open University Press and Halsted Press, pp. 72–106.
34. Vogelsang, D. (1995). Environmental Geophysics. *Geoelectrical Methods*. Springer-Verlag, New York, pp. 9–31.
35. Dragun, J. (1988). *The Soil Chemistry of Hazardous Materials*. Hazardous Materials Control Research Institute, pp. 75–262, Chapters 3–6.

MOBILITY OF HUMIC SUBSTANCES IN GROUNDWATER

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INTRODUCTION

Humic substances are a relatively stable part of the global carbon inventory. They are found mainly in solid sources, in both seabed and land sediments. High concentrations are found especially in lignite and peat. The most obvious source is the organic/humus inventory in soil. Humic substances are also found in natural water. The dissolved inventory is relatively small compared to that found in sediments. Nevertheless, this inventory is a key in the mobilization of numerous trace elements and pollutants, which includes the key influence in determining the stability of and interface reactions with minerals.

Some key information on the origin, stability, and mobility of dissolved aquatic humic substances is presented here. Also described are the experimental methods required, the approach for derivation of conclusions from experimental results, and background information. The focus is on the hydrophilic part of the total humic substance inventory. The hydrophilic aquatic humic substances originate from the same source as the stationary less hydrophilic ones, including partial oxidation from this stationary inventory. The hydrophilic nature is given by oxygen-containing functional groups. Some of these, especially carboxylic acids, may change the degree of hydrophilicity depending on physicochemical conditions, that is protonation, metal ion complexation and localization of counterions, pH, metal ion concentration, and ionic strength. Consequently, the whole inventory and changes in physicochemical conditions must be kept in mind when discussing the behavior of the hydrophilic aquatic part.

Humic acid is used both as a collective term for humic substances with a sufficiently high content of hydrophilic groups to dissolve in pH neutral range or specifically for the fraction that is dissolved in pH neutral range and flocculates in the acidic range with the complementary fraction of fulvic acid, soluble also under acidic conditions. Furthermore, a fraction of organic carbon found in soil not soluble in aqueous media (humin) but with some properties common with humic and fulvic acids is also frequently considered part of the overall term. This term may also be considered for rather hydrophobic humic material or humic acid precursor material also in sediments, including peat, lignite, and mineral-bound natural organic substances, such as clay organic matter. Below, humic and fulvic acids are used for the aquatic hydrophilic part of the overall inventory unless otherwise specified.

First, some basic relevant properties of humic substances are discussed. In order to study the origin, stability, and mobility of aquatic humic substances they must be isolated and purified. In order to ensure the quality of results, the success of isolation and purification must be verified by adequate characterization of the sampled humic material. Therefore, isolation, purification, and verification methods of aquatic humic substances are described as a prerequisite for interpretation of experimental results. Also discussed are the origin, stability, and mobility of aquatic humic acid followed by a summary.

BASIC RELEVANT PROPERTIES OF HUMIC ACID

The composition, mass distribution, and functional group content vary within limits, reflecting different origins and histories. Disregarding sulfur and nitrogen (present in varying low concentrations generally on the order of up to around 1% by weight), the atomic composition is dominated by carbon, oxygen, and hydrogen. The contributions of these substances vary around $CO_{0.5}H$; that is, the formal oxidation state of carbon is around zero. With respect to aquatic humic and fulvic acids, the mass distribution centers around approximately 500 mass units. In dissolved form, the molecules are highly hydrated and possibly form associates. The size distribution is generally determined to center slightly above 1 nm diameter.

Oxygen-containing functional groups and structural entities are abundant, as seen from the elemental composition. These oxygen-containing structural elements are of key importance for the hydrophilic character of humic substances. The oxygen to carbon ratio of aquatic humic and fulvic acids is somewhat higher than for the bulk sedimentary hydrophobic humic matter. The proton exchange capacity is on the order of 7 meq/g, where protonation/deprotonation takes place from about pH 10 down into the acidic range (below pH 3 a considerable number of the groups are still ionized). There is clear spectroscopic evidence for both carboxylic and phenolic types of proton exchanging groups. Carboxylic types of groups are normally quantified with about two-thirds of the total capacity. The hydrophilic character and thus the stability in aqueous solution, of humic and fulvic acids, vary with pH, ionic strength, and metal ion complexation.

ISOLATION AND PURIFICATION METHODS

Isolation

Isolation of humic and fulvic acids from natural water, including groundwater, is based on sorption chromatography. For this purpose, the XAD-8 resin is used where humic and fulvic acids sorb at low pH. Depending on the humic substance concentrations in the water sample, a pH of typically 1 or 2 will be used, the latter especially in order to limit the total amount of acid where the sample volumes are very large. Elution of both humic and fulvic acids is achieved by desorption at high pH. Typically, HCl and NaOH are used for adjustment of pH. In order to remove salt from the original sample, the column should be washed with HCl solution (pH not higher than that of the acidified water sample) prior to alkaline humic and fulvic acid elution. Where the humic acid concentration is sufficiently high, it, or at least a large part of it, will flocculate at low pH and thus is separated prior to sorption chromatography treatment.

The alkaline elute solution should be taken to pH neutral range within a relatively short time (ideally after not more than around 10 min) in order to prevent alkaline hydrolysis and sample oxidation. If desired, the humic and fulvic acid fractions are separated from each other from this concentrate by acidification, where the humic acid fraction flocculates and may be separated by centrifugation. The so obtained humic and fulvic acid concentrates are then further processed and purified. In many cases, however, preconcentration is desired, especially directly in the field.

The application of RO to humic and fulvic acid preconcentration makes use of the retention of these substances over the RO membrane. The retentate, containing salts, particles, and the humic and fulvic acids, is recirculated as long as practical with the clean water from penetration of the membrane being discarded. With increasing retentate salt concentration, the permeation of clean water through the RO membrane is decreased and finally ceases for all practical purposes (pressure buildup). Therefore, the level of preconcentration that can be obtained by RO depends on the salt content of the original water sample. Furthermore, where Ca ions and carbonate are present, calcite will precipitate unless the sample is slightly acidified and carbonic acid released. The concentrate obtained by RO is then treated by XAD-8 chromatography as described above, resulting in further sample concentration and removal of salt.

Purification

Purification has a number of objectives, including removal of organic and inorganic contaminants such as salt, complexed metal ions, and inorganic mineral constituents. For the purpose of dissolving Si-based minerals, NaF is added and the samples are left for typically 24 h. With respect to humic acid, subsequent purification is relatively simple. Humic acid is flocculated in HCl (pH 1) and centrifuged, and the supernatant is discarded, followed by dissolution in weak NaOH. The cycle is repeated until the flocculate is finally washed with HCl until no Na (from NaOH) is found. The sample is then in its protonated form and is brought to the final product by freeze-drying.

The fulvic acid does not flocculate at low pH and thus the procedure is more tedious. The fulvic acid is sorbed/desorbed on XAD-8 in a number of cycles. Finally, the slightly alkaline solution is acidified and protonated by cation exchange chromatography. The protonated fulvic acid in its final form is then obtained by freeze-drying of this solution.

The method described has successfully been applied for isolation of about 200 mg fulvic acid from about 10 m^3 of groundwater. Subsequent analysis was successfully used for ^{14}C dating and determination of general characteristic properties (1). Details on the isolation and purification of humic and fulvic acids, including description of the RO technique, can be found in Artinger et al. (2).

Verification

Verification of the purity of humic and fulvic acids is done by characterization of the final products. It should also be borne in mind that trust in published results on the mobility of humic and fulvic acids requires evidence for successful separation and purification from the source. Characterization of humic and fulvic acids can be done by a broad spectrum of methods. For the purpose of study concerning the present topic, the quality of the samples needs to be demonstrated by a minimum of characterization methods. The elemental composition, the concentrations of inorganic constituents, and UV/Vis and IR spectra should be compared with expectation values from the literature.

Inorganic constituents will be exhibited if inorganic minerals and complexed metal ions are removed to an acceptable level. The UV/Vis absorption increases uniformly with decreasing wavelength and the logarithm of the absorption should be close to linear with the wavelength. For fulvic acids the absorption ratio of 300–400 nm is expected to fall in the range between about 5 and 8 (abs. units/g and cm), whereas the values for humic acids are lower and are expected to fall around 2.5–4. These indicators show whether the UV/Vis absorbing carbon inventory is in agreement with humic and fulvic acids.

IR spectroscopy shows a number of characteristic bands. Comparison to published spectra will reveal if there are considerable amounts of non-UV/Vis absorbing organic contaminants. Presence of such contaminants may also be identified by strong deviation from an atomic ratio around $CO_{0.5}H$.

For the purpose of determining the origin and age of humic and fulvic acids, the ^{14}C concentration is essential. In this context the ^{13}C concentration is a good indicator for possible contaminants. The ^{13}C concentration should be close to −27‰ (rel. PDB) for C-3 plant cycle origin and around −13‰ for C-4 plant cycle origin.

Again, only if a sufficient purity of the isolated substances is demonstrated can the results be considered trustworthy.

ORIGIN, STABILITY, AND MOBILITY OF AQUATIC HUMIC ACID

Determination of the origin, stability (with respect to decomposition and sorption), and mobility of aquatic humic and fulvic acids in groundwater is based on several indicators. The origin can be determined based on ^{14}C content, functional entity distribution, and general information on climatic conditions, vegetation history for soil recharge, and sedimentary and groundwater composition. Another important indicator is the cogeneration with dissolved inorganic carbon (DIC) of biogenic origin, where deviations from such a correlation show that either the DIC or the humic and fulvic acid inventory deviates from ideal tracer transport and stability behavior.

Origin

The principal origin of humic and fulvic acids is plant material. In sea sediments, marine organisms may also play a role. From the viewpoint of aquatic humic and fulvic acids in a groundwater, two principal sources may be distinguished. These are introduction from the soil zone with recharge groundwater and *in situ* generation by conversion of organic sediment material. In the former case, the source term will depend on climatic conditions and the type of vegetation, including extensive vegetation versus, for example, intense modern agriculture and land conditions such as wetland and peat deposits. In the case of *in situ* generation, an oxidizing agent and partial oxidation of the hydrophobic source material by microbial activity are required (3,4).

The different origin can be distinguished by some characteristic properties and especially the ^{14}C content (5). In aquifer systems where the groundwater residence time is sufficiently low, compared to the half-life of ^{14}C (57,300 years), the ^{14}C content of recharge humic and fulvic acids is that of the soil recharge source. Numbers deduced for fulvic acid for conditions prior to nuclear atmospheric testing are around 55 pmc (percent modern carbon) (5), basically the same as for the cogenerated dissolved inorganic carbon of biogenic origin (6). Depending on local conditions, however, this value may vary. One example is modern agriculture, where the turnover of the organic soil inventory may be higher and thus the ^{14}C concentration is higher, reflecting the lower average residence time. The ^{14}C concentration of fulvic acid and cogenerated DIC from *in situ* generation is basically zero. The relative fractions of *in situ* generated and recharge originating fulvic acid can be deduced by the overall ^{14}C concentration (5).

Another important indicator for the origin of aquatic humic and fulvic acids is the concentration varying with recharge conditions. Drainage of wetland results in a decrease in the inflow of both aquatic humic and fulvic acids and the cogenerated dissolved inorganic carbon of biogenic origin (7), which is an indicator of changes in the land use and also of changes in climatic conditions with a drastic impact on land structure and vegetation. Recharge humic and fulvic acids can only be found in water originating from areas with vegetation. For this reason, the absence of humic and fulvic acids is an indicator for vegetation free recharge conditions, also indicative of climatic changes.

In one study ^{14}C groundwater dating on the DIC indicated ages well beyond 15,000 years for the most distant part of the groundwater flow system (1). Not only did the ^{14}C concentration of fulvic acid show that these age determinations were wrong, but also the pure presence of fulvic acid showed that the groundwater at the end of the flow path could not be older than 15,000 years. The reason is that, in this area, vegetation started to develop around 15,000 years ago at the decline of the Pleistocene conditions.

Some characteristic properties of aquatic humic and fulvic acids reflect their origin. Both spectroscopic properties and basic functional entity distribution are sufficiently insensitive to the physicochemical environment to retain origin-related properties, which is especially true for the ^{14}C content, which solely depends on the concentration upon their generation and subsequent decay with a half-life of approximately 5730 years. Extraction of hydrophilic

humic and fulvic acids from clay sediments revealed that the distribution of functional entities and photodynamic behavior vary with marine and terrestrial origin of the clay sediments (8,9). Other characteristic properties reflect chemical reactions of functional groups, especially redox reactions. It should thus be kept in mind that not all characteristic properties can be used as indicators for the origin of aquatic humic or fulvic acid. The content and redox state of sulfur functional entities partly reflect the redox conditions and presumably also the microbial sulfate reduction as part of the in situ generation process (5).

Stability and Mobility

In groundwater systems where the in situ generation is negligible, the fulvic acid inventory is given solely by recharge and possible follow-up geochemical reactions. Where the residence time is considerable compared to the half-life of ^{14}C, the age of the fulvic acid can be determined. A linear increase in ^{14}C age of fulvic acid with flow distance from recharge was found, with the maximum age of fulvic acid of about 15,000 years (cf. above and Ref. 1). The agreement with groundwater flow velocity calculations and the age of fulvic acid shows that the fulvic acid has an ideal tracer transport behavior over this time period, which is direct evidence for the stability and mobility with an ideal tracer behavior of aquatic fulvic acid over 15,000 years.

In the case of *in situ* generation of fulvic acid, the quantification of the recharge originating inventory by ^{14}C content and supporting spectroscopic and composition information is required. The outcome of one study is that in situ generated fulvic acid is flocculated in deeper brines, whereas the recharge originating fulvic acid remains stable in the brines. Both the conserved ^{14}C concentration and structural entity content by C-XANES show that the fulvic acid in the deeper brines (200–250 m depth) originates from recharge. The flocculation of in situ generated fulvic acid in the high ionic strength brines is shown to be the result of their less hydrophilic nature compared to the recharge fulvic acid. The similar concentrations in recharge and in the deep brines show the stability and mobility of these fulvic acids over at least several hundreds years and, furthermore, that the recharge conditions have not changed dramatically within this time period. In addition, the close correlation between the DIC of biogenic origin and humic and fulvic acids in the broad spectrum of groundwater samples shows that there is no considerable decomposition or retention of fulvic acid from either recharge or in situ generation. This correlation is also found for deep groundwater from a former wetland. This shows also that the elevated concentration from this previous source is not subject to sorption or decomposition but the dissolved humic and fulvic acids remain stable and mobile over long time periods (7).

Studies on clay organic matter show that the organic matter sorbed on the sediments are mainly of hydrophobic character and are strongly bound to mineral surfaces. Studies where humic or fulvic acid is in contact with fresh mineral surfaces frequently show strong sorption. The natural situation, however, is that active sites on sediments are coated with organic substances and subsequent introduction of hydrophilic aquatic humic and fulvic acids will behave differently and remain in solution rather than competing with sorbed hydrophobic/sediment bound organic material. Care must therefore be taken when analyzing experimental data that the real situation is reflected. Strong sorption may be expected where a recent increase in the inflow of humic acid/fulvic acid is given, such as a deposit leaking organic material into sediment previously in contact with very low organic carbon concentrations. Under stable groundwater conditions, no indication is given for retention or decomposition of humic and fulvic acids from recharge.

CONCLUSION

With respect to the origin of aquatic humic and fulvic acids, a large number of studies have shown that they are cogenerated with inorganic carbon of biogenic origin from microbial processes and that there is a strong variation in the concentration of humic and fulvic acids in natural groundwater—an indicator for recharge conditions, including climatic changes. With respect to the stability and mobility, there is no indication for decomposition of aquatic humic and fulvic acids under natural groundwater conditions for as long as 15,000 years and no indication for their retardation. An exception is the selective flocculation of less hydrophilic in situ generated fulvic acid in high ionic strength brines.

BIBLIOGRAPHY

1. Buckau, G. et al. (2000). Development of climatic and vegetation conditions and the geochemical and isotopic composition in the Franconian Albvorland aquifer system. *Appl. Geochem.* **15**(8): 1191–1201.
2. Artinger, R. et al. (2000). Characterization of groundwater humic substances: influence of sedimentary organic carbon. *Appl. Geochem.* **15**(1): 97–116.
3. Buckau, G. et al. (2000). Groundwater in-situ generation of aquatic humic and fulvic acids and the mineralization of sedimentary organic carbon. *Appl. Geochem.* **15**(6): 819–832.
4. Buckau, G. et al. (2000). Origin and mobility of humic colloids in the Gorleben aquifer system. *Appl. Geochem.* **15**(2): 171–179.
5. Schäfer, T., Buckau, G., Artinger, R., Wolf, M., Kim, J.I., Geyer, S., Bleam, W.F., Wirick, S., and Jacobsen, C. (2004). Vertical exchange of Gorleben fulvic acids of different origin, Annex 1. In: *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field (Second Technical Progress Report)*. G. Buckau (Ed.). Report FZKA 6969, Research Center, Karlsruhe, Germany.
6. Buckau, G. et al. (2000). ^{14}C Dating of Gorleben groundwater. *Appl. Geochem.* **15**(5): 583–597.
7. Buckau, G., Wolf, M., Geyer, S., Artinger, R., and Kim, J.I. (2003). Origin and mobility of aquatic humic substances from wetland recharge in the Gorleben aquifer system. In: *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field (First Technical Progress Report)*. G. Buckau (Ed.). Report FZKA 6800, Research Center, Karlsruhe, Germany.
8. Claret, F., Schäfer, T., Rabung, Th., Bauer, A., Wolf, M., and Buckau, G. (2004). Complexation properties of humic and

fulvic acids extracted from Callovo-Oxfordian and opalinus clay, Annex 23. In: *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field (Second Technical Progress Report)*. G. Buckau (Ed.). Report FZKA 6969, Research Center, Karlsruhe, Germany.

9. Claret, F. et al. (2005). Differences in characteristic properties and Cm(III) complexation between terrestrial and marine origin of humic and fulvic acids from Callovo-Oxfordian and opalinus clay. *Appl. Geochem.*

ASSESSMENT OF GROUNDWATER QUALITY IN DISTRICT HARDWAR, UTTARANCHAL, INDIA

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The groundwater quality of District Hardwar in the state of Uttaranchal (India) has been assessed to see the suitability of groundwater for domestic use. Forty-eight groundwater samples from shallow and deep aquifers were collected each during pre- and postmonsoon seasons during the year 2002. Various water quality constituents, pH, conductance, total dissolved solids, alkalinity, hardness, sodium, potassium, calcium, magnesium, chloride, sulphate, phosphate, fluoride, total coliforms, and fecal coliforms were determined. The data were analyzed with reference to BIS and WHO standards, and hydrochemical facies were determined. The concentration of total dissolved solids exceeded the desirable limit of 500 mg/L in about 25% of the samples analyzed, but the values were well within the maximum permissible limit of 2000 mg/L. The alkalinity exceeded the desirable limit of 200 mg/L in about 50% of the samples, but these were also within the maximum permissible limit of 600 mg/L. From the hardness viewpoint, about 80–85% of the samples were within the desirable limits. One sample of the study area exceeded the maximum permissible limit of 100 mg/L for nitrate. Other constituents such as chloride, sulphate, and fluoride were within the desirable limits. The bacteriological analysis of the groundwater samples indicated bacterial contamination in about 40% of the samples analyzed. Inadequate maintenance of hand pumps, improper sanitation, and unhygienic conditions around the structure may be responsible for bacterial contamination in groundwater of the region and is a cause of concern. It is recommended that the water drawn from such sources be properly disinfected before being used for drinking and other domestic purposes. The grouping of samples according to their hydrochemical facies indicates that all the samples of the study area fall under Ca–Mg–HCO_3 hydrochemical facies.

INTRODUCTION

Water is an essential and vital component of our life support system. In tropical regions, groundwater plays an important role in the context of fluctuating and increasing contamination of water resources. Groundwater has unique features, which render it particularly suitable for public water supply. It has excellent natural quality; is usually free from pathogens, color and turbidity; and can be consumed directly without treatment. Groundwater is widely distributed and can be frequently developed incrementally at points near water demand, thus avoiding the need for large-scale storage, treatment, and distribution systems. It is particularly important because it accounts for about 88% of safe drinking water in rural areas, where the population is widely dispersed and the infrastructure for treating and transporting surface water does not exist.

Unfortunately, the availability of groundwater is not unlimited, nor it is protected from deterioration. In most instances, extracting excessive quantities of groundwater has resulted in drying of wells, damaged ecosystems, land subsidence, saltwater intrusion, and depletion of the resource. It has been estimated that once pollution enters the subsurface environment, it may remain concealed for many years, becoming dispersed over wide areas of groundwater aquifer and rendering groundwater supplies unsuitable for consumption and other uses. The rate of depletion of groundwater levels and deterioration of groundwater quality are of immediate concern in major cities and towns of the country.

The creation of the new state of Uttaranchal has posed many challenges for planners and policy makers. Problems such as drinking water, transportation, power, housing and construction, and safety against natural hazards are very serious and require immediate attention. For sustainable development of a society, it is essential that the natural resources are used judiciously for the benefit of the existing population and also to meet the needs and aspirations of future generations. Drinking water is one such precious commodity for which a planned strategy is needed for immediate demands and also for sustainability for future needs. A large part of the state of Uttaranchal lies in the hills, where distribution of drinking water supply and its quality is a major problem that needs immediate attention. About 90% of the rural population of this region depends on natural springs for their daily water. However, due to population pressure, unplanned construction, garbage disposal, and changes in land use patterns, the water of these springs is becoming contaminated, and the discharge of these springs is declining.

A wide number of activities are associated with, the human introduction of foreign chemical and biological materials into the subsurface environment. In the long run, the most potentially hazardous of these may be the chemical fertilizers and pesticides used in agriculture. But it is possible that tremendous use of chemical fertilizers as plant nutrients may be a more significant problem, causing an increasing buildup of nutrients in some groundwaters. Bacteriological parameters are of great importance from the human point of view. It is essential to examine the presence of toxic substances and pathogenic organisms in potable water. Experience has established the significance of coliform group density as a criterion of the degree of pollution and thus of sanitary quality. The significance

of the various tests and the interpretation of results are well authenticated and have been used as a basis for standards of the chemical and bacteriological quality of water supplies. In this article, the groundwater quality of District Hardwar has been assessed to see the suitability of groundwater for drinking, which will provide a proper basis for judicial management of drinking water supplies in the state.

STUDY AREA

District Hardwar, part of the Indo-Gangetic plains, lies between latitude 29°30′ and 30°20′ N and longitude 77°40′ to 78°25′ E in the state of Uttaranchal (Fig. 1). It is the largest district (in population) of Uttaranchal State and occupies an area of about 2360 km^2. Per the 2001 census, the population of District Hardwar is 14,44,213, a population density of 612 per km^2.

Physiographically, the area is generally flat except for the Siwalik Hills in the north and northeast. The area is devoid of relief features of any prominence except for deep gorges cut by gullies and rivers flowing through the area. The area is bounded by River Yamuna in the west and River Ganga in the east. The climate of the area is characterized by moderate subtropical monsoons. The average annual rainfall in the region is about 1000 mm; the major part is received during the monsoon period. The major land use is agriculture, and there is no effective forest cover. The soils of the area are loam to silty loam and are free from carbonates. The most common groundwater use is achieved by hand pumps and tube wells. Based on the lithologic logs and water table fluctuation data,

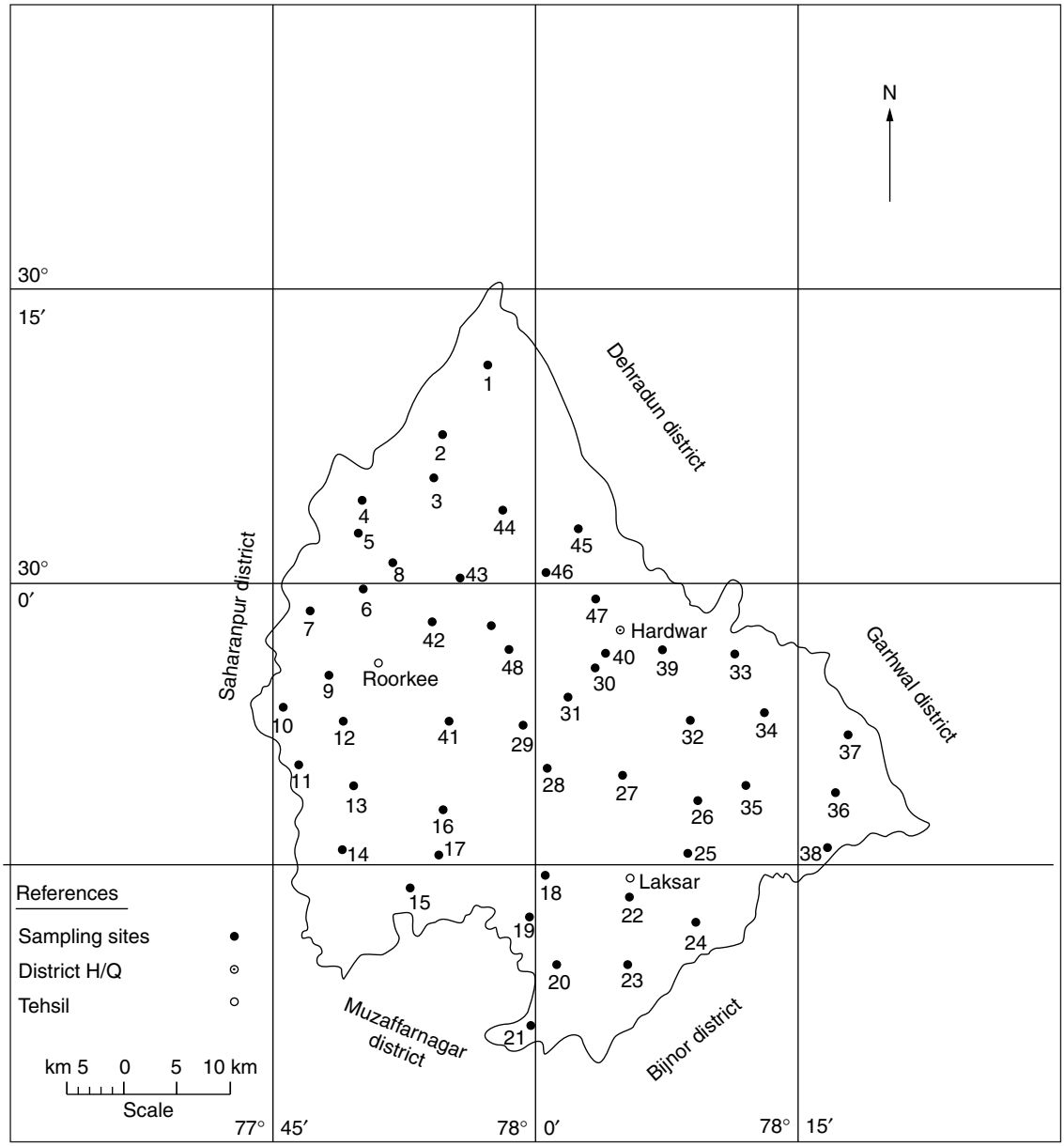


Figure 1. Study area showing location of sampling sites, District Hardwar.

two types of aquifers have been delineated in the area. The upper one is the shallow unconfined aquifer which generally extends to depths of around 25 m. The deeper one consists of semiconfined aquifers located at a depth of about 25 to 150 m below ground level separated by three to four aquifers at average depths of 25 to 55, 65 to 90, and 120 to 150 m. Water table contours in the area indicate a southward trend of groundwater flow in both unconfined and confined aquifers.

EXPERIMENTAL METHODOLOGY

Forty-eight groundwater samples from District Hardwar were collected each during pre- (June 2002) and post-monsoon (October 2002) seasons from various abstraction sources at various depths covering extensively populated area, commercial, industrial, agricultural, and residential colonies so as to obtain a good areal and vertical representation. The samples were preserved by adding an appropriate reagent (1,2). The hand pumps and tube wells were continuously pumped prior to sampling to ensure that the groundwater to be sampled was representative of the groundwater aquifer. The water samples for bacteriological analysis were collected in sterilized high-density polypropylene bottles covered with aluminum foil. All samples were stored in sampling kits maintained at 4 °C and brought to the laboratory for detailed chemical and bacteriological analysis. The details of sampling locations and source and depthwise distribution are given in Tables 1 and 2, respectively.

The physicochemical analysis was performed following standard methods (1,2). The total coliforms and fecal coliforms were determined by the multiple tube fermentation technique using MacConkey broth and EC medium, respectively.

Table 1. Description of Groundwater Sampling Locations in District Hardwar

S. No.	Location	Source	Depth, m	S. No.	Location	Source	Depth, m
1	Mohand	OW	10	25	Sultanpur	HP	15
2	Banjarewala	OW	10	26	Shahpur	HP	25
3	Buggawala	HP	30	27	Pathri	HP	15
4	Kheri	HP	38	28	Subashgarh	HP	20
5	Dadapatti	HP	38	29	Marghubpur	HP	30
6	Bahbalpur	HP	15	30	Bahadarabad	HP	20
7	Sikandarpur	HP	25	31	Alipur	HP	20
8	Bhagwanpur	HP	30	32	Katarpur	HP	10
9	Chudiala	HP	40	33	Kankhal	HP	25
10	Balswa Ganj	HP	25	34	Shyampur	HP	30
11	Manakpur	HP	40	35	Rasiya Garh	HP	40
12	Iqbalpur	HP	30	36	Gandikhatta	HP	10
13	Jharera	HP	30	37	Laldhang	HP	90
14	Sherpur	HP	30	38	Kottawali	HP	40
15	Narsen	HP	30	39	Hardwar	HP	30
16	Manglour	HP	35	40	Jwalapur	HP	30
17	Libarheri	HP	35	41	Roorkee	HP	10
18	Mahesari	HP	20	42	Gumanwala	HP	30
19	Sahipur	HP	35	43	Manubas	HP	10
20	Khanpur	HP	15	44	Bandarjud	HP	15
21	Chandpuri Kalan	HP	15	45	Beriwala	HP	5
22	Laksar	HP	15	46	Hazara	HP	10
23	Kalsiya	HP	10	47	Aurangbad	HP	10
24	Niranjanpur	HP	15	48	Daulatpur	HP	35

OW: Open well.
HP: Hand pump.

Table 2. Source and Depthwise Distribution of Sampling Sites in District Hardwar

	Depth Range			
Source Structure	<0–20 m	20–40 m	>40 m	Total Number
Hand pumps	6,18,20,21,22, 23,24,25,27,28, 30,31,32,36,41, 43,44,45,46,47	3,4,5,7,8,9, 10,11,12,13, 14,15,16,17,19, 26,29,33,34,35, 38,39,40,42,48	37	46
Tube wells	–	–	–	–
Open wells	1,2	–	–	2
Total	22	25	1	48

RESULTS AND DISCUSSION

During 1983, the Bureau of Indian Standards (BIS), earlier known as Indian Standards Institution (ISI), laid down standard specifications for drinking water which have been revised and updated from time to time. To enable the users to exercise their discretion toward water quality criteria, the maximum permissible limit was prescribed especially where no alternate source was available. The national water quality standards describe the essential and desirable characteristics that must be evaluated to assess the suitability of water for drinking (3). The hydrochemical data for the two sets of samples collected from District Hardwar during pre- and postmonsoon seasons are presented in Table 3.

General Characteristics

The pH of the groundwater of District Hardwar is mostly confined within the range 6.22 to 7.58 during the premonsoon season and 6.70 to 7.70 during the postmonsoon season. The pH values of all samples are well within the limits prescribed by the BIS (3) and the WHO (4) for various uses, including drinking and other domestic supplies.

The measurement of electrical conductivity is directly related to the concentration of ionized substances in water and may also be related to excessive hardness and/or other mineral contamination. The conductivity values in the groundwater samples of District Hardwar vary from 233–1440 μS/cm during the premonsoon season and from 221–1442 μS/cm during the postmonsoon season; about 10% of the samples had conductivity values above 1000 μS/cm during both pre- and postmonsoon seasons. The maximum conductivity of 1440 and 1442 μS/cm was observed at village Manubas (hand pump, 10 m depth) during pre- and postmonsoon season, respectively.

In natural waters, dissolved solids consists mainly of inorganic salts such as carbonates, bicarbonates, chlorides, sulfates, phosphates, and nitrates of calcium, magnesium, sodium, potassium, iron, etc. and small amounts of organic matter and dissolved gases. In the present study, the values of total dissolved solids (TDS) in the groundwater varied from 149–922 mg/L during the premonsoon season and from 141–923 mg/L during the postmonsoon season, indicating low mineralization in the area. More than 75% of the samples analyzed were within the desirable limit of 500 mg/L, and about 25% of the samples were above the desirable limit but within the maximum permissible limit of 2000 mg/L. An almost similar trend was observed during the postmonsoon season. The TDS content at deeper levels (>40 m depth) is comparatively low and lies well within the desirable limit of 500 mg/L. The TDS distribution maps for the pre- and postmonsoon seasons are shown in Fig. 2a,b. Water containing more than 500 mg/L of TDS is not considered desirable for drinking water, though more highly mineralized water is also used where better water is not available. For this reason, 500 mg/L as the desirable limit and 2000 mg/L as the maximum permissible limit have been suggested for drinking water (3). Water containing more than 500 mg/L TDS causes gastrointestinal irritation (3). No sample of District Hardwar exceeded the maximum permissible limit of 2000 mg/L.

Table 3. Hydrochemical Data for Groundwater Samples from District Hardwar[a]

Characteristics	Min	Max	Average
pH	6.22 (6.70)	7.58 (7.70)	6.87 (7.10)
Conductivity, μS/cm	233 (221)	1440 (1442)	642 (647)
TDS, mg/L	149 (141)	922 (923)	411 (414)
Alkalinity, mg/L	78 (71)	460 (482)	213 (215)
Hardness, mg/L	81 (80)	464 (427)	209 (212)
Chloride, mg/L	0.1 (1.2)	32 (35)	9.0 (9.0)
Sulphate, mg/L	0.5 (0.7)	72 (62)	22 (21)
Nitrate, mg/L	0.1 (0.1)	140 (130)	13 (13)
Phosphate, mg/L	0.01 (0.02)	0.41 (1.60)	0.03 (0.25)
Fluoride, mg/L	0.01 (0.01)	0.94 (0.88)	0.36 (0.42)
Sodium, mg/L	5.0 (4.5)	69 (71)	26 (25)
Potassium, mg/L	0.8 (0.2)	42 (32)	7.0 (7.4)
Calcium, mg/L	22 (24)	140 (135)	55 (56)
Magnesium, mg/L	5.0 (5.0)	36 (38)	18 (17)
Boron, mg/L	0.12 (0.12)	0.92 (0.87)	0.50 (0.49)

[a]Values given in parenthesis represent postmonsoon data.

Carbonates, bicarbonates, and hydroxides are the main cause of alkalinity in natural waters. Bicarbonates represent the major form because they are formed in considerable amounts by the action of carbonates upon the basic materials in the soil. The alkalinity in the groundwater varies from 78–460 mg/L during the premonsoon season and from 71–482 mg/L during the postmonsoon season. About 50% of the samples of the study area fall within the desirable limit of 200 mg/L both during the pre- and postmonsoon seasons, and the remaining 50% of the samples exceeds the desirable limit but are within the maximum permissible limit of 600 mg/L. No sample of the study area exceeded the maximum permissible limit of 600 mg/L. The high alkalinity may be due to the action of carbonates upon the basic materials in the soil.

Calcium and magnesium along with their carbonates, sulfates, and chlorides make the water hard. A limit of 300 mg/L has been recommended for potable water (3). The total hardness values in the study area range from 81–464 mg/L during the premonsoon season and from 80–427 mg/L during the postmonsoon season. About 80% of the samples of the study area fall within the desirable limit of 300 mg/L and the remaining samples exceed the desirable limit but are well within the maximum permissible limit of 600 mg/L. From the point of view of hardness all samples of District Hardwar were within the permissible limit of 600 mg/L.

The desirable limits for calcium and magnesium for drinking water are 75 and 30 mg/L, respectively (3). In the groundwater of the study area, the values for calcium and magnesium range from 22–140 mg/L and 5.0–36 mg/L, respectively, during the premonsoon season. An almost similar trend was observed during the postmonsoon season. In groundwater, the calcium content generally exceeds the magnesium content in accordance with their relative abundance in rocks. The increase in magnesium is proportionate to calcium in both seasons. All the

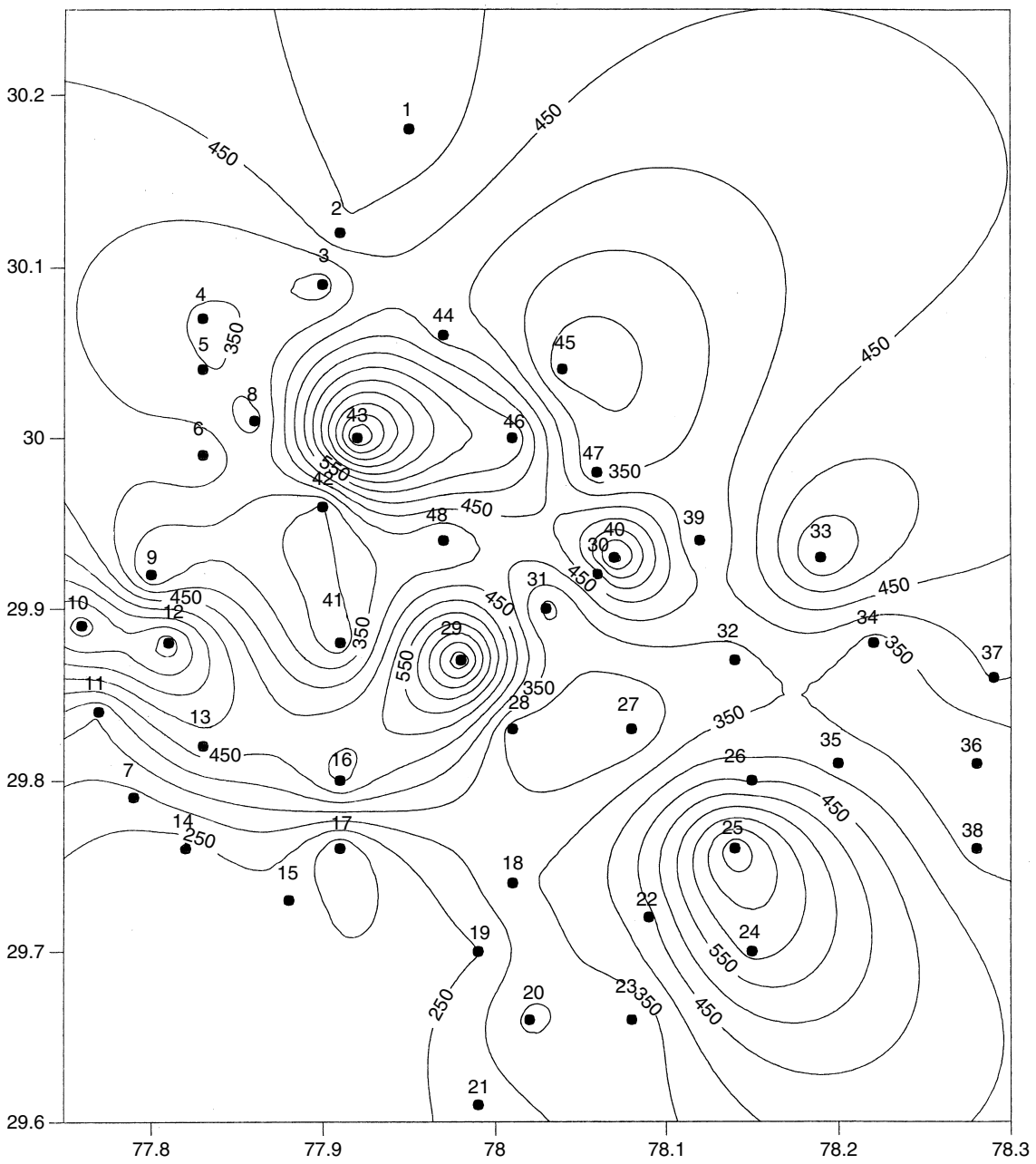


Figure 2. (**a**) Distribution of TDS in groundwater from District Hardwar (premonsoon 2002). (**b**) Distribution of TDS in groundwater from District Hardwar (postmonsoon 2002).

samples of the study area fall within the desirable limit at most places.

The concentration of sodium in the study area varied from 5.0–69 mg/L during the premonsoon season and from 4.5–71 mg/L during the postmonsoon season. The violation of BIS limits could not be ascertained for sodium as no permissible limit of sodium has been prescribed in BIS drinking water specifications. Groundwater high in sodium is not suitable for irrigation due to the sodium sensitivity of crops/plants.

The concentration of potassium in the groundwater of District Hardwar varied from 0.8–42 mg/L during the premonsoon season and from 0.2–32 mg/L during the postmonsoon season. Potassium, an essential element for humans, plants, and animals, is derived in the food chain mainly from vegetation and soil. The main sources of potassium in groundwater include rainwater, weathering of potash silicate minerals, use of potash fertilizers, and use of surface water for irrigation. It is more abundant in sedimentary rocks and commonly present in feldspar, mica, and other clay minerals. The Bureau of Indian Standards has not included potassium in drinking water standards. However, the European Economic Community has prescribed a guideline level of 10 mg/L potassium in drinking water. Per EEC criteria, about 10–15% of the samples of the study area exceeded the 10 mg/L

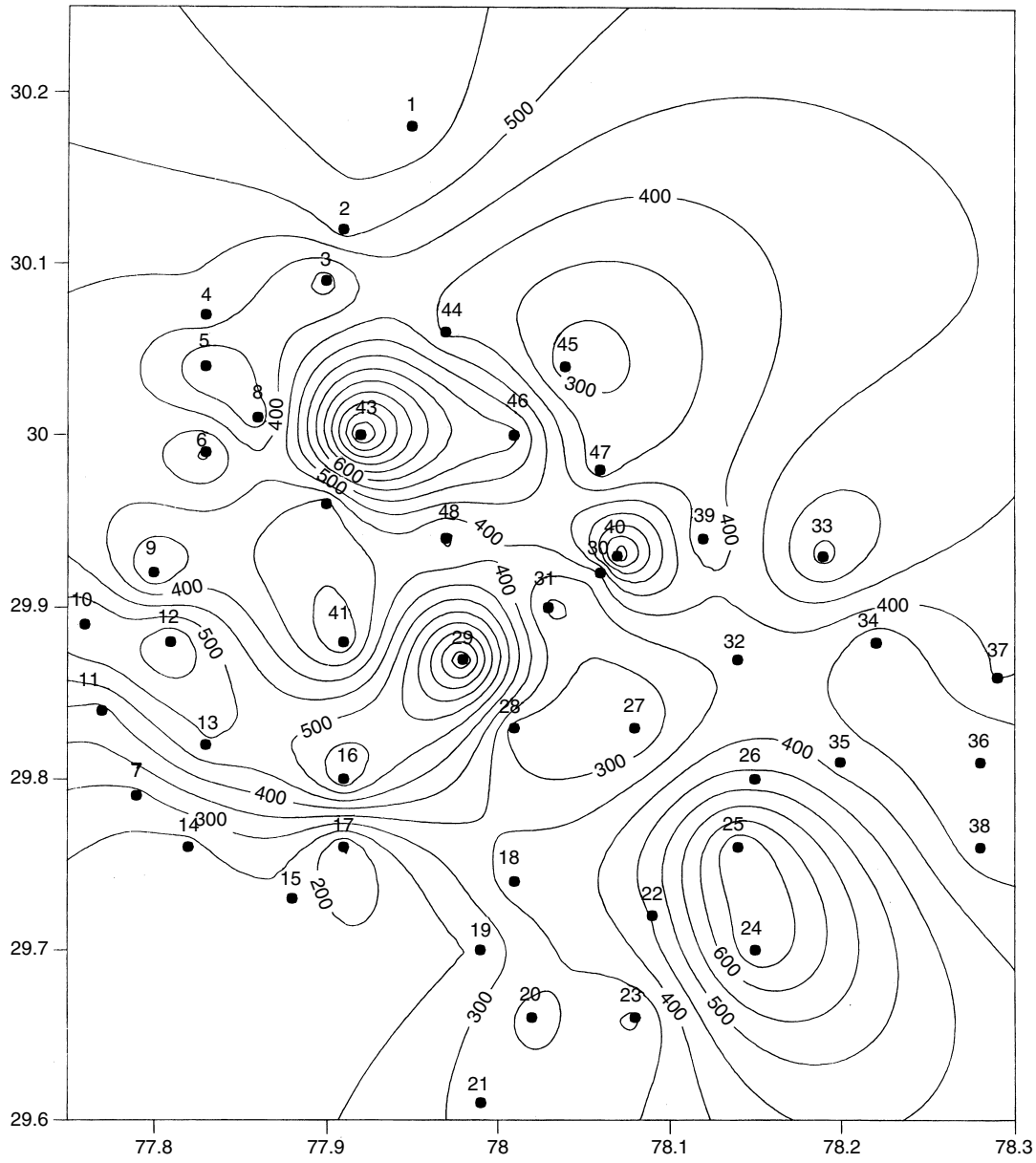


Figure 2. (*Continued*)

guideline level. Though potassium is found extensively in some igneous and sedimentary rocks, its concentration in natural waters is usually quite low because potassium minerals offer resistance to weathering and dissolution. A higher potassium content in groundwater is indicative of groundwater pollution.

The concentration of chloride in the study area is quite low and varies from 0.1–32 mg/L during the premonsoon season. An almost similar trend was observed during the postmonsoon season. The limits of chloride have been laid down primarily from taste considerations. A limit of 250 mg/L chloride has been recommended as a desirable limit for drinking water supplies (3,4). However, no adverse health effects on humans have been reported from intake of waters containing an even higher chloride content. No sample in the study area exceeded the desirable limit of 250 mg/L.

The sulfate content of groundwater generally occurs as soluble salts of calcium, magnesium, and sodium. The sulfate content changes significantly with time during infiltration of rainfall and groundwater recharge, which takes place mostly from stagnant water pools and surface runoff water collected in low-lying areas. The concentration of sulfate in the study area varied from 0.5–72 mg/L during the premonsoon season and from 0.7–62 mg/L during the postmonsoon season. It is clearly evident from the distribution maps that all the samples from District Hardwar fall within the desirable limit of 200 mg/L prescribed for drinking water supplies.

Excess nitrate content in drinking water is considered dangerous for its adverse health effects. The occurrence of high levels of nitrate in groundwater is a prominent problem in many parts of the country. The nitrate content in District Hardwar varies from 0.1–140 mg/L during the premonsoon season and from 0.1–130 mg/L during the postmonsoon season. About 95% of the samples shows nitrate content less than the desirable limit of 45 mg/L. Only one sample from Jwalapur exceeded the maximum permissible limit of 100 mg/L during both pre- and postmonsoon seasons. The nitrate distribution maps for the pre- and postmonsoon seasons are shown in Fig. 3a,b. The higher level of nitrate at Jwalapur may be attributed to improper sanitation and unhygienic conditions around the structure.

Nitrate is an effective and moderately toxic plant nutrient. A limit of 45 mg/L has been prescribed by the WHO (4) and the BIS (3) for drinking water. Its

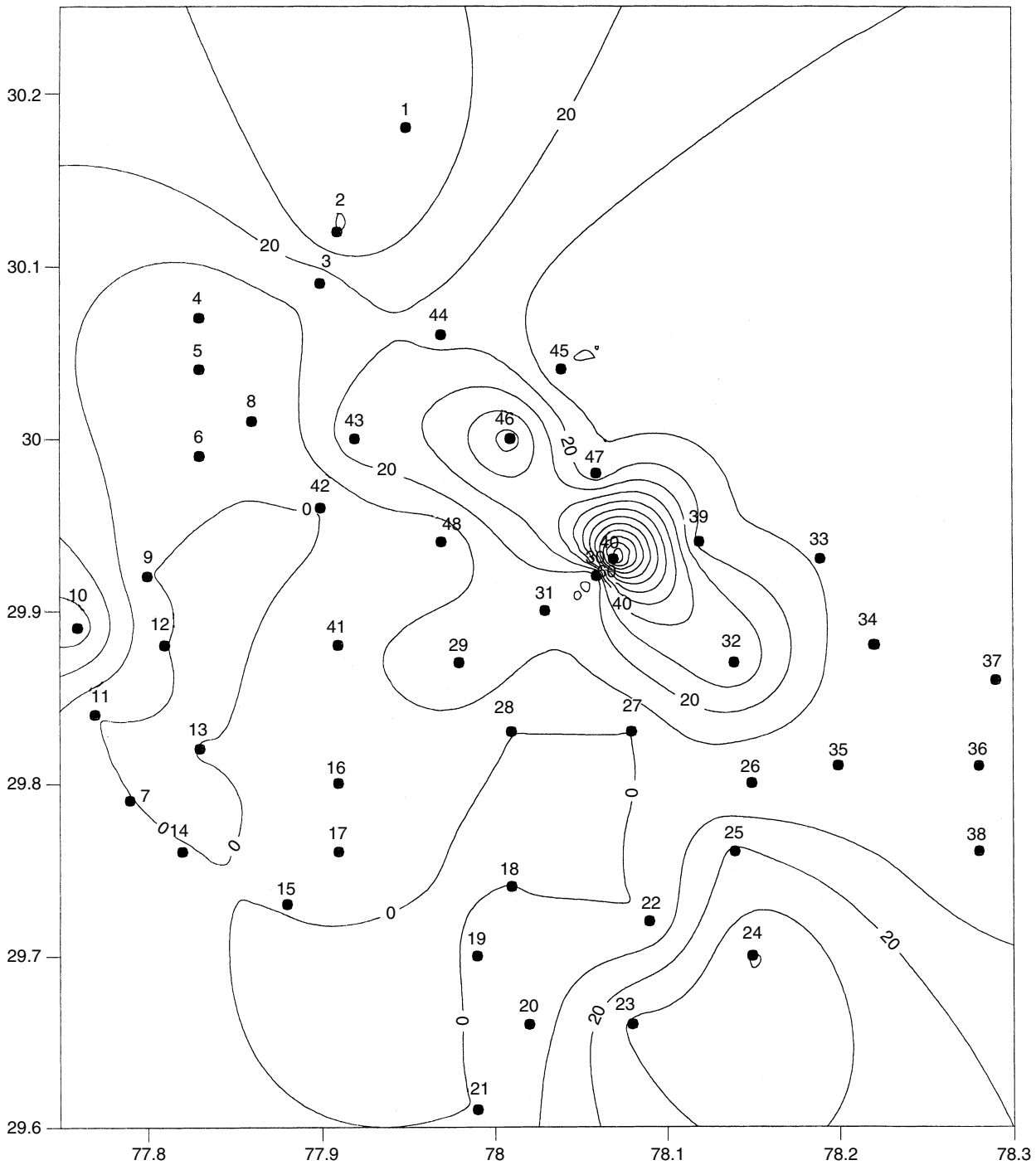


Figure 3. (**a**) Distribution of nitrate in groundwater from District Hardwar (premonsoon 2002). (**b**) Distribution of nitrate in groundwater from District Hardwar (postmonsoon 2002).

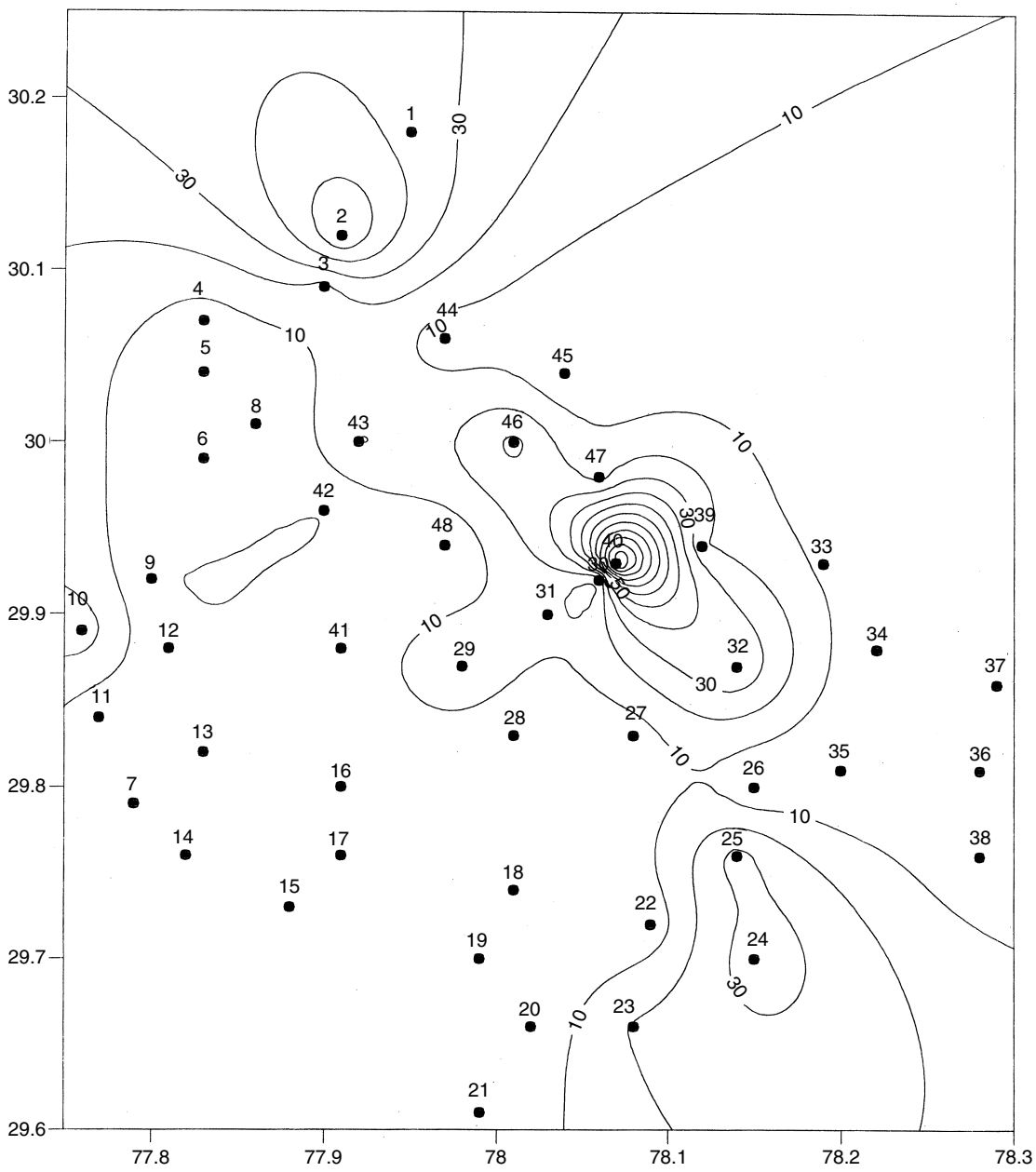


Figure 3. (*Continued*)

concentration above 45 mg/L may prove detrimented to human health. In higher concentrations, nitrate may produce a disease known as methemoglobinemia (blue babies) which generally affects bottle-fed infants. Repeated heavy doses of nitrates by ingestion may also cause cancer.

The concentration of phosphate in the study area is generally low at all locations. Phosphorous is an essential plant nutrient that is used extensively as a fertilizer. Phosphate is adsorbed or fixed as aluminium or iron phosphate in acidic soils or as calcium phosphate in alkaline or neutral soils; as a result, the concentration of phosphate in groundwater is usually low, but various chemical processes in soil strata may induce the mobility of phosphate in sub-soil and groundwater.

The fluoride content in the groundwater of District Hardwar varies from 0.01–0.94 mg/L during the pre-monsoon season and from 0.01–0.88 mg/L during the postmonsoon season; it lies well below the desirable limit of 1.0 mg/L in all samples. The fluoride distribution maps for pre- and postmonsoon seasons are shown in Fig. 4a,b.

The presence of fluoride in groundwater may be attributed to the localized effects of natural sources. Fluoride present in soil strata is from geological formations, such as fluorspar, and fluorapatite, and amphiboles, such as hornblende, tremolite, and mica. Weathering of igneous and sedimentary alkali silicate rocks, especially shales, contribute a major portion of fluorides to groundwaters. In addition to natural sources, considerable amounts of fluoride may be contributed by human activities. Fluoride

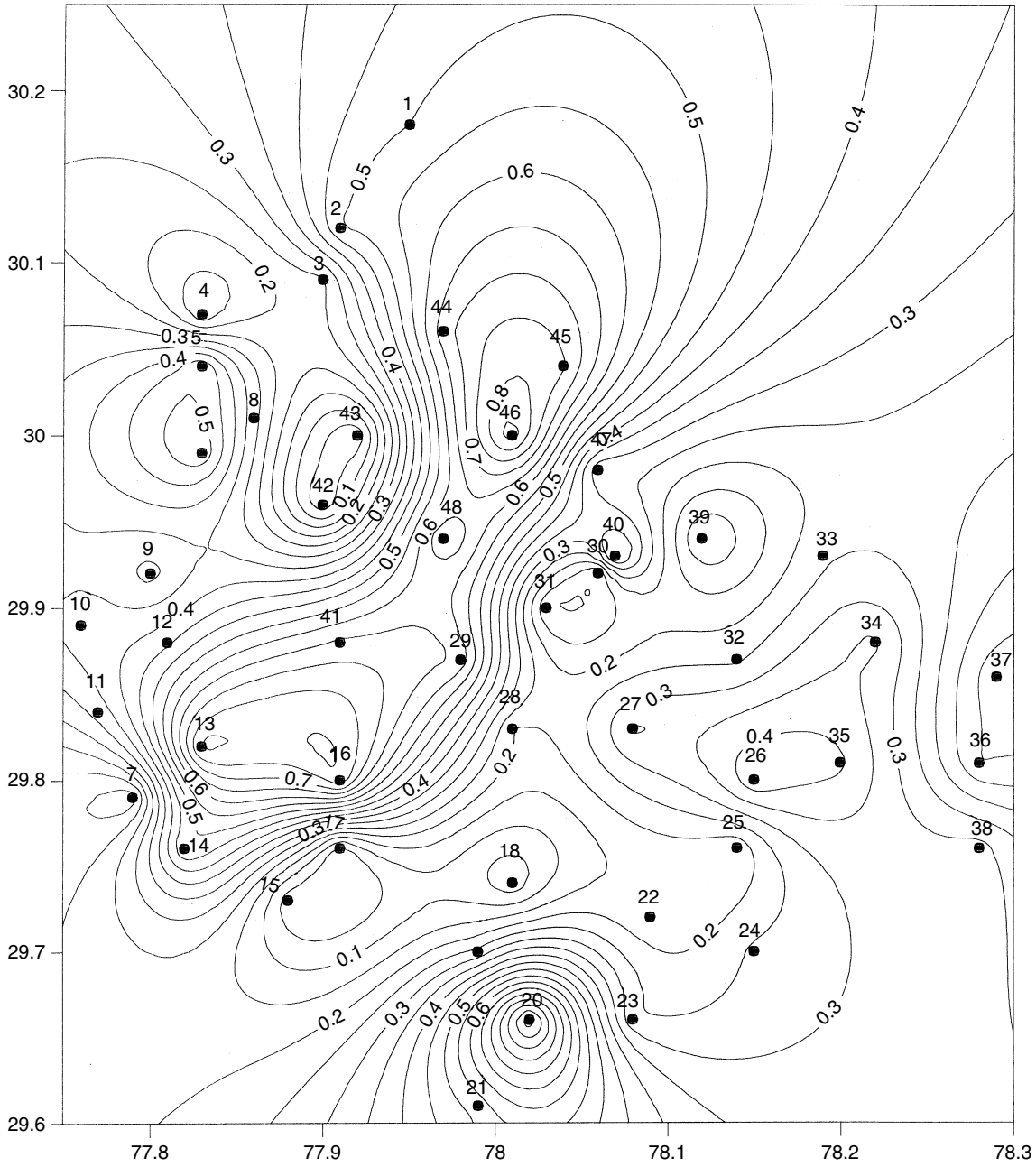


Figure 4. (**a**) Distribution of fluoride in groundwater from District Hardwar (premonsoon 2002). (**b**) Distribution of fluoride in groundwater from District Hardwar (postmonsoon 2002).

salts are commonly used in the steel, aluminum, brick, and tile industries. Fluoride containing insecticides and herbicides may be contributed through agricultural runoff. Phosphatic fertilizers, which are extensively used, often contain fluorides as impurities, and these may increase the levels of fluoride in soil. The accumulation of fluoride in soil eventually results in leaching it by percolating water, thus increasing the fluoride concentration in groundwater.

The study has clearly indicated that the concentration of total dissolved solids exceeds the desirable limit of 500 mg/L in about 25% of the samples analyzed, but the values are well within the maximum permissible limit of 2000 mg/L in all samples. The alkalinity exceeds the desirable limit of 200 mg/L in about 50% of the samples, but the levels are well within the maximum permissible limit of 600 mg/L. Total hardness exceeds the desirable limit of 300 mg/L in about 15% of the samples. The nitrate content exceeds the maximum permissible limit of 100 mg/L in only one sample (Jwalapur) of the study area. The fluoride content is well within the desirable limit in all samples analyzed.

Bacteriological Parameters

The coliform group of bacteria is the principal indicator of the suitability of water for domestic, industrial, and other uses. The density of the coliform group is the criterion for

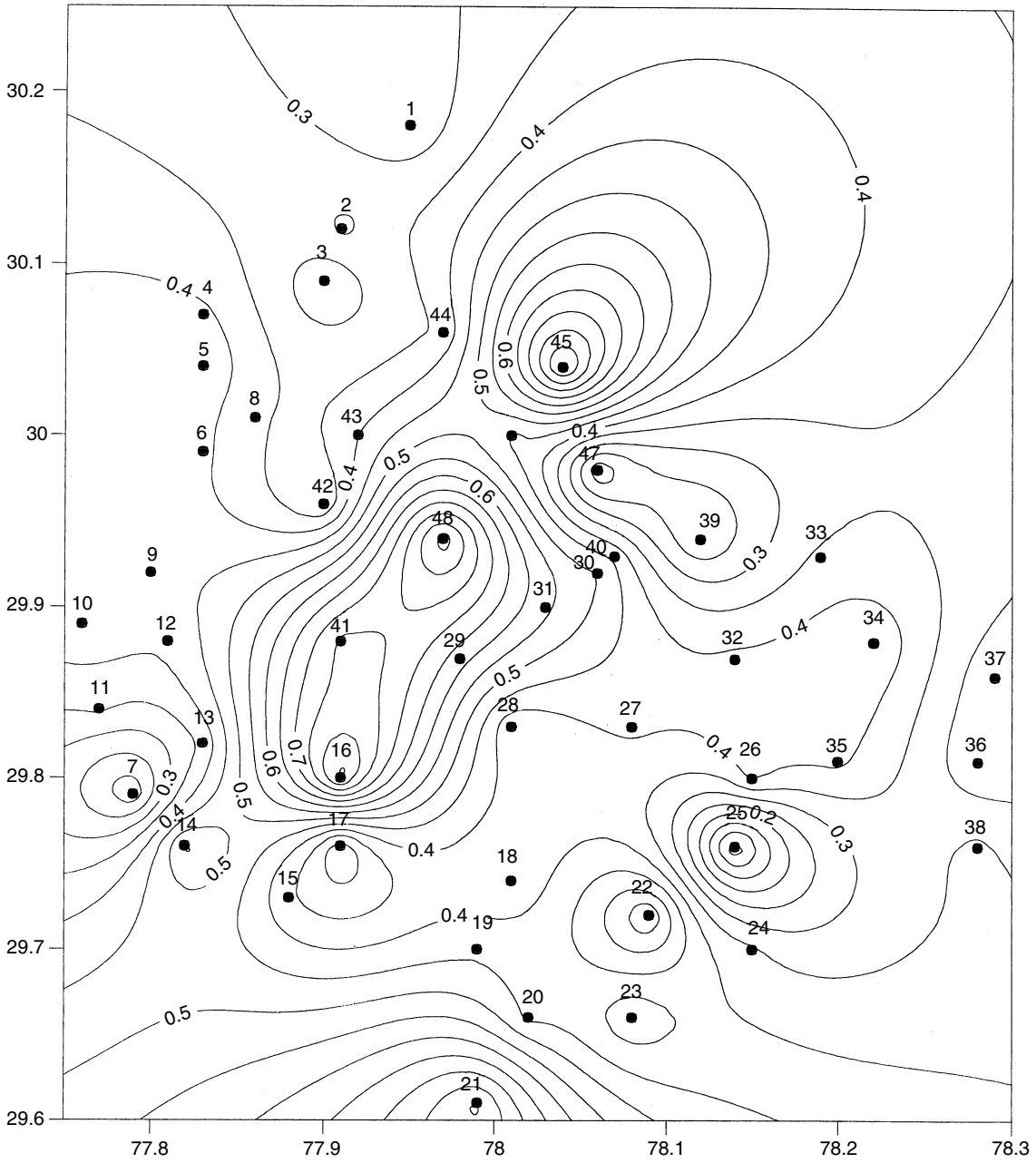


Figure 4. (*Continued*)

the degree of contamination and has been the basis for the bacteriological water quality standard. In ideal conditions, all samples taken from the distribution system should be free from coliform organisms, but in practice, this is not always attainable, and therefore, the following standard for water has been recommended (4):

— 95% of water samples should not contain any coliform organisms in 100 mL throughout the year.

— No water sample should contain *E. coli* in 100 mL water.

— No water sample should contain more than 10 coliform organisms per 100 mL.

— Coliform organisms should not be detected in 100 mL of any two consecutive water samples.

However, from bacteriological considerations, the objectives should be to reduce the coliform count to less than 10 per 100 mL, and more importantly, the absence of fecal coliform should be ensured. The presence of coliforms in water is an indicator of contamination by human or animal excrement. The presence of fecal colifirms in groundwater indicates a potential public health problem because fecal matter is a source of pathogenic bacteria and viruses. Groundwater contamination from fecal coliform bacteria is generally caused by percolation from sources of contamination (domestic sewage and

septic tanks) into the aquifers and also from poor sanitation. Shallow wells are particularly susceptible to such contamination. Indiscriminate land disposal of domestic waste on the surface and improper disposal of solid waste, and leaching of wastewater from landfill areas further increase the chances of bacterial contamination in groundwater. The results of the bacteriological analysis of groundwater samples from District Hardwar are given in Table 4.

Bacteriological analysis of the groundwater samples collected from District Hardwar indicates bacterial contamination in about 40% of the samples analyzed. About 20% of the samples even exceed the permissible limit of 10 coliforms per 100 mL of sample. Inadequate maintenance of hand pumps, improper sanitation, and unhygienic conditions around structures may be responsible for bacterial contamination in the groundwater of the region and is a cause of concern. The water from such sources should be

Table 4. Bacteriological Contamination in Groundwater from District Hardwar

		Premonsoon 2002		Postmonsoon 2002	
S. No.	Location	Total Coliform per 100 mL	Fecal Coliform per 100 mL	Total Coliform per 100 mL	Fecal Coliform per 100 mL
1	Mohand	Nil	Nil	Nil	Nil
2	Banjarewala	Nil	Nil	Nil	Nil
3	Buggawala	4	Nil	Nil	Nil
4	Kheri	9	Nil	Nil	Nil
5	Dadapatti	23	Nil	Nil	Nil
6	Bahbalpur	75	Nil	4	Nil
7	Sikandarpur	7	Nil	Nil	Nil
8	Bhagwanpur	23	Nil	Nil	Nil
9	Chudiala	Nil	Nil	Nil	Nil
10	Balswa Ganj	9	Nil	Nil	Nil
11	Manakpur	14	Nil	Nil	Nil
12	Iqbalpur	28	Nil	4	Nil
13	Jharera	15	Nil	Nil	Nil
14	Sherpur	Nil	Nil	Nil	Nil
15	Narsen	4	Nil	Nil	Nil
16	Manglour	4	Nil	Nil	Nil
17	Libarheri	Nil	Nil	Nil	Nil
18	Mahesari	4	Nil	Nil	Nil
19	Sahipur	Nil	Nil	Nil	Nil
20	Khanpur	Nil	Nil	Nil	Nil
21	Chandpuri Kalan	Nil	Nil	4	Nil
22	Laksar	43	Nil	Nil	Nil
23	Kalsiya	23	Nil	15	Nil
24	Niranjanpur	4	Nil	Nil	Nil
25	Sultanpur	4	Nil	Nil	Nil
26	Shahpur	Nil	Nil	Nil	Nil
27	Pathri	Nil	Nil	Nil	Nil
28	Subashgarh	4	Nil	Nil	Nil
29	Marghubpur	Nil	Nil	Nil	Nil
30	Bahadarabad	4	Nil	Nil	Nil
31	Alipur	Nil	Nil	Nil	Nil
32	Katarpur	Nil	Nil	Nil	Nil
33	Kankhal	Nil	Nil	Nil	Nil
34	Shyampur	Nil	Nil	Nil	Nil
35	Rasiya Garh	Nil	Nil	Nil	Nil
36	Gandikhatta	Nil	Nil	Nil	Nil
37	Laldhang	Nil	Nil	Nil	Nil
38	Kottawali	Nil	Nil	Nil	Nil
39	Hardwar	Nil	Nil	Nil	Nil
40	Jwalapur	Nil	Nil	Nil	Nil
41	Roorkee	Nil	Nil	Nil	Nil
42	Gumanwala	Nil	Nil	Nil	Nil
43	Manubas	Nil	Nil	Nil	Nil
44	Bandarjud	Nil	Nil	Nil	Nil
45	Beriwala	23	Nil	Nil	Nil
46	Hazara	Nil	Nil	Nil	Nil
47	Aurangbad	Nil	Nil	Nil	Nil
48	Daulatpur	Nil	Nil	Nil	Nil

properly disinfected before being used for drinking and other domestic purposes.

Classification of Ground Water

The groundwater of District Hardwar has been classified per Chadha's diagram (5). The diagram is a somewhat modified version of the Piper trilinear diagram (6). In the Piper diagram, the milliequivalent percentages of the major cations and anions are plotted in two base triangles, and the type of water is determined on the basis of the position of the data in the respective cationic and anionic triangular fields. The plottings from the triangular fields are projected further into the central diamond field, which represents the overall character of the water. A Piper diagram allow comparisons among numerous analyses, but this type of diagram has a drawback, as all trilinear diagrams do, in that it does not portray actual ion concentration. The distribution of ions within the main field is unsystematic in hydrochemical process terms, so the diagram lacks a certain logic. This method is not very convenient when plotting a large volume of data. Nevertheless, this shortcoming does not lessen the usefulness of the Piper diagram in representing some geochemical processes.

In contrast, in Chadha's diagram, the difference in milliequivalent percentage between alkaline earths

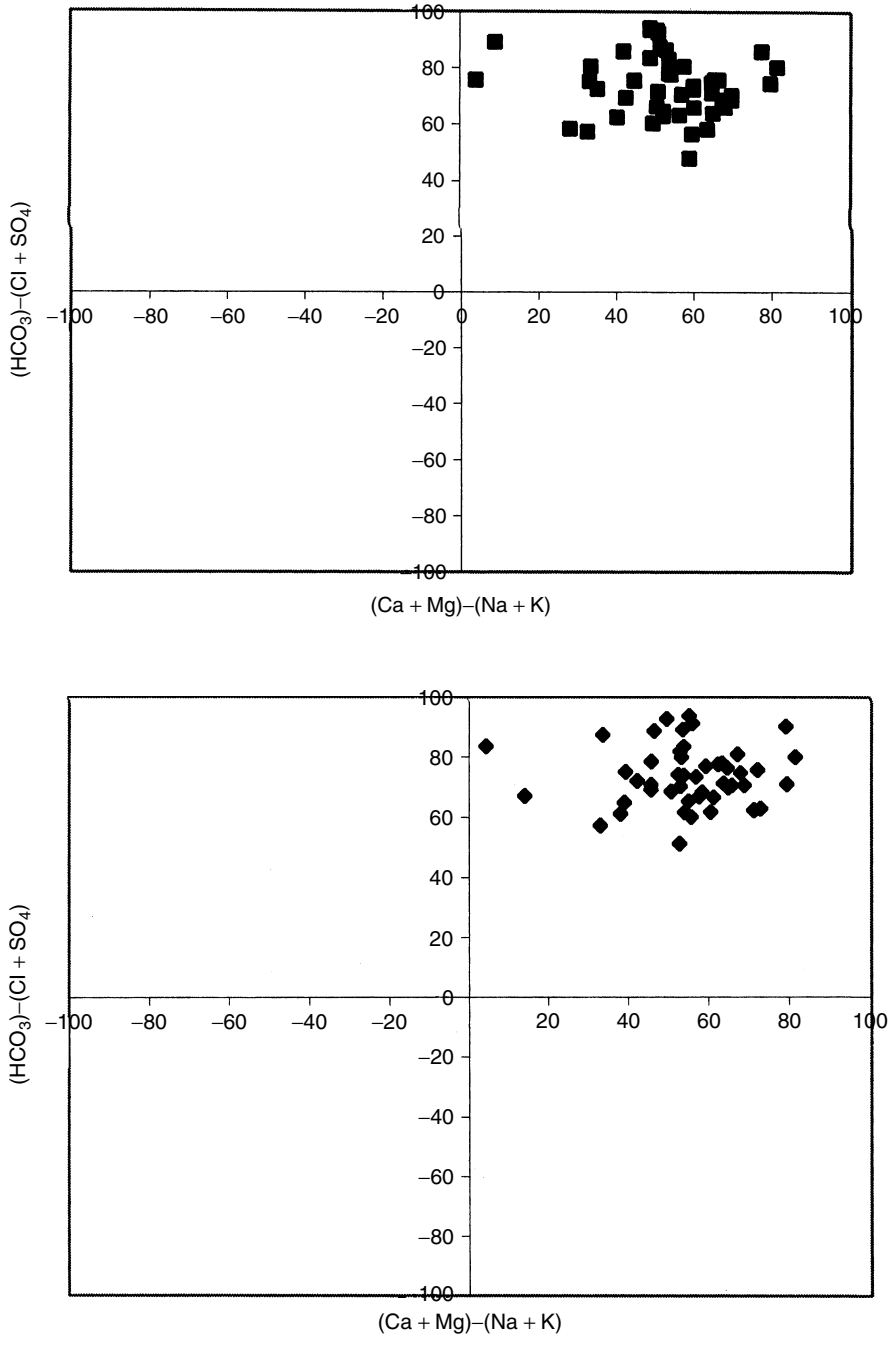


Figure 5. (**a**) Chadha's diagram showing the chemical character of groundwater in District Hardwar, Uttaranchal (premonsoon 2002). (**b**) Chadha's diagram showing the chemical character of groundwater in District Hardwar, Uttaranchal (postmonsoon 2002).

(calcium plus magnesium) and alkali metals (sodium plus potassium), expressed as a percentage of reacting values, is plotted on the x-axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulfate) is plotted on the y-axis. The resulting field of study is a square or rectangle depending upon the size of the scales chosen for the x and y coordinates. The milliequivalent percentage differences between alkaline earth and alkali metals and between weak acidic anions and strong acidic anions would plot in one of the four possible subfields of the diagram. The main advantage of this diagram is that it can be produced easily on most spreadsheet software packages.

The square or rectangular field describes the overall character of the water. The diagram has all the advantages of the diamond-shaped field of the Piper trilinear diagram and can be used to study various hydrochemical processes, such as base cation exchange, cement pollution, mixing of natural waters, sulfate reduction, saline water (end product water), and other related hydrochemical problems (5). The chemical analysis data of all samples collected from District Hardwar have been plotted on Chadha's diagram (Fig. 5a,b).

It is evident from the results that all samples of the study area fall in Group 5 ($Ca-Mg-HCO_3$ type) during both pre- and postmonsoon seasons. Chadha's diagram has all the advantages of the diamond-shaped field of the Piper trilinear diagram and can be conveniently used to study various hydrochemical processes. Another main advantage of this diagram is that it can be produced easily on most spreadsheet software packages.

CONCLUSIONS AND RECOMMENDATIONS

The groundwater quality in District Hardwar varies from place to place and with the depth of the water table. The water drawn for domestic use should be tested and analyzed to ensure the suitability of groundwater for human consumption. The groundwater abstraction sources and their surroundings should be properly maintained to ensure hygienic conditions; no sewage or polluted water should be allowed to percolate directly to a groundwater aquifer. Proper cement platforms should be constructed surrounding the ground water abstraction sources to avoid direct wellhead pollution, and the surrounding surface area should be frequently chlorinated by using bleaching powder. The hand pumps and wells, which have been identified as of suspect water quality, should be painted red to indicate and warn the public that the water drawn from the source is not fit for human consumption. In the absence of an alternate safe source of water, the water with excessive undesirable constituents must be treated by a specific treatment process before it is used for human consumption. The untreated sewage and sewerage flowing in various open drains are one of the causes of groundwater quality deterioration. A proper underground sewage system must be laid in inhabited areas, and the untreated sewage should not be allowed to flow in open drains. A proper system of collection and transportation of domestic waste should be developed. Landfill site(s) should be identified and must be scientifically designed. A mass awareness should be generated about water quality, its effect on human health, and the responsibilities of the public to safeguard water resources.

BIBLIOGRAPHY

1. Jain, C.K. and Bhatia, K.K.S. (1988). *Physico-Chemical Analysis of Water and Wastewater, User's Manual, UM-26*. National Institute of Hydrology, Roorkee, India.
2. American Public Health Association. (1992). *Standard Methods for the Examination of Water and Waste Waters*. 18th Edn. American Public Health Association, Washington, DC.
3. Bureau of Indian Standards. (1991). *Specifications for Drinking Water*. IS:10500:1991. Bureau of Indian Standards, New Delhi, India.
4. World Health Organization. (1996). *Guidelines for Drinking Water*. Vol. 2, Recommendations. World Health Organization, Geneva, Switzerland.
5. Chadha, D.K. (1999). A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol. J.* **7**(5): 431–439.
6. Piper, A.M. (1944). A graphical procedure in the geochemical interpretation of water analysis. *Trans. Am. Geophys. Union* **25**: 914–923.

IRRIGATION WATER QUALITY IN DISTRICT HARDWAR, UTTARANCHAL, INDIA

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The groundwater quality of District Hardwar in the state of Uttaranchal (India) was assessed to determine the suitability of groundwater for irrigation. Two sets of 48 groundwater samples from shallow and deep aquifers were collected during pre- and postmonsoon seasons in the year 2002, and the suitability of the groundwater for irrigation was evaluated based on salinity, sodium adsorption ration (SAR), residual sodium carbonate (RSC), and boron content. The values of SAR ranged from 0.24–1.75 during the premonsoon season and from 0.22–1.92 during the postmonsoon season, respectively. Values of the SAR indicate that the majority of samples of the study area falls under the category of low sodium hazard, indicating no risk of sodification. In general, the groundwater of District Hardwar is safe for irrigation. According to the U.S. Salinity Laboratory classification of irrigation water, the majority of the samples (70%) falls under water type C2-S1 followed by the C3-S1 type.

INTRODUCTION

The intensive use of natural resources and the large production of wastes in modern society often pose a threat to groundwater quality and have already resulted in many incidents of groundwater contamination. Pollutants are

being added to groundwater systems by human activities and natural processes. Solid waste from industrial units is being dumped near factories, is subjected to reaction with percolating rainwater, and reaches the groundwater level. The percolating water picks up a large amount of dissolved constituents, reaches the aquifer system, and contaminates the groundwater.

Groundwater plays an important role in agriculture for both watering crops and for irrigating dry season crops. It is estimated that about 45% of the irrigation water requirement is met from groundwater sources. Indiscriminate use of fertilizers and pesticides in agricultural fields has become common practice in India and has already resulted in very high concentrations of these constituents in groundwater, which in the long term, may create the greatest hazard to groundwater.

Many problems originate from inefficient management of water for agricultural use, especially when it carries high salts. The problem of groundwater contamination in several parts of the country has become so acute that unless urgent steps for detailed identification and abatement are taken, extensive groundwater resources may be damaged. Keeping in view the severity of the problem, the groundwater quality of District Hardwar in the newly created state of Uttaranchal (India) was studied to examine the suitability of groundwater for irrigation.

STUDY AREA

District Hardwar is part of the Indo-Gangetic plains and lies between latitude 29°30′ to 30°20′ N and longitude 77°40′ to 78°25′ E in the state of Uttaranchal (Fig. 1). It is the largest district (populationwise) of Uttaranchal State and occupies an area of about 2,360 km^2. Per the 2001 census, the population of the District Hardwar is 14,44,213, and the population density is 612 per km^2.

Physiographically, the area is generally flat except for the Siwalik Hills in the north and north east. The area is devoid of relief features of any prominence except for deep gorges cut by drains and rivers flowing through the area. The area is bounded by River Yamuna in the west and River Ganga in the east. The climate of the area is characterized by a moderate type of subtropical monsoon. The average annual rainfall in the region is about 1000 mm; the major part is received during the monsoon period. The major land use is for agriculture, and there is no effective forest cover. The soils of the area are loam to silty loam and are free from carbonates. The most common groundwater use is achieved by hand pumps and tube wells. Based on lithologic logs and water table fluctuation data, two types of aquifers have been delineated in the area. The upper is the shallow unconfined aquifer which generally extends to depths around 25m. The deeper one is confined to semiconfined and located at

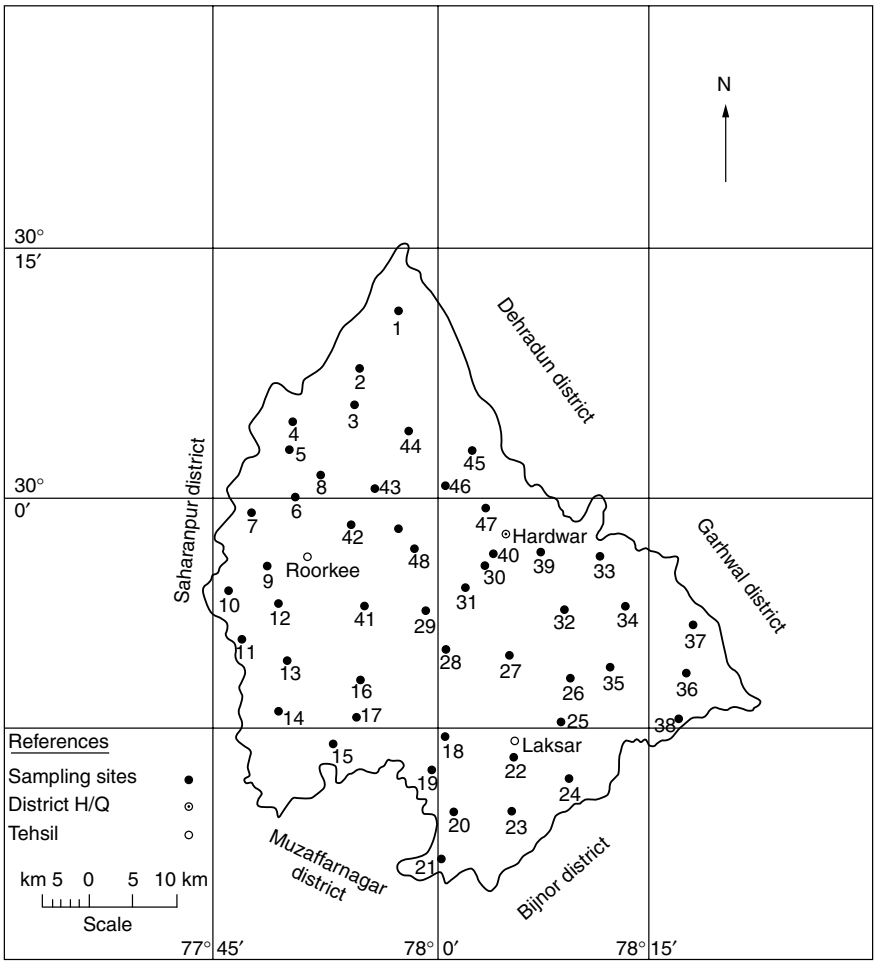


Figure 1. Study area showing location of sampling sites in District Hardwar.

a depth about 25 to 150m below ground level, separated by three to four aquifers at average depths of 25–55, 65–90, and 120–150m. Water table contours in the area indicate a southward trend of groundwater flow in both unconfined and confined aquifers.

EXPERIMENTAL METHODOLOGY

Two sets of 48 groundwater samples from District Hardwar were collected during pre- and postmonsoon seasons in the year 2002 from various abstraction sources at various depths. They were preserved by adding an appropriate reagent (1,2). The hand pumps and tube wells were continuously pumped prior to sampling to ensure that groundwater sampled was representative of the groundwater aquifer. The details of sampling locations and source and depth distribution are given in Tables 1 and 2, respectively. The physicochemical analysis was performed following standard methods (1,2).

RESULTS AND DISCUSSION

The hydrochemical data for the two sets of samples collected during pre- and postmonsoon seasons are presented in Table 3. The suitability of groundwater for domestic use was discussed in an earlier report (3). The quality of water plays an important role in irrigated agriculture. Many problems originate from inefficient management of water for agricultural use, especially when it carries high salts. The concentration and composition of dissolved constituents in water determine its quality for irrigation. The quality of water is an important consideration in any appraisal of salinity or alkaline conditions in an irrigated area. Good quality water has can provide maximum yield under good soil and water management practices. The most important characteristics of water which determine suitability of ground water for irrigation are

1. Salinity
2. Relative proportion of sodium to other cations (SAR)
3. Residual sodium carbonate (RSC)
4. Boron content

The safe limits of electrical conductivity for crops of different degrees of salt tolerance under varying soil textures and drainage conditions are given in Table 4.

Table 2. Source and Depth Distribution of Sampling Sites in District Hardwar

Source Structure	Depth Range <0–20 m	20–40 m	>40 m	Total Number
Hand pumps	6, 18, 20, 21, 22, 23, 24, 25, 27, 28, 30, 31, 32, 36, 41, 43, 44, 45, 46, 47	3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 19, 26, 29, 33, 34, 35, 38, 39, 40, 42, 48	37	46
Tube wells	—	—	—	—
Open wells	1,2	—	—	2
Total	22	25	1	48

Table 1. Description of Groundwater Sampling Locations in District Hardwar

S.No.	Location	Source	Depth, m	S.No.	Location	Source	Depth, m
1	Mohand	OW	10	25	Sultanpur	HP	15
2	Banjarewala	OW	10	26	Shahpur	HP	25
3	Buggawala	HP	30	27	Pathri	HP	15
4	Kheri	HP	38	28	Subashgarh	HP	20
5	Dadapatti	HP	38	29	Marghubpur	HP	30
6	Bahbalpur	HP	15	30	Bahadarabad	HP	20
7	Sikandarpur	HP	25	31	Alipur	HP	20
8	Bhagwanpur	HP	30	32	Katarpur	HP	10
9	Chudiala	HP	40	33	Kankhal	HP	25
10	Balswa Ganj	HP	25	34	Shyampur	HP	30
11	Manakpur	HP	40	35	Rasiya Garh	HP	40
12	Iqbalpur	HP	30	36	Gandikhatta	HP	10
13	Jharera	HP	30	37	Laldhang	HP	90
14	Sherpur	HP	30	38	Kottawali	HP	40
15	Narsen	HP	30	39	Hardwar	HP	30
16	Manglour	HP	35	40	Jwalapur	HP	30
17	Libarheri	HP	35	41	Roorkee	HP	10
18	Mahesari	HP	20	42	Gumanwala	HP	30
19	Sahipur	HP	35	43	Manubas	HP	10
20	Khanpur	HP	15	44	Bandarjud	HP	15
21	Chandpuri Kalan	HP	15	45	Beriwala	HP	5
22	Laksar	HP	15	46	Hazara	HP	10
23	Kalsiya	HP	10	47	Aurangbad	HP	10
24	Niranjanpur	HP	15	48	Daulatpur	HP	35

OW: open well; HP: hand pump.

Table 3. Hydrochemical Data for Groundwater Samples from District Hardwar[a]

Characteristics	Min	Max	Average
pH	6.22 (6.70)	7.58 (7.70)	6.87 (7.10)
Conductivity, μS/cm	233 (221)	1440 (1442)	642 (647)
TDS, mg/L	149 (141)	922 (923)	411 (414)
Alkalinity, mg/L	78 (71)	460 (482)	213 (215)
Hardness, mg/L	81 (80)	464 (427)	209 (212)
Chloride, mg/L	0.1 (1.2)	32 (35)	9.0 (9.0)
Sulfate, mg/L	0.5 (0.7)	72 (62)	22 (21)
Nitrate, mg/L	0.1 (0.1)	140 (130)	13 (13)
Phosphate, mg/L	0.01 (0.02)	0.41 (1.60)	0.03 (0.25)
Fluoride, mg/L	0.01 (0.01)	0.94 (0.88)	0.36 (0.42)
Sodium, mg/L	5.0 (4.5)	69 (71)	26 (25)
Potassium, mg/L	0.8 (0.2)	42 (32)	7.0 (7.4)
Calcium, mg/L	22 (24)	140 (135)	55 (56)
Magnesium, mg/L	5.0 (5.0)	36 (38)	18 (17)
Boron, mg/L	0.12 (0.12)	0.92 (0.87)	0.50 (0.49)

[a]Values in parentheses represent postmonsoon data.

The quality of water is commonly expressed by classes of relative suitability for irrigation with reference to salinity levels. The recommended classification with respect to electrical conductivity, sodium content, sodium absorption ratio (SAR), and residual sodium carbonate (RSC) are given in Table 5. The values of sodium percentage (% Na), SAR, and RSC in the groundwater of District Hardwar are given in Table 6.

Salinity

Salinity is broadly related to total dissolved solids (TDS) and electrical conductivity (EC). High concentrations of TDS and electrical conductivity in irrigation water may increase the soil salinity, which affects the salt intake of a plant. The salts in the water affect the growth of plants directly and also affect the soil structure, permeability, and aeration, which indirectly affect plant growth. Soil water passes into a plant through the root zone by osmotic pressure. As the dissolved solid content of the soil water in the root zone increases, it is difficult for the plant to overcome the osmotic pressure and the plant root membranes are able to assimilate water and nutrients. Thus, the dissolved solids content of the residual water in the root zone also has to be maintained within limits by proper leaching. Negative effects are visible in plants by stunted growth, low yield, discoloration, and even leaf burns at margin or top. The electrical conductivity values for water in District Hardwar are well within the prescribed limits of 1500 μS/cm and are therefore safe for irrigation.

Relative Proportion of Sodium to Other Cations

A high salt concentration in water leads to saline soil, and high sodium leads to development of an alkaline soil. The sodium or alkaline hazard in using water for irrigation is determined by the absolute and relative concentration of cations, expressed in terms of the sodium adsorption ratio (SAR). If the proportion of sodium is high, the alkaline hazard is high, and conversely, if calcium and magnesium predominate, the hazard is less. There is a significant relationship between SAR values of irrigation water and the extent to which sodium is absorbed by the soil. If water used for irrigation is high in sodium and low in calcium, the cation-exchange complex may become saturated with sodium. This can destroy the soil structure owing to dispersion of the clay particles. A simple method of evaluating the danger of high-sodium water is the sodium adsorption ratio (SAR) (4):

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})/2}}$$

The sodium percentage is calculated from

$$\%\mathrm{Na} = \frac{\mathrm{Na}^+ + \mathrm{K}^+}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+} \times 100$$

where all ionic concentrations are expressed in milliequivalents per liter.

Table 5. Guidelines for Evaluation of Irrigation Water Quality

Water Class	Sodium (Na), %	Electrical Conductivity, μS/cm	SAR	RSC, meq/L
Excellent	<20	<250	<10	<1.25
Good	20–40	250–750	10–18	1.25–2.0
Medium	40–60	750–2250	18–26	2.0–2.5
Bad	60–80	2250–4000	>26	2.5–3.0
Very bad	>80	>4000	>26	>3.0

Table 4. Safe Limits of Electrical Conductivity for Irrigation Water

S. No.	Nature of Soil	Crop Growth	Upper Permissible Safe Limit of EC in Water, μS/cm
1.	Deep black soil and alluvial soil whose clay content is more than 30% in soils that are fairly to moderately well drained	Semitolerant	1500
		Tolerant	2000
2.	Textured soil of clay content of 20–30% in soils that are well drained internally and have a good surface drainage system	Semitolerant	2000
		Tolerant	4000
3.	Medium textured soils whose clay is 10–20% internally very well drained and has a good surface drainage system	Semitolerant	4000
		Tolerant	6000
4.	Lightly textured soils whose clay is less than 10% of soil that has an excellent internal and surface drainage system	Semitolerant	6000
		Tolerant	8000

Table 6. SAR, % Na, and RSC Values in the Groundwater of District Hardwar

		Premonsoon			Postmonsoon		
S.No.	Location	SAR	% Na	RSC	SAR	% Na	RSC
1	Mohand	1.02	27.4	0.40	0.97	27.1	−0.05
2	Banjarewala	0.81	22.7	−0.32	0.49	16.4	−0.62
3	Buggawala	0.31	11.1	−0.18	0.30	10.3	−0.05
4	Kheri	0.56	17.5	−0.17	0.67	18.3	−0.03
5	Dadapatti	0.86	25.4	0.77	0.76	25.2	0.60
6	Bahbalpur	0.89	23.4	0.61	0.96	23.5	0.47
7	Sikandarpur	0.72	24.5	0.48	0.66	23.2	0.51
8	Bhagwanpur	0.79	25.3	0.67	0.68	22.4	0.49
9	Chudiala	0.72	24.4	0.60	0.64	21.9	0.42
10	Balswa Ganj	0.90	25.0	−0.27	0.71	22.5	−0.52
11	Manakpur	0.69	23.0	0.54	0.73	23.3	0.52
12	Iqbalpur	1.04	23.7	0.48	0.97	23.4	0.55
13	Jharera	0.77	21.3	−0.10	0.76	20.8	−0.33
14	Sherpur	0.54	23.0	0.28	0.51	21.5	0.07
15	Narsen	0.50	21.0	0.14	0.56	23.0	0.26
16	Manglour	0.80	21.6	−0.38	0.90	22.1	−0.35
17	Libarheri	0.24	14.9	−0.06	0.22	13.5	−0.19
18	Mahesari	1.11	33.1	0.69	1.18	33.1	1.01
19	Sahipur	0.74	28.9	0.59	0.71	27.1	0.48
20	Khanpur	1.75	45.5	1.48	1.92	47.8	1.54
21	Chandpuri Kalan	1.60	47.9	1.11	1.51	42.9	0.93
22	Laksar	1.30	33.2	0.74	1.19	30.3	0.66
23	Kalsiya	0.71	24.4	−0.17	0.64	23.7	−0.18
24	Niranjanpur	1.28	33.5	0.01	1.39	33.5	0.26
25	Sultanpur	1.31	35.7	1.04	1.14	30.9	0.11
26	Shahpur	0.46	19.8	0.14	0.44	18.1	0.13
27	Pathri	0.25	9.9	−0.36	0.24	10.2	−0.45
28	Subashgarh	0.45	17.3	−0.37	0.42	17.1	−0.17
29	Marghubpur	1.53	29.7	0.12	1.57	30.4	0.18
30	Bahadarabad	0.54	14.9	−0.70	0.61	20.3	0.17
31	Alipur	0.49	17.0	−0.16	0.53	17.7	−0.07
32	Katarpur	0.42	17.4	−0.69	0.39	16.0	−0.77
33	Kankhal	0.63	20.0	−0.91	0.62	19.7	−0.40
34	Shyampur	0.59	19.8	0.07	0.50	17.5	−0.06
35	Rasiya Garh	0.52	16.1	−0.11	0.51	15.5	−0.17
36	Gandikhatta	0.54	18.0	−0.35	0.58	19.3	−0.23
37	Laldhang	0.54	15.7	−0.55	0.48	14.3	−0.65
38	Kottawali	0.48	16.1	−0.07	0.41	13.9	−0.31
39	Hardwar	0.54	20.3	−0.46	0.64	23.6	−0.36
40	Jwalapur	1.05	23.7	−1.76	1.07	22.9	−2.11
41	Roorkee	0.46	16.6	−0.19	0.48	18.8	0.05
42	Gumanwala	0.58	19.7	−0.15	0.72	24.6	0.31
43	Manubas	1.09	24.5	−0.10	1.37	28.8	1.09
44	Bandarjud	0.30	9.1	−0.45	0.28	9.2	−0.40
45	Beriwala	0.72	25.4	0.46	0.66	23.1	0.25
46	Hazara	1.03	28.5	0.15	0.62	21.1	−0.62
47	Aurangbad	0.99	32.2	0.32	0.75	27.1	0.24
48	Daulatpur	0.79	24.10	0.44	0.88	26.7	0.64

Calculation of SAR for a given water provides a useful index of the sodium hazard of that water for soils and crops. A low SAR (2 to 10) indicates little danger from sodium; medium hazards are between 7 and 18, high hazards between 11 and 26, and very high hazards above that. The lower the ionic strength of the solution, the greater the sodium hazards for a given SAR (4).

The values of SAR in the groundwater of District Hardwar vary from 0.24–1.75 during the premonsoon season and from 0.22–1.92 during the postmonsoon season. As evident from the SAR values, the groundwater of the study area falls under the category of low sodium hazard, which reveals that the groundwater of the study area is free from any sodium hazard. The sodium percentage in the study area varies from 9.1–47.9% during the premonsoon season and from 9.2–47.8% during the postmonsoon season. All samples are well within the permissible limit for irrigation water and are free of any sodium hazard.

Residual Sodium Carbonate

In addition to total dissolved solids, the relative abundance of sodium with respect to alkaline earths and boron and the quantity of bicarbonate and carbonate in excess of alkaline earths also influence the suitability of water for irrigation. This excess is denoted residual sodium carbonate (RSC) and is determined by the following formula:

$$\mathrm{RSC} = (\mathrm{HCO_3}^- + \mathrm{CO_3}^{2-}) - (\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})$$

where all ionic concentrations are expressed in meq/L. Groundwater containing high concentrations of carbonate and bicarbonate ions tends to precipitate calcium and magnesium as carbonate. As a result, the relative proportion of sodium increases and is fixed in the soil thereby decreasing soil permeability. If the RSC exceeds 2.5 meq/L, the water is generally unsuitable for irrigation. Excessive RSC causes the soil structure to deteriorate, as it restricts the water and air movement through soil. If the value is between 1.25 and 2.5, the water is of marginal quality; values less than 1.25 meq/L indicate that the water is safe for irrigation. During the present study, the RSC values clearly indicate that the groundwater of District Hardwar does not have any residual sodium carbonate hazard.

Boron

Boron is essential to the normal growth of all plants, but the concentration required is very small and if exceeded may cause injury. Plant species vary in boron requirement and in tolerance to excess boron, so that concentrations necessary for the growth of plants that have high boron requirements may be toxic to plants sensitive to boron. Although boron is an essential nutrient for plant growth, generally it becomes toxic beyond 2 mg/L in irrigation water for most field crops. It does not affect the physical and chemical properties of the soil, but at high concentrations, it affects the metabolic activities of the plant. During the present study, the boron content in the groundwater clearly indicates that the groundwater is safe for irrigation.

U.S. Salinity Laboratory Classification

The U.S. Salinity Laboratory classification (5) is used to study the suitability of groundwater for irrigation. In classifying irrigation waters, it is assumed that the water will be used under average conditions with respect to soil texture, infiltration rate, drainage, quantity of water used, climate, and salt tolerance of the crop. Sodium concentration is an important criterion in irrigation-water

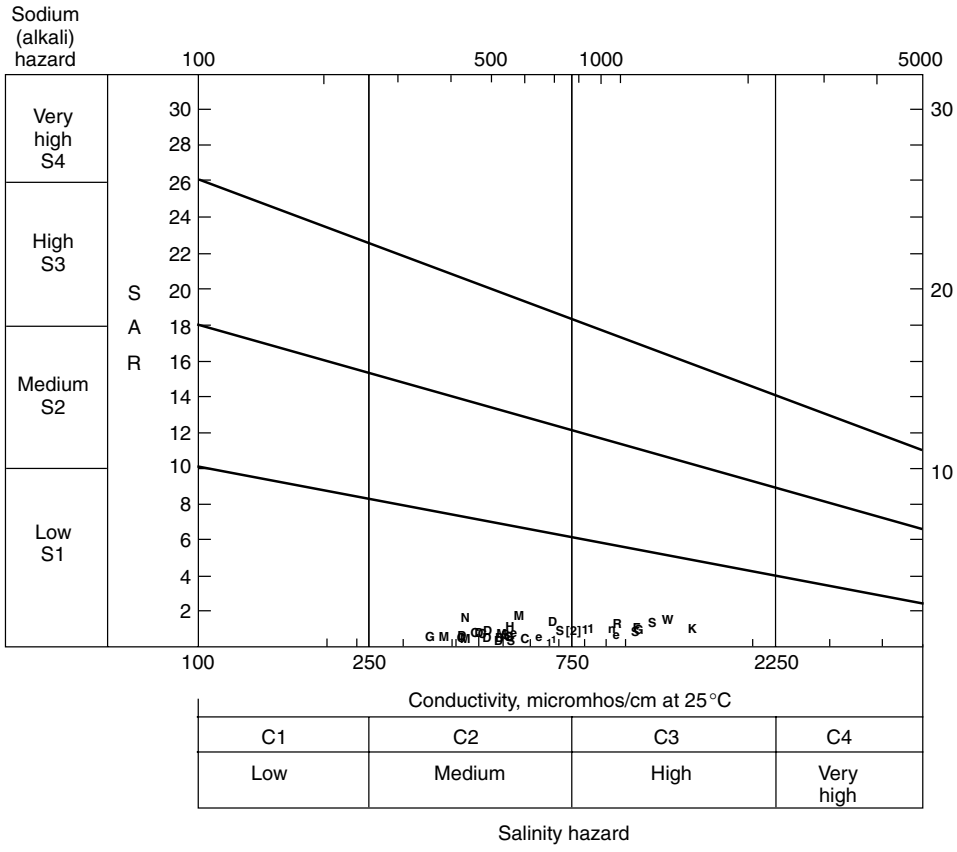


Figure 2. U.S. Salinity Laboratory classification, District Hardwar (premonsoon 2002).

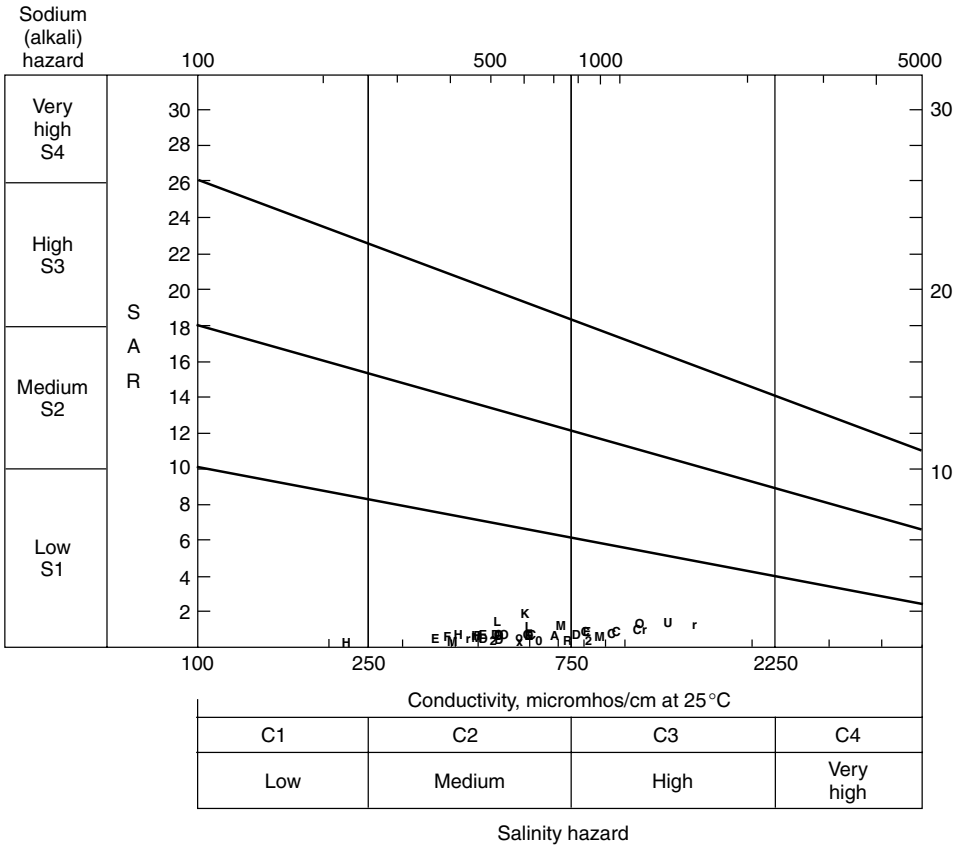


Figure 3. U.S. Salinity Laboratory classification, District Hardwar (postmonsoon 2002).

Table 7. Summarized Results of U.S. Salinity Laboratory Classification

	Sample Numbers	
Classification/Type	Premonsoon 2002	Postmonsoon 2002
C1-S1	17	17
C2-S1	3, 4, 5, 6, 7, 8, 9, 11, 14, 15, 18, 19, 20, 21, 22, 23, 26, 27, 28, 31, 32, 34, 35, 36, 37, 39, 40, 41, 42, 44, 45, 47, 48	3, 4, 5, 7, 8, 9, 11, 14, 15, 18, 19, 20, 21, 22, 23, 26, 27, 28, 30, 31, 32, 34, 35, 36, 37, 38, 39, 41, 42, 44, 45, 47, 48
C3-S1	1, 2, 10, 12, 13, 16, 24, 25, 29, 30, 33, 38, 43, 46	1, 2, 6, 10, 12, 13, 16, 24, 25, 29, 33, 40, 43, 46

classification because sodium reacts with the soil to create sodium hazards by replacing other cations. The extent of this replacement is estimated by the sodium adsorption ratio (SAR). A diagram for use in studying the suitability of groundwater for irrigation is based on the sodium adsorption ratio (SAR) and the electrical conductivity of water expressed in μS/cm. The chemical analytical data on groundwater samples from District Hardwar were processed as per the U.S. Salinity Laboratory classification for the two sets of data (Figs. 2 and 3), and the results are summarized in Table 7.

It is evident from the results that majority of the samples (about 70% of total samples) falls under water type C2-S1 (medium salinity and low SAR); such water can be used if a moderate amount of leaching occurs, and plants with moderate salt tolerance can be grown in most cases without special practices for salinity control. About 30% of the samples falls under water type C3-S1 (high salinity and low SAR); such water cannot be used on soils where drainage is restricted. Even with adequate drainage, special management for salinity control may be required, and plants with good tolerance should be selected. An almost similar trend was observed during the postmonsoon season.

CONCLUSIONS

Groundwater quality varies from place to place and with the depth of the water table. The SAR values indicate that the majority of samples from the study area falls under the category of low sodium hazard indicating no risk for sodification. In general, the groundwater of District Hardwar is safe for irrigation. According to the U.S. Salinity Laboratory classification of irrigation water, the majority of the samples (70%) falls under water type C2-S1 followed by the C3-S1 type.

BIBLIOGRAPHY

1. American Public Health Association. (1992). *Standard Methods for the Examination of Water and Waste Waters*, 18th Edn. American Public Health Association, Washington, DC.
2. Jain, C.K. and Bhatia, K.K.S. (1988). *Physico-Chemical Analysis of Water and Wastewater, User's Manual, UM-26*. National Institute of Hydrology, Roorkee, India.
3. Jain, C.K. (2003). *Ground Water Quality in District Hardwar, Uttaranchal, Technical Report*. National Institute of Hydrology, Roorkee, India.
4. Richards, L.A. (Ed.). (1954). *Diagnosis and Improvement of Saline and Alkali Soils, Agricultural Handbook 60*. U.S. Dept. Agric., Washington, DC.
5. Wilcox, L.V. (1955). *Classification and Use of Irrigation Water*. U.S. Dept. of Agric. Circular 969, Washington, DC.

INFILTRATION AND SOIL WATER PROCESSES

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Water at the soil surface is drawn into the soil pores under the influence of both suction and gravity. Suction (or tension/capillary) forces are largest in the small pore spaces between soil particles. Therefore, small pores fill first, and large pores empty first. As a soil becomes saturated, suction forces approach zero. As a soil dries, suction forces dominate, and there is little or no gravitational flow. For a dry soil during the early stages of wetting, the effect of soil pore suction is predominant. However, as the depth of wet soil increases, the suction gradient decreases (the same difference in suction is spread over an ever increasing depth interval) and the gravitational head gradient becomes the main driving force (1).

Infiltration processes cannot easily be separated from the processes involved in movement of water within soil because the rate of infiltration is partly controlled by the rate of soil water movement below the surface. Soil water movement continues after an infiltration, as the infiltrated water is redistributed. Infiltration and soil water processes play a key role in surface runoff, groundwater recharge, ecology, evapotranspiration, soil erosion, and transport of nutrients and other solutes in surface and subsurface waters.

Bodman and Colman (2) suggested that for a uniform soil, there would be a series of zones in the wetting part of the soil profile during an infiltration. The zone nearest the surface is a saturated zone (typically in the upper centimeter of the soil profile). As water penetrates more deeply, a zone of uniform water content, the transmission zone, develops behind a well-defined wetting front (Fig. 1).

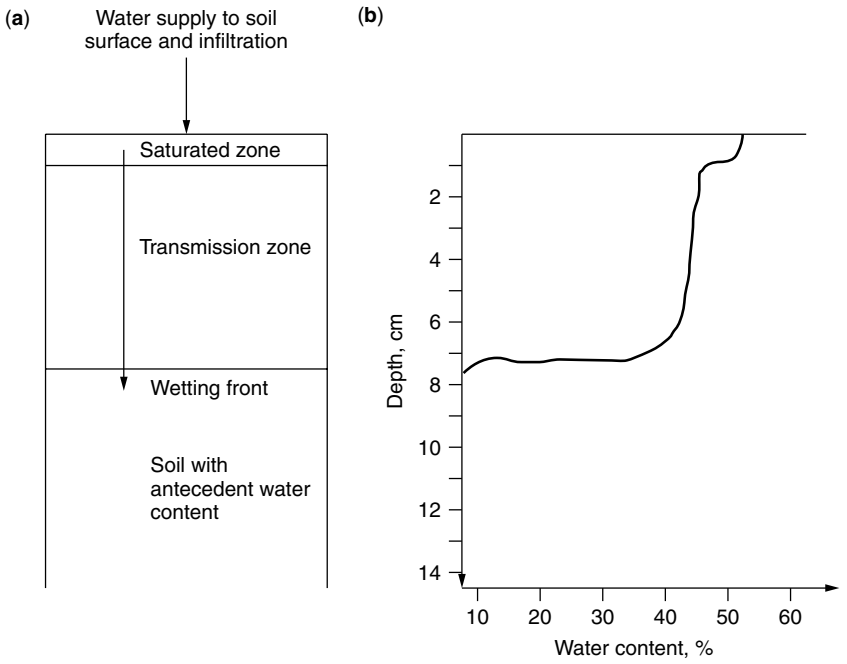


Figure 1. Soil water zones during infiltration: (**a**) theoretical zonation, (**b**) measured water content for a sandy soil 4 minutes after ponded infiltration commenced.

There is a sharp change in water content at the wetting front because the water at the boundary takes up a preferred position of minimum potential energy in the narrowest pores, for which the hydraulic conductivity is very low, and does not move at an appreciable rate until the large pores begin to fill. Figure 1 shows the water content versus depth for a sandy soil 4 minutes after ponded infiltration at the surface. The sharp transition in water content can be seen at the wetting front. Note that the soil below the wetting front still has some pre-event moisture. There is also a sharp transition in the moisture profile between the upper saturated zone and the transmission zone, sometimes called the transition zone (1).

Gravitational and suction gradients result in continued downward movement of water within the soil profile which may occur long after infiltration at the surface has ceased. As a result, the transmission zone which existed during infiltration becomes a draining zone that releases water from the wetter upper layers of the soil to deeper drier layers. As the draining zone becomes drier, the hydraulic conductivity reduces, and so the rate of soil water redistribution slows down. The suction gradient also weakens as the soil water content becomes more uniform. While the wetting front continues to advance into deeper soil layers, its movement is reduced over time until eventually the water content changes only very slowly and the soil is said to be at field capacity (1). In some soils, this may take several days (2). Theoretically, soil water redistribution following rainfall would continue until gravity and soil suction forces were in balance (4,5). At this stage and at all depths, there would be equal soil water potential. Therefore, without a hydraulic gradient, there would be no soil water movement, which is rarely observed in the field because soils are highly heterogeneous, rainfall itself is rarely an on–off uniform event (a theoretical model examining this issue was applied to a range of soil types by Ref. 6), and because evaporation from soil and plants can result in drying of surface soil layers.

Evaporation at the soil surface encourages upward movement of soil water, which therefore reduces downward movement of water over time. There is probably a two-way effect whereby drainage reduces the amount of evaporation and evaporation reduces the amount of drainage (3). During water redistribution following infiltration, the upper part of the soil profile may be drying through drainage and evaporation while the lower part is still becoming wetter, which complicates the water content–soil moisture tension (suction) relationship within the soil because it will depend on the history of wetting and drying in any given part of the soil profile (soil water hysteresis; 4,7,8).

Often, the soil water redistribution that follows an infiltration is complicated by the nonuniform nature of most soils. In addition to the effects of soil layering, many studies, for example, often assume that the water table has little impact on postinfiltration water redistribution. However, in many soils, the water table may be shallow (e.g., peats), and this may exert considerable influence on the distribution of water in a soil profile (9). Trapped soil gases may also affect water redistribution by blocking pores and preventing water entry (10). Furthermore, noncapillary macropores or voids such as decayed root channels, worm holes, and structural cracks that are open at the soil surface can capture the free water available at the surface during rainfall and overland flow. This causes the water flowing through the macropores to bypass the soil matrix. Often, water and solutes (e.g., fertilizer applications) can infiltrate into the soil via macropores but then are quickly transferred to much deeper parts of the soil profile where the water and nutrients are not readily available to plants (11,12). Bypassing flow also causes some parts of the soil profile at any given depth

to wet well before other parts of the soil that are at the same depth.

BIBLIOGRAPHY

1. Ward, R.C. and Robinson, M. (2000). *Principles of Hydrology*. McGraw-Hill, London.
2. Bodman, G.B. and Colman, E.A. (1943). Moisture and energy conditions during downward entry of water into soils. *Proceedings of the Soil Science Society of America* **8**: 116–122.
3. Gardner, W.R., Hillel, D., and Benyamini, Y. (1970). Post irrigation movement of soil water, 2, Simultaneous redistribution and evaporation. *Water Resources Research* **6**: 1148–1153.
4. Childs, E.C. (1969). *An Introduction to the Physical Basis of Soil Water Phenomena*. John Wiley & Sons, London.
5. Rawls, W.J., Ahuja, L.R., Brakensiek, D.L., and Shirmohammadi, A. (1993). Infiltration and soil water movement. In: *Handbook of Hydrology*. D.R. Maidment (Ed.). McGraw-Hill, New York, pp. 5.1–5.51.
6. Corradini, C., Melone, F., and Smith, R.E. (1997). A unified model for infiltration and redistribution during complex rainfall patterns. *Journal of Hydrology* **192**: 104–124.
7. Vachaud, G. and Thony, J.L. (1971). Hysteresis during infiltration and redistribution in a soil column at different initial water contents. *Water Resources Research* **9**: 160–173.
8. Beese, F. and van der Ploeg, R.R. (1976). Influence of hysteresis on moisture flow in an undisturbed soil monolith. *Proceedings of the Soil Science Society of America* **40**: 480–484.
9. Evans, M.G., Burt, T.P., Holden, J., and Adamson, J. (1999). Runoff generation and water table fluctuations in blanket peat: evidence from UK data spanning the dry summer of 1995. *Journal of Hydrology* **221**: 141–160.
10. Beckwith, C.W. and Baird, A.J. (2001). Effect of biogenic gas bubbles on water flow through poorly decomposed blanket peat. *Water Resources Research* **37**: 551–558.
11. Beven, K.J. and Germann, P. (1982). Macropores and water flow in soils. *Water Resources Research* **18**: 1311–1325.
12. Germann, P.F. (1990). Macropores and hydrologic hillslope processes. In: *Process Studies in Hillslope Hydrology*. M.G. Anderson and T.P. Burt (Eds.). John Wiley & Sons, Chichester, pp. 327–363.

INFILTRATION/CAPACITY/RATES

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Infiltration is the process of water entry into the surface of a soil. It involves surface water entry, transmission through the soil, and depletion of the soil water storage capacity. Surface water entry is influenced by surface vegetation cover, soil texture, soil porosity, soil structure (e.g., cracks, surface crusting), and compaction. Land management can influence all of these parameters and therefore influence infiltration.

The infiltration rate is the volume of water passing into the soil per unit area per unit time and therefore has dimensions of velocity (e.g., m s^{-1}; mm h^{-1}). The infiltration rate is often measured using an infiltrometer (INFILTROMETERS) and is one of the most easily and frequently measured soil water processes. Despite the units of velocity, the values of infiltration rate are actually volume fluxes expressed as volume flux density and therefore do not indicate the effective velocity of vertical water movement in the soil (1).

The maximum rate at which water soaks into or is absorbed by the soil is the infiltration capacity. Infiltration capacity may be very important in determining the proportion of incoming rainfall that runs off as infiltration-excess overland flow and the proportion that moves into the soil. The infiltration capacity is different from the infiltration rate. Infiltration may be limited by the rate of supply of rainfall (or other water supply) or the capacity of the soil to absorb water. In the former case, infiltration is limited by the water supply to the soil surface, and in the latter case, infiltration is restricted by the infiltration capacity of the soil. Use of the term infiltration rate therefore indicates that infiltration is proceeding at less than the infiltration capacity (2). If infiltration is occurring at less than the infiltration capacity, then all rain reaching the soil surface that is not held as surface storage will infiltrate into the soil. Thus, there will be a direct relationship between infiltration rate and rainfall intensity. However, when rainfall intensity exceeds the infiltration capacity of the soil surface, this relationship breaks down and may be inverted, as infiltration capacity declines through a storm as the soil wets (2). Excess rainwater that cannot infiltrate into the soil because the surface water supply is greater than the infiltration capacity will pond on the soil surface and eventually run over the surface as infiltration-excess overland flow.

The infiltration capacity of a soil generally decreases during rainfall, rapidly at first and then more slowly, until a more or less stable value has been attained (Fig. 1). Water initially crosses the soil surface interface at an initial rate (f_o), depending on existing soil moisture content. As the rainfall or other water supply to the soil surface continues, the rate of infiltration decreases (because it is limited by decreasing infiltration capacity) as the soil becomes wetter and less able to take up water. Philip (3) put forward the theory that the infiltration capacity of a soil declines over time in a manner described by the equation,

$$f = A + Bt^{-0.5}$$

where $f =$ infiltration capacity at time t, and A and B are constants. This equation may be solved using simultaneous equations, allowing constants A and B to be evaluated:

$$B = (f_1 - f_0)/(t_1^{-0.5} - t_0^{-0.5})$$
$$A = (f_0 t_1^{-0.5} - f_1 t_0^{-0.5})/(t_1^{-0.5} - t_0^{-0.5})$$

The curve of infiltration rate over time shown in Fig. 1 reduces to a constant value f_c, which is the infiltration capacity at time t_c. The Philip model is useful for short infiltration events, but other models (e.g., those based on the Richards equation) are more reliable for longer periods (4,5).

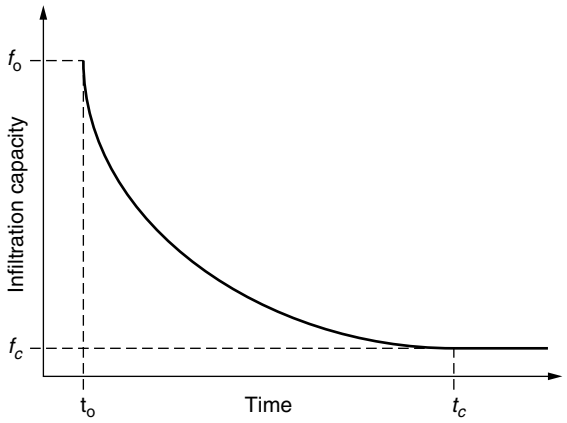


Figure 1. The decline of infiltration capacity during a rainfall.

Soil surface conditions may impose an upper limit on the rate at which water can be absorbed, despite a large available capacity of the lower soil layers to receive and to store additional infiltrating water. Often, the infiltration capacity is reduced by surface sealing resulting from compaction, washing of fine particles into surface pores, and by frost (6,7). Frozen moisture will block soil pores, and the greater the frozen moisture content, the lower the infiltration rate upon melt, as the larger pores remain blocked for longest. Holden and Burt (8) noted that infiltration capacity increases with the depth of standing water on the surface because of increased water head (9,10) and unblocking of pores due to flotation of fines (11). The number of cracks and fissures at the surface and the ground slope also influences infiltration capacity. Cultivation techniques may either increase or decrease infiltration capacity (12). Field plowing can increase soil infiltration capacity, whereas raindrop compaction subsequent to field plowing can reduce infiltration capacities when splashed silt and clay soil particles clog soil pores as the aggregates break down. Organic matter also binds aggregates together. New vegetation, however, tends to increase the infiltration capacity of a soil by retarding surface water movement, stabilizing loose particles, reducing raindrop compaction, and improving soil structure. Soils with well developed humus and litter layers tend to have high infiltration capacities. Most forest floors that have a litter layer tend, for example, to have higher infiltration than that beneath grass (2).

The infiltration capacity of a soil is dependent on surface properties and also on transmission through the soil below the surface and the storage capacity of the soil. Water cannot be absorbed by the soil surface unless the underlying soil profile can conduct the infiltrated water away. Transmission rates depend on soil texture, porosity, pore size distribution, soil stratification, antecedent soil moisture content, initial gradient of soil water potential, salinity, and biotic activity. Storage capacity depends on pore size distribution, porosity, and antecedent moisture conditions. Where the soil profile contains a relatively impermeable layer at some distance below the surface, the curve of infiltration capacity against time may display a sudden reduction of infiltration capacity because when available storage in the surface soil horizons has been filled, infiltration will be governed by the rate at which water can pass through the underlying impeding layer.

Soil properties are highly heterogeneous. Infiltration capacities and infiltration rates vary greatly even within a small area and in a short time. The effect of spatial variability on infiltration produces a difference between point infiltration values and apparent infiltration rates associated with measurements from large plots, composite areas, and estimates from watershed calculations, which may provide a reason that mean infiltration capacity across a plot increases with rainfall intensity (13,14; see also RAIN SIMULATORS). In other words, the nonuniform nature of soil across a large plot may cause in the surface of one part of the plot to have a higher infiltration capacity than the rest of the plot. Therefore, as Hawkins (13) demonstrated numerically, the mean infiltration rate across a plot will increase with rainfall intensity simply because a greater flux of water is occurring through the parts of the plot surface that have higher relative infiltration capacities. It must be acknowledged, therefore, that only a fraction of the area within a plot or hillslope need contribute to overland flow, even when the rainfall rate exceeds the mean infiltration capacity across the plot or hillslope, which also suggests that the spatial variability in infiltration parameters has more effect at lower rainfall rates, closer to the saturated hydraulic conductivity of the soil (5).

BIBLIOGRAPHY

1. White, R.E. (1997). Principles and practice of soil science. *The Soil as a Natural Resource*. Blackwell Science Ltd, Oxford.
2. Ward, R.C. and Robinson, M. (2000). *Principles of Hydrology*. McGraw-Hill, London.
3. Philip, J.R. (1957). The theory of infiltration 1. The infiltration equation and its solution. *Soil Science* **83**: 345–357.
4. Kirkby, M.J. (1985). Hillslope hydrology. In: *Hydrological Forecasting*. M.G. Anderson and T.P. Burt (Eds.). John Wiley, Chichester, pp. 37–75.
5. Rawls, W.J., Ahuja, L.R., Brakensiek, D.L., and Shirmohammadi, A. (1993). Infiltration and soil water movement. In: *Handbook of Hydrology*. D.R. Maidment (Ed.). McGraw-Hill, New York, pp. 5.1–5.51.
6. Poesen, J. (1986). Surface sealing as influenced by slope angle and position of simulated stones in the top layer of loose sediments. *Earth Surface Processes and Landforms* **11**: 1–10.
7. Romkens, M.J.M., Prasad, S.N., and Parlange, J.Y. (1990). Surface seal development in relation to rainsform intensity. *Catena Supplement* **17**: 1–11.
8. Holden, J. and Burt, T.P. (2002). Infiltration, runoff and sediment production in blanket peat catchments: Implications of field rainfall simulation experiments. *Hydrological Processes* **16**: 2537–2557.
9. Schiff, L. (1953). The effect of surface head on infiltration rates based on the performance of ring infiltrometers and ponds. *Transactions of the American Geophysical Union* **34**: 257–266.
10. Philip, J.R. (1958). The theory of infiltration 6. Effect of water depth over soil. *Soil Science* **85**: 278–286.

11. Bowyer-Bower, T.A.S. (1993). Effects of rainfall intensity and antecedent moisture on the steady-state infiltration rate in a semi-arid region. *Soil Use and Management* **9**: 69–76.
12. Imeson, A.C. and Kwaad, F.J.P.M. (1990). The response of tilled soils to wetting by rainfall and the dynamic character of soil erodibility. In: *Soil Erosion on Agricultural Land*. J. Boardman, I.D.L. Foster, and J.A. Dearing (Eds.). John Wiley, Chichester, pp. 3–14.
13. Hawkins, R.H. (1982). Interpretations of source area variability in rainfall-runoff relations. In: *Rainfall-runoff relationship*. *Proceedings of the International Symposium on rainfall runoff modelling held May 18–21, 1981, Mississippi State University*. Water Resources Publications, Littleton, CO, pp. 303–324.
14. Smith, R.E. (1983). Flux infiltration theory for use in watershed hydrology. In: *Advances in Infiltration*. American Society of Agricultural Engineers, St. Joseph, MI, pp. 313–323.

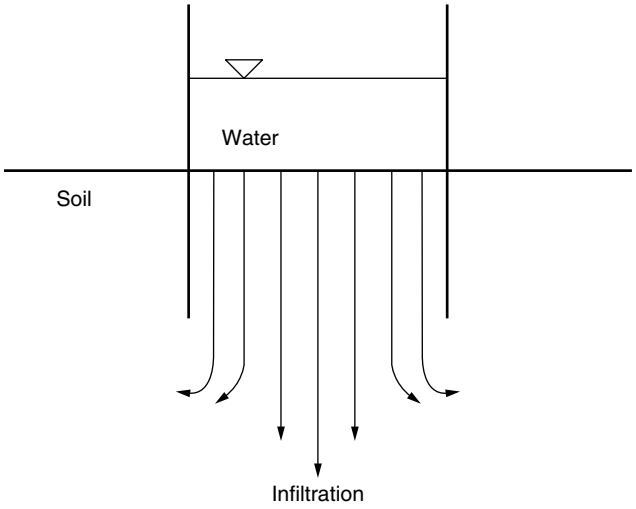


Figure 1. Infiltration from a single ring infiltrometer.

INFILTROMETERS

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Infiltrometers allow measuring of the rate of infiltration of water into a given medium. Rain simulators, a particular type of infiltrometer, are discussed elsewhere (see entry RAIN SIMULATORS). Unlike rain simulators, other infiltrometers do not simulate raindrop activity but measure the rate of infiltration from a reservoir of water at the ground surface. Their main advantage is their simplicity and ease of use. There are two main types of infiltrometer, a ponded ring infiltrometer and a disk infiltrometer.

PONDED RING INFILTROMETER

A ponded ring infiltrometer is the most common type of infiltrometer used. It is inexpensive to construct or operate and requires relatively little water for measurements. One person can set up and run several tests simultaneously. A cylindrical ring of stainless steel or plastic pipe is used, and the ring is pushed a few centimeters into the ground (Fig. 1). Care is taken to minimize disturbing the soil surface and soil structure during installation. Water is then flooded into the ring. The water inside the ring gradually infiltrates the soil, so measurements of the depth of water in the ring over time can be used to provide an infiltration rate usually in units of length per unit time (e.g., mm hr^{-1}) allowing easy comparison with rainfall intensity data. If the ring empties, it can be easily refilled.

There are two main problems in this method: (1) lateral flow below the ring; (2) changing pressure of water in the ring as the water level decreases in the ring during infiltration. To get around the lateral flow problem, it is advisable to use two concentric rings; the larger ring forms a buffer compartment around the inner ring (Fig. 2). While water is topped up in the outer ring, measurements are taken only of infiltration from the inner ring. It is preferable that a constant head of water is maintained

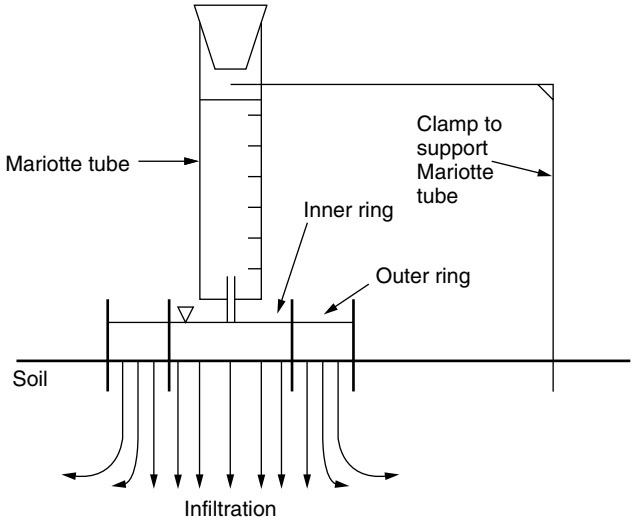


Figure 2. Double-ring infiltrometer with constant-head supply.

within the rings to avoid changing pressures. The head of water should also be less than 5 cm deep. The constant head can be supplied by a Mariotte bottle placed above the rings, and readings of water usage can be made from the Mariotte bottle (Fig. 2). Thus the optimum design for a ring infiltrometer is a constant-head, double-ring device whose rings have large diameters, so that they can represent the soil surface more readily. A plot of water uptake against time should show a leveling off as the infiltration capacity is reached. It often takes several hours before a constant rate of infiltration is achieved from the infiltrometer, depending on soil type, texture, and antecedent soil moisture.

The method of placement is serious limitation to the use of ring infiltrometers. Knocking rings into the ground can result in destruction of the soil structure or compression. If a soil is shattered, it can disturb the contact between the ring edge and the soil, resulting in leakage and high infiltration rates. Research has demonstrated that

ring infiltrometers give higher infiltration rates than rain simulators because of the effect of a pond on the soil surface, lateral seepage, and soil cracking.

DISK INFILTROMETER

Tension disk infiltrometers are a standard tool for in situ determination of saturated and near-saturated soil hydraulic properties. These infiltrometers have a porous membrane disk at their base which rests on the soil surface of interest. To assess the role of matrix and macropore flow, a tension infiltrometer allows infiltration of water into the soil matrix, while preventing flow into larger pores that may otherwise dominate the infiltration process. The infiltrometer provides a source of water at a small negative pore water pressure at the surface. The supply pressure head is controlled with a Mariotte bottle. A schematic diagram of a tension disk infiltrometer is given in Fig. 3. As for a ring infiltrometer, infiltration rates can be measured manually by observing the volume of water lost from the Mariotte bottle over time. The negative pressure prevents the larger pores that fill at greater pore water pressures from wetting and short-circuiting the flow. Hence, by subtraction, the hydrological role of larger pores during the infiltration process can be evaluated. Further details on designs for these infiltrometers are given in Ankeny et al. (1) and Zhang et al. (2). Most studies using tension disk infiltrometers have been conducted at the soil surface, although Azevedo et al. (3) looked at infiltration properties of an Iowa loamy soil at 0.15 m depth, and Logsdon et al. (4), and Messing and Jarvis (5) conducted measurements at different depths under different agricultural tillages.

Careful preparation of the soil surface is required to use a disk infiltrometer, which is to ensure even and sound contact of the disk with the soil surface. At each location, vegetation must be cut back to the soil surface, and a fine layer of moist fine sand of the same diameter as the circular base of the infiltrometer should be applied, which must be smoothed out to remove any irregularities at the soil surface and improve contact between the disk and soil surface. Moist sand is essential as air-dry sand may readily fall down into surface-vented macropores, forming 'wicks' (5). The infiltrometer is then placed on the sand. The weight of the infiltrometer must not be too great so as compress the soil surface significantly, as this will restrict the water flux. Therefore, it is usual to make the water supply reservoir narrow so that the total volume of water held in the infiltrometer is low, resulting in reduced weight and also aiding accurate measurements of discharge.

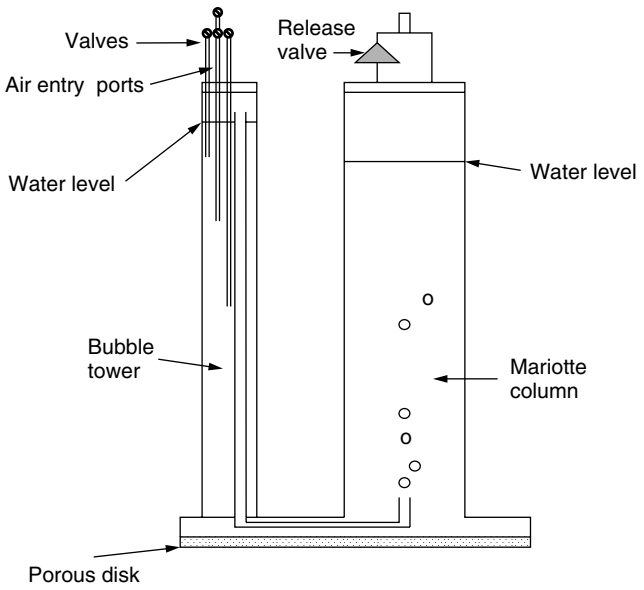


Figure 3. Schematic diagram of a tension disk infiltrometer.

If a range of supply heads is to be used, then infiltration tests are normally conducted with the lowest supply head first. Reversal of this may lead to hysteresis where drainage occurs close to the disk while wetting continues near and at the infiltration front (6). Infiltration measurements should proceed until a steady state is achieved. Users should be careful to ensure that sunlight does not heat the supply reservoir significantly: this can be reduced by shading.

Methods for analyzing the data from disk infiltrometers (e.g., hydraulic conductivity values and macropore contribution to infiltration) are given in Reynolds and Elrick (6). Typically, Wooding's (7) solution for infiltration from a shallow pond is combined with Gardner's (8) unsaturated hydraulic conductivity function. A range of assumptions is involved in using of these techniques, including that the hydraulic conductivity before the test is much less than that imposed under the infiltration experiment and that the soil below the tension disk is homogeneous, isotropic, and uniformly saturated, which are unlikely to be satisfied fully in most soils, and so it is necessary to evaluate the potential errors involved (9).

Water levels in supply bottles for both the ring and disk infiltrometers can be measured automatically by using electronic pressure sensors with data recorders, thus allowing an experiment to continue unattended for several hours if the infiltration rates are very low.

BIBLIOGRAPHY

1. Ankeny, M.D., Kaspar, T.C., and Horton, R. (1988). Design for an automated tension infiltrometer. *Journal of the Soil Science Society of America* **52**: 893–896.
2. Zhang, Y., Smith, R.E., Butters, G.L., and Cardon, G.E. (1999). Analysis and testing of a concentric-disk tension infiltrometer. *Soil Science Society of America Journal* **63**: 544–553.
3. Azevedo, A.S., Kanwar, R.S., and Horton, R. (1998). Effect of cultivation on hydraulic properties of an Iowa soil using tension infiltrometers. *Soil Science* **163**: 22–29.
4. Logsdon, S.D., Jordahl, J.L., and Karlen, D.L. (1993). Tillage and crop effects on ponded and tension infiltration rates. *Soil and Tillage Research* **28**: 179–189.
5. Messing, I. and Jarvis, N.J. (1993). Temporal variation in the hydraulic conductivity of a tilled clay soil as measured by tension infiltrometers. *Journal of Soil Science* **44**: 11–24.
6. Reynolds, E.D. and Elrick, D.E. (1991). Determination of hydraulic conductivity using a tension infiltrometer. *Journal of the Soil Science Society of America* **55**: 633–639.

7. Wooding, R.A. (1968). Steady infiltration from a shallow circular pond. *Water Resources Research* **4**: 1259–1273.
8. Gardner, W.R. (1958). Some steady state solutions of the unsaturated moisture flow equation with application to evaporation from a water table. *Soil Science* **85**: 228–232.
9. Holden, J., Burt, T.P., and Cox, N.J. (2001). Macroporosity and infiltration in blanket peat: the implications of tension disc infiltrometer measurements. *Hydrological Processes* **15**: 289–303.

SUMMARY OF ISOTOPES IN CONTAMINANT HYDROGEOLOGY

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INTRODUCTION

The word contaminant is a general term to describe dissolved constituents, nonaqueous phase liquids (NAPLs), or industrial solvents which, when added to water as a result of human activities, impair groundwater quality. To an important extent, the complexity of a groundwater contamination problem can be determined by whether or not NAPLs are present (1). Obviously, contaminants related to anthropogenic activities are one of the major threats facing groundwater resources today. Groundwater contamination can have a significant impact on the present and future use of groundwater resources as a source of drinking water for an increasing population living in cities and rural areas (2).

In the investigation of problems posed by contaminants in the hydrologic environment, the modern approach is to use a combination of tracers. These tracers include radioactive isotopes (such as ^{3}H, ^{13}C, ^{14}C,), stable isotopes (^{18}O, ^{2}H), and dissolved geochemical constituents (Cl^{-}, SO_4^{2-}, NO_3^{-} and some cations). An important facet of contaminant hydrogeology is the movement of liquids that are immiscible with water through the vadose zone as well as below the water table. Such liquids are usually called nonaqueous phase liquids. There are numerous cases of groundwater contamination involving organic liquids that are either insoluble or partially soluble in water. When the densities of these liquids are greater than that of water, they are called dense nonaqueous phase liquids (DNAPLs). Those whose densities are less than that of water are light nonaqueous phase liquids (LNAPLs). They could also be partially soluble in water, such that both dissolved and nonaqueous phases may be present (3–7).

The major groups of contaminants in hydrogeology include radionuclides, trace metals, and nutrients. They could also be classified as inorganic and organic contaminants. These include synthetic organic compounds, hydrocarbons, and pathogens (7). Some types of these contaminants are inorganic chemicals that are either metallic or nonmetallic (1,8). Included in the group of organic contaminants are NAPLs, which naturally subdivide into LNAPLs and DNAPLs (7).

A wide variety of materials have been identified as contaminants found in groundwater. An extensive listing of these compounds is tabulated in (Reference 7, pp. 3–10). Many of these materials will dissolve in water to different degrees. Some of the organic compounds are only slightly soluble and will exist in both dissolved form and as an insoluble phase, which can also migrate through the ground (7). According to (2), the main relevant organic compounds of the LNAPLs are benzene, toluene, ethylbenzene, and xylenes (BTEX) from spills at gas stations and industrial facilities. The most common compounds of the group found in groundwater are perchloroethene (PCE), trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), and dichloroethane (DCA) (9). In terms of environmental contamination, the major concern is focused on those organic compounds that are not readily degraded by bacteria, either in the soil zone or in sewage treatment facilities. The presence of these substances in the surface environment is becoming increasingly pervasive (8).

The sources that contribute to groundwater contamination are varied. Among these are land disposal of solid wastes, inorganic substances, metal and nonmetal trace elements. Other sources of groundwater contamination are from introducing of salts on roads to combat ice in winter, the infiltration of leachate from tailings in the mining industry, seepage from industrial water lagoons and septic tanks of urban waste disposal systems, wastewater discharge into rivers and lakes, agricultural wastes and fertilizers, saline or geogenic polluted water attracted by overexploitation of groundwater, and fossil fuels (1,7,8,10,11). Inorganic cations and anions occur in nature and may come from natural as well as anthropogenic sources. Some of the radionuclides are naturally occurring; others are man-made and come from the production and testing of nuclear weapons.

There are three important attributes that distinguish sources of groundwater contamination: (1) their degree of localization, (2) their loading history, and (3) the kinds of contaminants emanating from them (1). From the work of Domenico and Schwartz (1) contaminants are organized by groups according to reaction type and mode of occurrence. Six categories have been tabulated:

Category 1—Sources designed to discharge substances, for example, subsurface percolation (from septic tanks and cesspools), injection wells (hazardous and nonhazardous wastes), and land application.

Category 2—Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release, for example, landfills, open dumps (including illegal dumping waste), residential or local disposal wastes, waste tailings, material stockpiles (nonwaste), graveyards, animal burial, surface and underground storage tanks, and containers.

Category 3—Sources designed to retain substances during transport or transmission, for example, pipelines and materials transport and transfer operations.

Category 4—Sources discharging substances as a consequence of other planned activities, for example,

irrigation practices, pesticide applications, fertilizer applications, animal feeding operations, deicing salt applications, urban runoff, percolation of atmospheric pollutants, and mining and mining drainage.

Category 5—Sources providing conduits or inducing discharge through altered flow patterns, for example, production wells (oil/gas wells, geothermal and heat recovery wells, water supply wells), other nonwaste wells (monitoring and exploration wells), and construction excavation.

Category 6—Naturally occurring sources whose discharge is created and/or exacerbated by human activity, for example, groundwater–surface water interactions, natural leaching, saltwater intrusions and brackish water upconing, or intrusion of other poor-quality natural water.

For details of sources and background concentrations of contaminants in groundwater, refer to Forstner and Wittman (10). More information on inorganic contaminants is available in Reference 7 (Chapter 6), Reference 1 (Chapter 17); methods of detecting groundwater contamination are fully discussed in Domenico and Schwartz (1), and the sources and hydrochemical behavior of contaminants are described in Chapter 9 of Reference 8 as well as Chapter 1 of Reference 11. As a general introduction to groundwater contamination and related literature, the following are suggested for further reading: Baetsle (12), Fuhriman and Barton (13), Hall (14), Scalf et al. (15), Miller et al. (16), Summers and Spiegal (17), Cherry et al. (18), Back and Cherry (19), Fried (20), Todd and McNulty (21), Wilson et al. (22), Freeze and Cherry (8), IAEA (23, 24), Pearson et al. (25), Fetter (7), Pankow and Cherry (9), Domenico and Schwartz (1), and Seiler (11).

ENVIRONMENTAL ISOTOPES IN CONTAMINANT HYDROGEOLOGY

Introduction

For many years, environmental isotopes have been used in hydrogeology to address a range of issues such as evaluation of recharge areas, determination of groundwater residence time, and evaluation of surface water–groundwater interactions. Isotope studies applied to a wide spectrum of hydrologic problems related to both surface and groundwater resources as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, called "Isotope Hydrology." However, it is now becoming increasingly popular to use environmental isotopes as tracers to provide information about sources of contaminants and processes that affect these compounds in the groundwater flow system (2).

In essence, isotope techniques are becoming an integral part of many hydrologic investigations and sometimes a unique tool in studies related to groundwater contamination. Stable and radioactive environmental isotopes have now been used for more than four decades to study hydrologic systems, particularly in determining the hydrodynamics of aquifers, and have proved useful for understanding groundwater systems. The applications of isotopes in hydrogeology are based on the general concept of "tracing," in which either intentionally introduced isotopes or naturally occurring (environmental) isotopes are employed.

Environmental isotopes (either radioactive or stable) have the distinct advantage over injected (artificial) tracers in that they facilitate the study of various hydrologic processes on a much larger temporal and spatial scale through their natural distribution in a hydrologic system. Thus, environmental isotope methodologies are unique in regional studies of water resources to obtain the time and space integrated characteristics of groundwater systems. The use of artificial tracers generally is effective for site-specific, local applications (26,27). Environmental isotopes can now be used to trace the pathways as well as spatial distribution and temporal changes in pollution patterns for assessing pollution migration scenarios and planning for aquifer remediation (27,28).

Recent research and the development of new analytical methods have led to fast expansion of the application of isotopes in hydrogeology. In particular is the introduction of techniques that make it possible to measure isotopic ratios of individual compounds at low concentrations (29). These have opened new and exciting possibilities for using isotopes in organic contaminant studies in groundwater. For example, nitrogen and carbon isotopes can now provide information regarding such attenuation processes as the denitrification and biodegradation of halogenated solvents, respectively (28).

Environmental isotopes have, therefore, become useful tools in differentiating between different sources of organic contaminants or in assessing biotic and abiotic transformation processes associated with natural attenuation or engineered groundwater remediation techniques (30–32). The isotope method used to evaluate the degradation of organic contaminants relies on the frequent occurrence of small differences in the degradation rate between molecules of the same contaminant that contain different isotopes. Usually, the rate is slightly faster for molecules that contain light isotopes (e.g., ^{12}C) compared to those that contain heavy isotopes (e.g., ^{13}C) because bonds between light isotopes are weaker. As a result, degrading contaminants should contain increasingly more of the heavier isotope (^{13}C) as degradation proceeds, and thus the ratio between heavy and light isotopes ($^{13}C/^{12}C$) is expected to increase (2). Oxygen-18 in dissolved oxygen also has a significant potential as a tracer to evaluate the fate of oxygen in contaminated plumes.

The sequel to these environmental isotope studies has focused on the light elements and their isotopes: hydrogen (^{1}H, ^{2}H, ^{3}H), carbon (^{12}C, ^{13}C, ^{14}C), nitrogen (^{14}N, ^{15}N), oxygen (^{16}O, ^{18}O), and sulfur (^{32}S, ^{34}S). These are the most important elements in biological systems that occur in relatively great abundance and also participate in most geochemical reactions (33). Other less important and less abundant isotopes (^{17}O, ^{33}S, ^{36}S) are not often employed in environmental studies but have significance in very specific studies. Table 1 lists the isotopes of major elements used in environmental studies and their average abundances in natural compounds.

Table 1. Isotopes of Major Elements Used in Environmental Studies[a]

Element	Isotopes	Average Terrestrial Abundance, (%)	Comments[b]
Hydrogen	^{1}H	99.984	
	^{2}H	0.015	
	^{3}H	10^{-14} to 10^{-16}	Radioactive, $t_{1/2} = 12.35$ years
Carbon	^{12}C	98.89	
	^{13}C	1.11	
	^{14}C	$\sim 10^{-10}$	Radioactive, $t_{1/2} = 5730$ years
Oxygen	^{16}O	99.76	
	^{17}O[c]	0.037	
	^{18}O	0.1	
Nitrogen	^{14}N	99.34	
	^{15}N	0.366	
Sulphur	^{32}S	95.02	
	^{33}S[c]	0.75	
	^{34}S	4.21	
	^{36}S[c]	0.02	
Strontium	^{84}Sr[c]	0.56	
	^{86}Sr	9.86	
	^{87}Sr	~7.02	
	^{88}Sr[c]	82.56	
Uranium	^{234}U	~0.0056	Radioactive, $t_{1/2} = 2.47\times10^{5}$ years
	^{235}U[c]	0.7205	Radioactive, $t_{1/2} = 7.13\times10^{8}$ years
	^{238}U	99.274	Radioactive, $t_{1/2} = 4.51\times10^{9}$ years

[a] Reference 33.
[b] $t_{1/2}$ = half-life.
[c] These isotopes are not presently used in environmental studies.

Uses of Isotopes in Contaminant Hydrogeology

General uses of environmental isotopes in contaminant studies are often based on evaluating the various sources of contaminants in both surface and groundwater. The isotope approach to evaluating these sources relies mostly on the distinct isotope composition, that can characterize the different sources of contaminant (2,34). Environmental isotopes have found good use as tracers both artificially and naturally (26,35–38). For general review of the use of environmental isotopes in contaminant hydrogeology and potential future use of these tracers in vulnerability studies in groundwater, see References 2,27 and 28.

Environmental isotopes have been found widely applicable, especially in identifying the origin of water that is infiltrating an aquifer (28). Obviously, there is a relationship between recharge and the vulnerability of groundwater to contamination because the transport of many contaminants to the saturated zone of the aquifer occurs in the dissolved phase as part of the recharge process (39). Generally, ^{18}O and ^{2}H, among the various environmental isotopes, are most widely used in defining groundwater recharge areas as well as their origins. Changes in the isotopic relationships between $^{18}O/^{16}O$ and $^{2}H/^{1}H$, during the evaporation and condensation of water allow defining its origin (28).

New isotope applications are being developed in organic contaminant studies of groundwater. These studies have shown that carbon isotopes allow very sensitive evaluation of the fate of precursors and by-products of the biodegradation of chlorinated compounds, which are the most common organic contaminants found in groundwater. Potentially new applications include ^{18}O to evaluate the fate of oxygen in contaminant plumes and ^{11}B in salinization and nitrate studies of groundwater (2). Table 2 shows the potential/common applications of isotopes in groundwater pollution studies.

Boron-11, a stable isotope of boron, has also been used to differentiate nitrate from sewage and fertilizers as well as to trace the sources of salinity in groundwater. This approach was used to differentiate isotopic composition of injected treated wastewater and irrigation-affected water ($\delta^{11}B > 40‰$) distinctly and to trace the effect of injection into an alluvial aquifer near El Paso, Texas (40).

It has also been possible to approach the tracing of various organic pollutants (chlorinated hydrocarbons) in groundwater by using a combination of the isotopes $^{13}C/^{12}C$, $^{2}H/^{1}H$, and $^{37}Cl/^{35}Cl$. For example, the isotopic ratios $^{37}Cl/^{35}Cl$ and $^{10}B/^{11}B$ have been used recently in pollution studies of groundwater (41,42). The strontium isotopic ratio ($^{87}Sr/^{86}Sr$) is also a valuable tracer for studies related to the mixing and origin of mineralized groundwater. It is a tracer for the origin of salinity, groundwater movement, and water–rock interactions (43,44). In the past, a combination of stable and radioactive isotopes that has dissolved geochemical constituents has been used in tracing the migration of contaminants in groundwater (45–47).

According to Hirata and Varnier (28), isotope techniques are useful in determining groundwater pollution vulnerability, to the extent that they allow for better understanding of the degree of access provided for penetration of contaminants and the attenuative capacity offered by the geologic medium (Table 3).

The most frequently used environmental isotopes in contaminant hydrogeology include nitrogen isotopes ($^{14}N/^{15}N$), chlorine - 37, the sulphur isotope (^{34}S), carbon

Table 2. Common/Potential Isotopes Used in Groundwater Pollution Studies[a]

Isotope(s)	Potential/Common Applications
^{13}C in HCO_3^- and CH_4	Identifying of methane sources Monitoring CO_2 and CH_4 production in biodegradation studies
^{34}S and ^{18}O in SO_4^{2-}	Identifying of sources of pollution Acidification and acid mine drainage
^{15}N and ^{18}O in NO_3^-, NH_4^-, N_2	Origin of nitrates Sources of pollution Microbial denitrification processes
^{11}B in B $(OH)_4^-$ and B $(OH)_3^-$	Identifying of pollution sources Characteristics of brines, source of salinity
Chlorine-37 (^{37}Cl)	Identifying pollution sources Characteristics of brines, sources of salinity
Tritium (^3H)	Indicators of recent pollution/recharge Water transport in the unsaturated zone
Strontium isotope ratio ($^{87}Sr/^{86}Sr$)	Tracer for the origin of salinity, mixing, and origin of mineralized groundwater, groundwater movement, and water–rock interactions.
Uranium isotopes (^{234}U, ^{238}U)	Sensitive indicators of radioactive pollution in natural waters, Rock–water interaction, dating of old groundwater

[a] Modified from Reference 27.

Table 3. The Use of the Isotope Technique for Groundwater Pollution Vulnerability Characterization[a]

Component of Aquifer Pollution Vulnerability	Information Related to	Isotope Technique
Hydraulic accessibility of the saturated aquifer to penetration of pollutants	Identification of recharge/discharge areas	^{18}O in H_2O ^2H in H_2O
	Degree of aquifer confinement	^{85}Kr flow through fissured rock
	Definition of period of recharge	^3H in H_2O (environmental and applied tracer)
	Identification of paleowaters	^{51}Cr, ^{58}Co, ^{60}Co, ^{131}I (applied tracers)
	Interconnection of surface and groundwater	
Attenuative capacity of strata overlying the saturated zone, resulting from the physicochemical retention or reaction of pollutants	Determination of transit time of water through the saturated and unsaturated zones (advective flow)	Dating young water ^3H ^3He Dating midage water ^{39}Ar ^{14}C, correction with ^{13}C in HCO_3^- ^{81}Kr Dating old water ^{81}Kr ^{234}U
	Identification of physico chemical reactions of pollutants (degradation)	^{15}N and ^{18}O in NO_3^-, NH_4^+, N_2, microbial denitrification processes ^{13}C, biodegradation of synthetic solvents and fuel ^{34}S, oxidation/reduction of sulfur
Pollution hazard factors	*Information related to*	*Isotope technique*
Definition of pollutant origin	Identification of source of pollution	^{34}S and ^{18}O in SO_4^{2-}, acidification and acid mine drainage ^{37}Cl, ^{11}B, in $B(OH)_4^-$ and $B(OH)_3^-$ characteristics of brines; sources of salinity ^{15}N and ^{18}O in NO_3^-, NH_4^+, N_2 ^{18}O, ^2H in H_2O, salinization mechanisms, recycling of irrigation water ^{14}C and ^{13}C for origin of sources of organic compounds

[a] After Reference 28.

isotopes (^{13}C, ^{14}C), and the boron isotope (^{11}B). Those of the water molecules (^{18}O, ^2H) are also sometimes used with some of these isotopes in groundwater contamination studies. Following are brief descriptions of the isotopes commonly employed in contaminant hydrogeologic studies.

Nitrogen Isotopes ($^{14}N/^{15}N$). The most common contaminant identified in groundwater is dissolved nitrogen in the form of nitrate (NO_3^-). Other forms of inorganic nitrogen are nitrite (NO_2^-), nitrogen gas (N_2), ammonia (NH_4^+), and cyanide (CN^-). Nitrogen is also a major constituent

of organic matter as amino acids (7). These contaminants are becoming widespread due to increased agricultural activities worldwide and disposal of sewage on or beneath the land surface.

Nitrogen occurs as two isotopes in nature: ^{14}N(≈99.6%) and ^{15}N(≈0.36%). ^{14}N is more abundant in the atmosphere than ^{15}N. Hence, the $^{15}N/^{14}N$ ratio in nitrate can be used to distinguish the origin of nitrates either from animal/human wastes or from the application of chemical fertilizers (48,49). The origin of contamination by nitrates can be determined through the relationship between $^{15}N/^{14}N$ and standard values ($\delta^{15}N$). Combined isotope analyses of nitrogen and oxygen in NO_3^- leave fingerprints on natural and anthropogenic sources of nitrate; on microbial denitrification, nitrification and biological fixation processes; and on the nitrogen budget in groundwater (50–53).

Therefore, the $\delta^{15}N$ values of dissolved nitrates, ammonium, and organic nitrogen in soil water are well distinguished from one region to another. The $\delta^{15}N$ of animal waste is between +5 to 15‰, and fertilizers have a $\delta^{15}N$ of about 0‰. However, for nitrogenous fertilizers, these values lie between −4‰ and +4‰ (50,54).

For more information and related nitrogenous inputs in groundwater, refer to Foster and Crease (55), Kreitler and Jones (56), Létolle (57), Kreitler and Browning (58), White (59), Flipse et al. (60), Heaton (60), Mariotti (61), Flipse and Bonner (62), Tessendorff (63), Hübner (64), Mariotti (65), Böttcher et al. (51), Exner and Spalding (66), Aravena et al. (52), Buzek (67), Révész et al. (68), Pauwels et al. (69), Tore et al. (70), and Anwar and Ghosh (71).

Chlorine-37. Naturally, chlorine exists with two common stable isotopes: ^{35}Cl (≈75.7%) and ^{37}Cl (≈24.2%). Chloride ions are generally not reactive and as such, do not participate in redox reactions, are not sorbed onto mineral or organic surfaces, and do not form insoluble precipitates. As a result, ^{37}Cl is sometimes used as a conservative tracer in groundwater studies. Data are expressed as $\delta^{37}Cl$ with respect to the standard mean oceanic chloride (SMOC). The ratio $^{37}Cl/^{35}Cl$ is measured by isotope ratio mass spectrometry (IRMS). Precision must be better than ± 0.1‰ (72). $\delta^{37}Cl$ values contain information on the origin of chloride ions in fresh and polluted groundwater as well as in subsurface brines (30,41,42).

In geochemical studies generally, chlorine isotopes are not highly fractionated, but research has shown that measurable fractionations can be used to distinguish sources of groundwater mixing (73). The ^{37}Cl content of chloro contaminants in groundwater can fingerprint the sources of contaminants and salinity. It is therefore a potential tool in contaminant hydrogeology (27,43).

Sulphur Isotope (^{34}S). Sulphur has four stable isotopes: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%). The abundance ratio of ^{34}S and ^{32}S is generally given as a $\delta^{34}S$ value. Iron sulfide from the troilite phase of the Diablo Canyon iron meteorite (DCT) (that has a $^{32}S/^{34}S$ ratio of 22.220) is conventionally used as a standard (72). ^{34}S is one of the distinct isotopes that can be used to characterize different sources of sulfate contamination. For example, high sulfate in aquifers in areas close to mine tailings could be associated with the oxidation of sulfide minerals in the tailings. However, other sources of sulfate in aquifers such as gypsum of marine origin, input from volcanic sources, or sulfate from recirculated water from agriculture have been identified (2). Generally, sulfate produced from sulfide minerals is much more depleted in ^{34}S and ^{18}O than marine sulfate (74,75).

Moreover, owing to isotope fractionation during sulfate reduction, ^{34}S and ^{18}O in sulfate can also be used to evaluate the fate of sulfate in groundwater flow systems (76). The isotopic composition of sulfate can also be an indicator of anthropogenic pollution of groundwater (75).

Carbon Isotopes (^{13}C, ^{14}C). Carbon has three isotopes in nature: ^{12}C, ^{13}C, and ^{14}C. The heavy carbon isotope, ^{14}C, is unstable and decays radioactively into ^{14}N. The stable isotopes of carbon, ^{13}C and ^{12}C, have an average ratio of about 1:100 (72). The isotopic composition of carbon in the dissolved carbon constituents of groundwater is very variable. The sources of carbon dissolved in groundwater are soil CO_2, CO_2 of geogenic origin or from magmatic CO_2 (from deep crustal or mantle sources) or in fluid inclusions, living and dead organic matter in soils and rocks, methane, and carbonate minerals (53). Each of these sources has a different carbon isotopic composition and contributes to total dissolved carbon in various proportions. Therefore, the isotopic composition of dissolved inorganic carbon compounds in groundwater has a wide range of $\delta^{13}C$ values.

Carbon isotopes (^{13}C, ^{14}C) can be used to evaluate the origin of methane in landfills (2). The origin of methane is a common problem in landfills located in old quarries. Methane in this type of environment can be thermocatalytic in origin, associated with gases present in the bedrock or/and originating in the landfill itself (2). According to Schoell (77), gases of thermocatalytic origin are generally more enriched in carbon-13 ($\delta^{13}C > -50$‰) than methane of biogenic origin ($\delta^{13}C < -50$‰). In addition, Hackley et al. (78) proved that catalytic gases are devoid of carbon-14, whereas methane in landfills has a ^{14}C content higher than 100% modern carbon (pmc). Obviously, due to carbon-14 from thermonuclear explosions, any carbon in domestic waste that was deposited in a landfill after 1950 is usually characterized by a ^{14}C content higher than 100 pmc (2). Furthermore, carbon isotopes have also been employed in monitoring CO_2 and CH_4 production in biodegration studies in unsaturated areas impacted by organic contamination (79,80).

Boron Isotope (^{11}B). Natural boron has two stable isotopes, ^{11}B (≈80%) and ^{10}B (≈20%). The variation in the ratio of these two isotopes is expressed in $\delta^{11}B$ (‰) with respect to SRM-951 NBS standard (81). Generally, boron is present in groundwater mainly as trigonal undissociated boric acid, $B(OH)_3^0$, and its conjugate base, tetrahedral borate, $B(OH)_4^-$. Tetrahedrally coordinated boron is more isotopically depleted (i.e., lower in $\delta^{11}B$) relative to trigonally coordinated boron; thus the $\delta^{11}B$ of dissolved boron in groundwater is usually higher than that in aquifer rocks (81).

Boron is used as tracer in groundwater because of its high solubility in aqueous solution, natural abundance in all waters, and the lack of effects from evaporation, volatilization, and oxidation–reduction reactions. The concentrations of boron in pristine groundwaters are generally low (<0.05 mg/L), and contaminant sources are usually enriched in boron (e.g., sea water: 4.6 mg/L; domestic wastewater: 1 mg/L; flyash leachate: 14 mg/L; landfill leachate: 6 mg/L), so the $\delta^{11}B$ of groundwater is highly sensitive to the impact of contamination (81). The large isotopic variation of the potential sources can be used to trace the origin of contamination. Vengosh (81) reported that coastal aquifers affected by seawater intrusion and marine-derived fossil brines are characterized by high $\delta^{11}B$ values (up to 60‰). In contrast, domestic wastewater that has relatively high boron concentrations and a high B/Cl ratio has $\delta^{11}B$ values of 0‰ to 12.9‰. Boron stable isotope ratios have a potential to play a role in pollution studies (82). They also have applications in the characterization of brines and geothermal waters (83).

It will suffice at this point to say that some of these environmental isotopes are in themselves a source of groundwater contamination, especially radioactive isotopes. Radioactive isotopes, also known as radionuclides, are therefore discussed in the following section in relation to groundwater contamination.

Radioactive Contaminants

It is now well known that numerous human activities have created nuclear isotopes by detonating nuclear weapons and constructing nuclear reactors. A number of radionuclides are produced in the earth's atmosphere by nuclear reactions caused by cosmic rays. Cationic radionuclides may be subjected to ion exchange and other processes that sorb the radionuclides onto mineral organic surfaces in the soil (7). Examples of transition metals that have large distribution coefficients and hence low mobilities in waters are listed in References 7 and 84. ^{90}Sr, ^{137}Cs, and ^{226}Ra are involved in cation exchange similar to other exchangeable cations, for example, Ca^{2+} and Mg^{2+} (84).

Many of these radionuclides are frequently produced as fission products from the decay of ^{235}U and ^{239}Pu and from neutron activation of stable isotopes. These processes result in the production of more than 75 radionuclides such as ^{137}Cs, ^{134}Cs, ^{58}Co, ^{51}Cr, ^{54}Mn, ^{55}Fe, ^{3}H, and ^{131}I (1). Table 4 lists the various sources of environmentally important radioactive isotopes. These are elements that undergo spontaneous decay resulting in the release of energy as well as energetic particles and consequent formation of different isotopes. They occur either naturally or are created by bombardment of the earth by cosmic radiation (7) and undergo spontaneous decay resulting in the release of energy as well as energetic particles and consequent formation of different isotopes.

The nuclear industry has been the main generator of radioactive contaminants. However, potential sources occur throughout the nuclear fuel cycle, which involves mining and milling uranium, uranium enrichment and fuel fabrication, power plant operation, fuel reprocessing, and waste disposal (1). In the examples presented by Domenico and Schwartz, the United States, Japan, France, and Germany have large numbers of light-water reactors that use enriched uranium (^{235}U) as the predominant fuel source and possibly ^{239}Pu and ^{238}U. The process of enrichment and fuel fabrication is also accompanied by generation of the following radionuclides: ^{238}U, ^{235}U, ^{137}Cs, and ^{90}Sr, which are common contaminants.

Furthermore, there are potential radionuclide contaminants that result from the processing of raw uranium ore (during mining operation) alongside other nonradioactive pollutants, which include ^{238}U, ^{230}Th, ^{226}Ra, and ^{222}Rn. Examples of locations where this type of contamination occurs are Colorado, New Mexico, Texas, Utah, Wyoming, northern Saskatchewan, and Ontario (1).

PRACTICAL APPLICATIONS OF ENVIRONMENTAL ISOTOPES IN SOLVING GROUNDWATER CONTAMINATION PROBLEMS

Many examples exist in the literature on the use of environmental isotopes in solving groundwater contamination problems. There are also case studies in publications, which have addressed the applications of isotopes in contaminant hydrogeology. In this section, the results of the application of isotopes in groundwater contamination studies, particularly in solving specific problems are summarized. The case studies cut across continents and varied hydrogeologic settings. Some of these applications are based on single isotopes, and others combine several isotopes, particularly oxygen with nitrogen and sulfur to understand the origin and migration of contaminants in groundwater. However, some case studies applied an integrated approach (using isotope techniques and conventional hydrochemistry) to interpret contaminant sources and pathways. This is not an exhaustive listing but rather selected to demonstrate the applications of environmental isotopes in solving specific hydrogeologic problems.

Table 4. Various Sources of Environmentally Important Radioactive Isotopes[a]

Source	Radionuclides
Naturally occurring	^{40}K, ^{222}Rn, ^{226}Ra, $^{230,232}Th$, $^{235,238}U$
Cosmic irradiation	^{3}H, ^{7}Be, ^{14}C, ^{22}Na
Nuclear weapon tests	^{3}H, ^{90}Sr, ^{137}Cs, $^{239,240}Pu$
Mining wastes—uranium, phosphate, coal	^{222}Rn, ^{226}Ra, $^{230,232}Th$, $^{235,238}U$
Industrial wastes—nuclear power plants, weapons manufacturing, research and medical waste	$^{59,63}Ni$, ^{60}Co, ^{90}Sr, $^{93,99}Zr$, ^{99}Tc, ^{107}Pd, ^{129}I, ^{137}Cs, ^{144}Ce, ^{151}Sm, $^{152,154}Eu$, ^{237}Np, $^{239,240,242}Pu$, $^{241,243}Am$

[a] Reference 7.

For more information and examples, refer to the IAEA TECDOC series and other edited specialist volumes.

Fritz et al. (45) studied the possible movement of leachate from a sanitary landfill in Frankfurt am Main, Germany. Interpretation of results of both isotopic and chemical data in the pollution monitoring showed that δ^2H and δ^{18}O are most useful in tracing the leachate and mapping the pollution plume. Three groups were identified from δ^{18}O data: The first group (−8.6‰ to −8.0‰) is of uncontaminated groundwater; the second group (−6.7‰ to −6.3‰) is polluted groundwater, and the third group (−3.0‰ to −2.0‰) reflects recharge from lake water. The same δ^{18}O data have also been used (by these researchers) to calculate the percentage of leachate water in each well, and this was helpful in producing a map of the pollution plume at the landfill site.

Mazor et al. (85) conducted a study of groundwater contamination by a slaughterhouse at Lobatse, Botswana. The results of this study revealed that tritium and chloride were the most conservative tracers in this case. The slaughterhouse used water from a dam, and this water (when sampled and analyzed) had tritium concentrations that were significantly higher than those in the local groundwater. High tritium concentrations/contamination were observed in wells near the slaughterhouse and along the Peleng riverbed into which the effluent was released. Other wells (according to the researchers) showed low tritium and chlorine values, indicating that they were not contaminated.

Egboka (46), in the investigation of problems posed by contaminants in the hydrologic environment, used a combination of tracers: (radioisotopes, such as bomb tritium), stable isotopes (^{18}O and ^{2}H), and dissolved geochemical constituents (Cl, SO_4, NO_3 and some major cations). These isotopes, in combination with the dissolved geochemical constituents, have been used to delineate the aerial extent of spread of leachate plumes in landfills and spillage zones and around sewage lagoons. He presented two case studies where this multitechnique approach was used successfully to investigate environmental pollution and contamination. These include using bomb tritium, ^{18}O, ^{2}H, Cl^-, and SO_4^{2-} to investigate the leachate migration in an aquifer beneath an abandoned landfill at CFB Borden, Ontario (Canada) and the Lake Chad drainage basin (NE Nigeria), where ^{3}H, ^{18}O, ^{2}H, ^{14}C, and ^{13}C were extensively analyzed.

Song et al. (86) used ^{34}S in 66 water samples and 30 rock (anhydrite) samples to determine the origin of sulfate in the stable isotopic composition and geochemistry of fresh water and brine in Sichuan Basin, China. The results indicate that δ^{34}S values of saline waters are similar to those in the samples collected from different sections of the same sequence and differ from different strata. These authors considered that the evaporate of the early Triassic was formed in an enclosed and reductive beach and the facies belongs to the beach salt-lake in the environment of a supratidal zone and that of the middle Triassic belongs to lagoon-salt-lakes in the intertidal environment. The consistency of δ^{34}S in water and rock implies that they have a common source of sulphur.

Wassenaar (87) carried out a representative study in Abbotsford aquifer (a regional aquifer in Canada characterized by nitrate concentrations between 80 and 160 mg/L) using the isotopes of ^{15}N and ^{18}O. In this case, it was well documented that the main sources of nitrate were manure produced in the poultry industry and inorganic fertilizers used in cultivated fields. Based on the ^{15}N data, it was shown that most of the nitrate in the contaminated groundwater has δ^{15}N values greater than +8‰. Wassenaar (87) demonstrated that the main source of this nitrate was the manure piles that were deposited on top of the aquifer.

Similarly, a nitrate study carried out by Auge and Nagy (88) in the city of La Plata (Argentina) illustrates one of the applications of nitrogen isotopes in Latin America. The isotope study, which was part of a comprehensive hydrogeologic study of this aquifer, aimed to provide information about the sources of high nitrate observed in production wells in the city of La Plata. According to these researchers, the main potential sources of nitrate in this area are fertilizers and manure from agricultural and pasture areas located upgradient of the city of La Plata and leakage from the sewage system and possibly landfills located downgradient of the center of the city. A regional nitrate study showed a plume that had high nitrate concentration below the city. From the result, the nitrogen isotope pattern showed a clear trend toward enriched δ^{15}N values correlated with an increase in nitrate concentration. The high nitrate concentration (80–120 mg/L as nitrate) and enriched δ^{15}N values (14–15‰) correspond to groundwater located below the city. The low nitrate concentration (15–40 mg/L) and depleted δ^{15}N values (7–11‰) correspond to groundwater representing the agricultural areas and wells located upgradient on the high nitrate concentration plume. The enriched δ^{15}N values indicated input of nitrate from an enriched ^{15}N source associated with domestic wastes.

Aravena and Robertson (38) used multiple isotope tracers to evaluate denitrification in groundwater and documented that septic systems are point sources of nitrate in groundwater, which was documented in a nitrate plume generated in a large communal septic system operating at a campsite. As a result of oxygen consumption by the oxidation of pyrite and organic carbon in the unsaturated zone, the groundwater became anaerobic in the shallow part of the flow system. A steady decrease in nitrate concentrations from values around 80 mg N/L at the water table to nondetectable was observed versus depth along the groundwater system. A trend toward enriched δ^{15}N values accompanied these concentration changes, reaching values as high as +58‰, demonstrated that nitrate attenuation was controlled by denitrification. A linear correlation between δ^{15}N and δ^{18}O values in nitrate also supported denitrification as the mechanism for nitrate attenuation in the aquifer.

Tandia et al. (89), in the investigation of the origin, process, and migration of nitrate compounds in the aquifers of the Dakar region, Senegal, used environmental isotopes (^{18}O, ^{2}H, ^{3}H, ^{13}C, ^{14}C) along with major inorganic constituents and fecal coliform on yearly water samples. The samples were taken from piezometers, hand-pumped

wells, and dug wells in different areas of the Peninsula from 1987 to 1997. Results showed that only a limited area is affected by nitrate pollution in the confined layer. Stable isotopes, tritium and ^{14}C, gave a better understanding of nitrate contamination of groundwater in this region; tritium in groundwater indicates that nitrate concentration is recent. This has been confirmed by the presence of high activities of ^{14}C (80‰), in good agreement with recent analyses of recharge groundwater.

The distribution of the values of ^{18}O and ^{2}H (89) around the World Meteoric Water Line indicate that the recharge of the Dakar aquifer system originates from the monsoon rainfall after it has been exposed to evaporation. However, the cluster of points relating to ^{18}O and ^{2}H were also interpreted as contributions of nitrate contamination along the flow path from east to west.

Buzek et al. (67) investigated the nitrate pollution of a karstic groundwater system in Svaty Jan Pod Skalou in the Czech Republic using $\delta^{18}O$ in water and $\delta^{15}N$ in nitrate. Increasing agricultural activity in the republic after the 1960s resulted in contaminating both shallow and deep-water resources. Therefore, to identify the sources of nitrate contamination and evaluate the parameters of the karstic system, the stable isotopes $\delta^{15}N$ and $\delta^{18}O$ were used together with monitoring of the flow dynamics, water chemistry, and soil composition. The results of the isotopic investigation revealed the sources of nitrate contamination from $\delta^{15}N$ in soil solutes at sites that had different agronomic records (sequential use of organic and inorganic fertilizers). They further showed that spring-discharge nitrate is formed from an atmospheric source (an average nitrate content of 8 mg/L and $\delta^{15}N$ of −6‰) and two groundwater components that had nitrate content of 50 to 60 mg/L and $\delta^{15}N$ values from 2 to 7‰. However, the contribution of groundwater components varied in time more frequently than can be described by the model developed for flow dynamics and ^{18}O. From this case study, data from the flow dynamics, ^{18}O, and tritium gave sufficient information to estimate the volume of the karstic system and the residence times of the three contributions (direct infiltration, fast, and old components) to spring discharge. The estimated turnover time of the old component (about 22 years) could be used for calculating the spring nitrate content in the future.

Aggarwal et al. (90) initiated a study using a suite of different isotopes to fingerprint and determine the source of contaminants in groundwater systems in New Zealand. Four different isotope systems were examined: boron isotopes, oxygen and nitrogen isotopes in nitrates, oxygen isotopes in sulfates, and oxygen and sulfur isotopes in sulfates. In a case study of the semirural Manakau area as well as the South and North Islands (all in New Zealand) conducted to investigate the possibility of using nitrate isotopes to detect the source of nitrate contamination, results showed nitrogen isotope (+4 to +12‰) coupled with oxygen isotope measurements (+5 to +9‰) and demonstrated that nitrogen is not sourced from fertilizers but from some combination of septic and animal waste. However, for the case study of sulfate isotope used, sulfur and oxygen isotopic compositions of sulfate in river and lake water from seven major catchments of the North and South Islands of New Zealand were determined. The results of the isotope analyses allowed distinguishing between natural (geologic, geothermal, and volcanic) and anthropogenic (fertilizer) sulfur sources. Boron (B) isotope measurements were also carried out in the Bartholomew (Manawatu) and Petone waters in New Zealand. Results showed that the Cl/B ratio and the $\delta^{11}B$ of the water from Bartholomew may be interpreted as a consequence of mixing between saline water and freshwater. Seawater (included for comparison) showed a distinctly heavy B isotopic composition, relatively high B concentrations, and a high Cl/B ratio, whereas these two freshwaters contain a variable B isotope ratio that has a low B concentration and a much lower Cl/B ratio than that in the seawater.

Groundwater contamination in coastal aquifers of Israel, Italy, and the United States was determined by boron isotope systematics (81). This work reports isotopic results of contaminated groundwater from the coastal aquifers of the Mediterranean in Israel, the Cornia River in northwestern Italy, and the Salinas Valley in California. The interpretation of the results revealed different contamination sources; underlying saline water of a marine origin in saline plumes in the Mediterranean coastal aquifer of Israel ($\delta^{11}B = 31.7$ to 49.9‰; B/Cl ratio $\sim 1.5 \times 10^{-3}$), mixing of fresh and sea water ($\delta^{11}B = 25$ to 38‰; B/Cl ratio7×10^{-3}) in saline water associated with a saltwater intrusion into the Salinas Valley, California, and a hydrothermal contribution (high B/Cl of ~ 0.03; $\delta^{11}B = 2.4$ to 9.3‰) in groundwater from the Cornia River, Italy. Vengosh et al. (81) observed that the boron concentrations in pristine groundwaters are generally low (<0.05 mg/L), whereas contaminant sources (e.g., domestic wastewater) are enriched in boron; hence, boron isotopes can be used to evaluate the impact of anthropogenic boron on the environment. Moreover, the isotopic composition of contaminated groundwater has revealed the sources of pollution because different sources are characterized by distinguishable isotopic ratios. For example, seawater ($\delta^{11}B = 39$‰), saltwater intrusion, and marine-derived brines (40 to 60‰) sharply differ from hydrothermal fluids ($\delta^{11}B = -10$‰ to 10‰) and anthropogenic sources (sewage effluent: $\delta^{11}B = 0$‰ to 10‰; boron-fertilizer: $\delta^{11}B = -15$‰ to 7‰). This research further showed that some differences (up to 15‰) might exist between domestic wastewater and boron fertilizer.

Shivanna et al. (91) used environmental isotopes (^{18}O, ^{2}H, ^{3}H, ^{14}C, and ^{34}S) along with hydrogeology and hydrochemistry to investigate (1) the source of salinity and the origin of sulfate in the groundwater of coastal Orissa, Orissa state (India) and (2) to study the source of salinity in deep and saline groundwaters of charnockite terrain at Kokkilimedu, south of Chennai, India. The results of the first case indicate that the shallow groundwater (depth <50 m) is fresh and modern. Groundwater salinity in the intermediate aquifer (50–100 m) is due to the Flandrian transgression during the Holocene period. The saline groundwater found below the fresh deep aquifer has marine water entrapped during the late Pleistocene. The source of high sulfate in the groundwater (as identified by the researchers) is of marine origin. In most of the deep aquifers, saline samples showed enriched $\delta^{34}S$ values

(+20.8‰ to +43.8‰) compared with the seawater value, and radiocarbon ages are in the range of 12, 000 to 24, 000 years BP with negligible tritium.

However, in the second case, the results of isotope investigation showed that there are two different sources of salinity in this area: one, the salinity attributed to infiltration of seawater together with the contribution of solute from pseudotachylites observed along the fractures and shear zones in the host rock; second, salinity attributed to solutes mostly from sheared and fractured charnockite rock. The high tritium content observed in this case was interpreted as due mainly to effluent from the nuclear power plant located 0.5 km west of the site and partly due to mixing of surface water with groundwater.

Halas and Trembaczowski (92) applied stable isotopic analysis of oxygen and sulfur in sulfate to trace the sources of groundwater pollutants in the industrial area of Belchatow, central Poland, where a large brown coal deposit is exploited and the coal is burned in an electric power plant. The interpretation of isotope ratios allowed recognizing three groups of sulfates:

(1) from the leaching of a Permian salt dome,
(2) produced by the leaching of soluble sulfates from an ash pool, and
(3) produced by the oxidation of natural sulfides in water-bearing rocks.

It was obvious from the data presented in this work that the oxygen and sulfur isotopic ratios of the dissolved sulfates are informative of their origin.

Liu et al. (93) carried out an investigation of groundwater contamination due to uranium deposits in the Zhoujiashan district of the Xiangshan uranium ore field, China. Samples of groundwater collected from five completed exploration boreholes in the area revealed the pollution source. It was traced and analyzed by using isotope as well as radiohydrochemical techniques. The researchers experimentally proved that the uranium concentration and uranium isotope ratio $^{234}U/^{238}U$ in natural waters are two sensitive indicators of radioactive pollution in natural waters. It was concluded that, under present conditions, exploration of uranium deposits might not cause serious groundwater contamination by radioactive elements (U, Ra, Rn, and Tn). Activity ratios $^{226}Ra/^{228}Ra$ and $^{230}Th/^{232}Th$ in water can be used only as supplementary indicators.

Qureshi et al. (94) used stable carbon isotope ratios as water quality indicators in the coastal areas of Karachi, Pakistan. Stable carbon isotope ratios ($\delta^{13}C$) of total dissolved inorganic carbon (TDIC), total organic and inorganic carbon in bottom sediments, as well as sea plants in polluted water sources, nonpolluted Karachi seawater, and pollution recipients were used to elaborate the pollution scenario of the shallow marine environment (off the Karachi coast). Groundwater pollution in the coastal areas of Karachi is also reflected in the stable isotope composition of carbon ($\delta^{13}C$) in the TDIC pool of organic carbon in bottom sediments, mangrove leaves, and seaweed. These results were supplemented with stable isotope analysis of nitrogen ($\delta^{15}N$) in seaweed and mangroves. Isotopic data revealed that the mangrove ecosystem and its tidal fluctuations play a key role in controlling contamination inventories in the shallow seawater off the Karachi coast, specifically the Manora Channel. The Karachi harbor zone was reportedly the most heavily polluted marine site in Manora Channel during high as well as low tide.

De Vito et al. (95) carried out a study in a 200 meter long wetland located between agricultural fields and the Boyne River in southern Ontario (Canada) using ^{15}N and ^{18}O (in nitrate) to evaluate the role of denitrification as an attenuative mechanism in nitrate. Results showed that nitrate levels of 30 and 40 mg N/L characterize the groundwater impacting the wetland. A significant change in nitrate concentration was observed by the researchers along the groundwater flow system that reached values as low as 1 mg N/L in areas close to the river. This pattern is accompanied by an isotope trend toward enriched ^{15}N and ^{18}O. The isotopic data and the dissolved organic carbon that increases along the groundwater flow system were interpreted as demonstrating that denitrification is the main process responsible for nitrate attenuation in the area.

According to Aravena (2), applications of isotopes in organic contaminants have focused on evaluating carbon and hydrogen isotope fractionation in biological and physical processes that can affect organic contaminant concentration in groundwater. The results of these studies have shown that very little isotopic fractionation occurred during physical processes (96,97). However, recent analytical developments in stable isotope research have shown that carbon isotopes are very sensitive tracers for evaluating the biodegradation of chlorinated compounds in groundwater (31,32). However, they are not sensitive enough to document biodegradation of petroleum hydrocarbons in groundwater (98,99).

BIBLIOGRAPHY

1. Domenico, P.A. and Schwartz, F.W. (1998). *Physical and Chemical Hydrogeology* (Chapter 17), 2nd Edn. John Wiley & Sons, New York, p. 506.
2. Aravena, R. (2002). Use of environmental isotopes in contaminant studies in groundwater. In: *Groundwater and Human Development*. E. Bocanegra, D. Martinez, and H. Massone (Eds.). Mar de Plata, Argentina, pp. 293–298.
3. Schwille, F. (1981). Groundwater pollution in porous media by fluids immiscible with water. *The Science of the Total Environment* **21**: 173–185.
4. Schwille, F. (1984). Migration of organic fluids immiscible with water in the unsaturated zone. In: *Pollutant in Porous Media*. B. Yanon, G. Dagen, and J. Goldshmid (Eds.). Springer-Verlag, Berlin, pp. 27–48.
5. Schwille, F. (1988). *Dense Chlorinated Solvents in Porous and Fractured Media*. Translated by Pankow, J.F., Lewis Publishers, Chelsea, MI, p. 146.
6. McWhorter, D.B. and Sunada, D.K. (1990). Exact integral solutions for two-phase flow. *Water Res. Research* **26**(3): 399–413.
7. Fetter, C.W. (1993). *Contaminant Hydrogeology*. Prentice-Hall, Englewood Cliffs, NJ, p. 458.

8. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ, p. 604.
9. Pankow, A. and Cherry, J.A. (1996). *Dense Chlorinated Solvents and other DNAPLs in Groundwater*. Waterloo Press, Waterloo, Canada.
10. Forstner, U. and Wittman, T.W. (1981). *Metal Pollution in Aquatic Environment*. Springer-Verlag, Berlin, p. 486.
11. Seiler, K.P. (2000). Man's impact on groundwater systems. In: *Environmental Isotopes in the Hydrological Cycle (Principles and Applications)*. W.G. Mook (Ed.). Vol. V, UNESCO/IAEA Publ. Series, Paris/Vienna, p. 105.
12. Baetsle, L.H. (1969). Migration of radionuclides in porous media. In: *Progress in Nuclear Energy, Series XII, Health Physics*. A.M.F. Duhamel (Ed.). Pergamon Press, New York, pp. 707–730.
13. Fuhriman, D.K. and Barton, J.R., (1971). *Ground water pollution in Arizona, California, Nevada, and Utah*. Environ. Protect. Agency. Rept. 16060 ERU.
14. Hall, E.S. (1972). Some chemical principles of groundwater pollution. In: *Groundwater Pollution in Europe*. J.A. Cole (Ed.). Water Information Centre, Port Washington, NY, pp. 269–271.
15. Scalf, M.R., Keley, J.W., and Lafevers, C.J. (1973). *Groundwater pollution in the south central States*. U.S. Environ. Protect. Agency Rept. EPA -122-73-268.
16. Miller, D.W., Deluca, F.A., and Tessier, T.L. (1974). *Groundwater contamination in the northeast States*. U.S. Environ. Protect. Agency Rept. EPA 660/2-74-056.
17. Summers, W.K. and Spiegal, Z. (1974). *Groundwater Pollution: A Bibliography*. Ann Arbor Science Publishers, Ann Arbor, MI.
18. Cherry, J.A., Gillham, R.W., and Pickens, J.F. (1975). Contaminant hydrogeology: Part I: Physical processes. *Geosci. Can.* **2**: 76–84.
19. Back, W. and Cherry, J.A. (1976). Chemical aspects of present and future hydrogeologic problems. *Proc. Symp. Adv. Groundwater Hydrol. America Water Resour. Assoc*.
20. Fried, J.J. (1976). *Ground Water Pollution*. Elsevier, Amsterdam, pp. 1–47.
21. Todd, D.K. and McNulty, D.E.O. (1976). *Polluted Groundwater*. Water Information Centre, Port Washington, NY.
22. Wilson, J.L., Lenton, R.L., and Porter, J. (Eds.). (1976). *Groundwater pollution: technology economics and management*. Dept. Civil Eng., M.I.T., Rept. TR208.
23. International Atomic Energy Agency (IAEA). (1980). *Nuclear Techniques in Groundwater Pollution Research*. IAEA, Vienna, p. 286.
24. International Atomic Energy Agency (IAEA). (1983). *Isotope Techniques in the Hydrological Assessment of Potential Sites for the Disposal of High-level Radioactive Wastes*. IAEA, Vienna, p. 164.
25. Pearson, F.J., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, T.J., Schmassmann, H., and Gautschi, A. (1991). *Applied Isotope Hydrogeology, a Case Study in Northern Switzerland, Studies in Environ. Sci. 43*. Elsevier, Amsterdam, p. 439.
26. Kendal, C. and McDonnell, J.J. (1998). *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam, Lausanne, New York, p. 839.
27. Gourcy, L. and Aggarwal, P. (2002). Strengthening the use of isotope techniques for a sustainable groundwater management. In: *Groundwater and Human Development*. E. Bocanegra, D. Martinez, and H. Massone (Eds.). Mar de Plata, Argentina, pp. 299–304.
28. Hirata, R. and Varnier, C. (2002). The use of isotopic techniques in determining groundwater pollution vulnerability—A Latin America perspective. In: *Groundwater and Human Development*. E. Bocanegra, D. Martinez, and H. Massone (Eds.). Mar de Plata, Argentina, pp. 305–313.
29. Hunkeler, D. and Aravena, R. (2000). Determination of stable carbon isotope ratios of dissolved chlorinated solvents by GC-C-IRMS: Comparison of headspace and solid-phase micro extraction. *Environ. Sci. Technol*. **34**: 2839–2844.
30. van Warmerdam, E.M. et al. (1995). Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. *Applied Geochemistry* **10**: 547–552.
31. Hunkeler, D., Aravena, R., and Butler, B. (1999). Monitoring of microbial dechlorination of tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope ratios: Microcosm and field studies. *Environ. Sci. Technol.* **33**: 2733–2739.
32. Slater, G.F., Sherwood Lollar, B., Sleep, B., and Edwards, E. (2001). Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: Implications for field applications. *Environ. Sci. Technol.* **35**: 901–907.
33. Fritz, P. and Fontes, J.Ch. (1980). *Handbook of Environmental Isotope Geochemistry. Vol. 1, The Terrestrial Environment*, A. p. 545.
34. Hiscock, K.M., Dennis, P.F., Feast, N.A., and Fairbaim, J.D. (1997). Experience in the use of stable isotopes to distinguish groundwater contamination from leaking sewers in urban areas. In: *Groundwater in the Urban Area*, *Proc. of the XXVI IAH Congress*. Vol. 1, Balkema, Rotterdam, Brookfield, pp. 427–432.
35. Nuti, S., Calore, C., and Noto, P. (1981). Use of environmental isotopes as natural tracers in a reinjection experiment at Larderello. In: *Proc. 7th Stanford Geothermal Reservoir Engineering Workshop*, pp. 85–89.
36. International Atomic Energy Agency (IAEA). (1991). *Use of Artificial Tracers in Hydrology*. IAEA-TECDOC-601, Vienna, p. 229.
37. International Atomic Energy Agency (IAEA). (1998). *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA-TECDOC-1046, Vienna, p. 262.
38. Aravena, R. and Robertson, W. (1998). The use of multiple isotope tracers to evaluate denitrification in groundwater: A case study in a large septic system plume. *Ground Water* **36**: 975–982.
39. Foster, S. (1998). Groundwater recharge and pollution vulnerability of British aquifers: a critical overview. In: *Groundwater Pollution, Aquifer Recharge and Vulnerability*. N. Robins (Ed.). Special Publication. Geological Society, London, 130, pp. 7–22.
40. Vengosh, A., Heumann, K.G., Juraske, S., and Kasher, R. (1994). Boron isotope application for tracing sources of contamination on groundwater. *Environ. Sci. Technol.* **28**: 1968–1974.
41. Eggenkamp, H.G.M. (1994). The geochemistry of chlorine isotopes. *Geologica Ultraiectina, Mededelingen van de Faculteit Aardwetenschappen, Rijksunversiteit*. Utrecht, p. 116.
42. Frape, S.K., Bryant, G., Blomquist, R., and Ruskeeniemi, T. (1995). Evidence from stable chlorine isotopes for multiple sources of chlorine in groundwaters from crystalline shield environments. In: *Isotopes in Water Resources Management*. Vol. I, IAEA, Vienna, pp. 19–30.
43. Fritz, B., Clauer, N., and Sam, M. (1987). Strontium isotopic data and geochemical calculations as indicators of the origin of saline waters in crystalline rocks. In: *Saline Water and*

Gases in Crystalline Rocks. P. Fritz and S.R. Frape (Eds.). Special Paper 33, Geol. Assoc. of Canada, pp. 121–126.

44. McNutt, R.H. (1987). Sr^{87}/Sr^{86} as indicators for water-rock interactions: applications to brines found in Precambrian age rocks from Canada. In: *Saline Water and Gases in Crystalline Rocks*. P. Fritz and S.K. Frape (Eds.). Geol. Assoc. of Canada, Special Paper 33, pp. 81–88.
45. Fritz, P., Cherry, J.A., Weyer, R.V., and Sklash, M.G. (1976). Runoff analyses using environmental isotopes and major ions. In: *Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology*. IAEA, Vienna, pp. 111–130.
46. Egboka, B.C.E. (1981). Multitechnique approach using environmental tracers in hydrogeological studies. *J. Mining Geol.* **18**(1): 96–102.
47. Egboka, B.C.E., Cherry, J.A., Farvolden, R.N., and Frind, E.O. (1983). The migration of contaminants in groundwater at a landfill: a case study. *Journal of Hydrology* **63**: 51–80.
48. Aravena, R., Auge, M., Bucich, N., and Nagy, M.I. (1999). Evaluation of the origin of groundwater nitrate in the city of La Plata, Argentina, using isotope techniques. In: *Proceeding XXIX IAH Congress, Hydrogeology and Land Use Management*. Bratislava, September 6–10.
49. Flipse, W.J., Katz, B.G., Linder, J.B., and Markel, R. (1984). Sources of nitrate in groundwater in a sewered housing development, Central Long Island, New York. *Ground Water* **22**(4): 418–425.
50. Heaton, T.H.E. (1986). Isotopic study of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chemical Geology (Isotope. Geosci. Sect.)* **59**: 87–102.
51. Böttcher, J., Strebel, O., Voerkelius, S., and Schmidt, H.L. (1990). Using isotope fractionation of nitrate nitrogen and nitrate oxygen for evaluation of nitrate in a sandy aquifer. *J. Hydrol.* **114**: 413–424.
52. Aravena, R., Evans, M.L., and Cherry, J.A. (1996). Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Ground Water* **31**: 180–186.
53. Geyh, M. (2000). Groundwater: Saturated and unsaturated zone. In: *Environmental Isotopes in the Hydrological Cycle (Principles and Applications)*. Vol. IV, W.G. Mook (Ed.). UNESCO/IAEA Publ. Series, Paris/Vienna, p. 196.
54. Kendall, C. and Aravena, R. (1999). Nitrate isotopes in groundwater systems. In: *Environmental Tracers in Subsurface Hydrology*. P.G. Cook and A.L. Herczeg (Eds.). pp. 261–297.
55. Foster, S.S.D. and Crease, R.I. (1972). Nitrate pollution of chalk groundwater in East Yorkshire: a hydrogeological appraisal. In: *Groundwater Pollution in Europe*. J.A. Cole (Ed.). Water Information Center, Port Washington, NY, pp. 269–271.
56. Kreitler, C.W. and Jones, D.C. (1975). Natural soil nitrate: the cause of the nitrate contamination of groundwater in runnels county, Texas. *Ground Water* **13**(1): 53–61.
57. Létolle, R.. (1980). Nitrogen-15 in the natural environment. In: *Handbook of Environmental Geochemistry 1A*. P. Fritz and J.Ch. Fontes (Eds.). Elsevier Science Publ., Amsterdam, pp. 407–434.
58. Kreitler, C.W. and Browning, L.A. (1983). Nitrogen isotope analysis of groundwater nitrate in carbonate aquifers: Natural sources versus human pollution. *J. Hydrol.* **61**: 285–301.
59. White, R.J. (1983). Nitrate in British waters. *Aqua*. **2**: 51–57.
60. Heaton, T.H.E. (1984). Sources of the nitrate in phreatic groundwater in the western Kalahari. *J. Hydrol.* **67**: 249–259.
61. Mariotti, A. (1984). Utilisation des variations naturelles d'abondance isotopique en ^{15}N pour tracer l'origine des pollutions des aquiferes par les nitrates. In: *Isotope Hydrology 1983*. IAEA Vienna, 605–633.
62. Flipse, W.J. and Bonner, F.T. (1985). Nitrogen isotope ratios of nitrate in groundwater under fertilized fields, Long Island, New York. *Ground Water* **23**(1): 59–67.
63. Tessendorff, H. (1985). Nitrates in groundwater: A European problem of growing concern. *Aqua* **4**: pp. 192–193.
64. Hübner, H. (1986). Isotope effects of nitrogen in the soil and biosphere. In: *Handbook of Environmental Geochemistry IA*. Elsevier Science Publ., Amsterdam, pp. 361–426.
65. Mariotti, A., Landreau, A., and Simon, B. (1988). ^{15}N isotope biogeochemistry and natural denitrification process in groundwater: Application to the chalk aquifer of northern France. Geochim. *Cosmochim. Acta*. **52**: 1869–1878.
66. Exner, M.E. and Spalding, R.F. (1990). *Occurrence of pesticides and nitrate in Nebraska's groundwater, Report WC1, Water Centre, Inst. Agric. & Natural Resour.,* The University of Nebraska, Lincoln, NE, pp. 3–30.
67. Buzek, F., Kadlecová, R., and Zák, K. (1998). Nitrate pollution of a karstic groundwater system. In: *Isotope Techniques in the Study of Environmental Change*. IAEA, Vienna, pp. 453–464.
68. Révész, K., Böhlke, J.K., and Yoshinari, T. (1998). $\delta^{18}O$ and $\delta^{15}N$ determination in nitrate. In: *Isotope Techniques in the Study of Environmental Change Proc.* IAEA Vienna, pp. 851–854.
69. Pauwels, H., Foucher, J., and Kloppmann, W. (2000). Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. *Chemical Geology* **168**: 307–324.
70. Tore, C., Grilli, A., Aguirre, E., and Moya, P. (2001). Application of hydrochemistry and isotopic hydrology to identify recharge areas and characterize nitrate contamination in the Santiago aquifer. In: *Processing III Simposio Sudamericano de Geologia Isotopica*. Pucon, Chile, October, pp. 441–445.
71. Anwar, A.H.M.F. and Ghosh, P.K. (2002). Nitrate leaching to groundwater under an irrigation project. In: *Balancing the Groundwater Budget, Proc. IAH International Groundwater Conference*. Darwin, Australia, May 12–17.
72. Mook, W.G. (2000). *Environmental Isotopes in the Hydrological Cycle (Principles and Applications)*. Vol. I, UNESCO/IAEA Publ. Series, Paris/Vienna, p. 280.
73. Clark, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York, p. 328.
74. Krouse, H.R. (1980). Sulphur isotopes in our environment. In: *Handbook of Environmental Isotope Geochemistry*. Vol. I, P. Fritz and J.C. Fontes (Eds.). *The Terrestrial Environment*. Elsevier, Amsterdam, pp. 435–471.
75. Krouse, H.R. and Grinienko, V.A. (Eds.).(1991). Stable isotopes of natural and anthropogenic sulphur in the environment. *Scope 43*. John Wiley & Sons, New York.
76. Strebel, O., Boettcher, J., and Fritz, P. (1990). Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in a sandy aquifer. *J. Hydrol.* **121**: 155–172.
77. Schoell, M. (1980). The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica Cosmochimica Acta.* **44**: 649–661.
78. Hackley, K.C., Liu, C.L., and Coleman, D.D. (1996). Environmental isotope characteristics of landfill leachates and gases. *Ground Water* **34**: 827–836.
79. Landmeyer, J.E., Vroblesky, D.A., and Chapelle, F.H. (1996). Stable isotope evidence of biodegradation zonation in a

shallow jet-fuel contaminated aquifer. *Environ. Sci. Technol.* **30**: 1120.

80. Conrad, M.E., Templeton, A.S., Daly, P.F., and Alvarez-Cohen, L. (1999). Isotopic evidence for biological controls on migration of petroleum hydrocarbons. *Organic Geochemistry* **30**: 843–859.
81. Vengosh, A., Kolodny, Y., and Spivack, A.J. (1998). Groundwater pollution determined by boron isotope systematics. In: *Application of Isotope Techniques to Investigate Groundwater Pollution IAEA-TECDOC-1046*. IAEA, Vienna, pp. 17–38.
82. Davidson, G.R. and Bassett, R.L. (1993). Application of boron isotopes for identifying contaminants such as fly ash leachate in groundwater. *Environ. Sci. Techn.* **27**: 172–176.
83. Eggenkamp, H.G.M. and Coleman, M.L. (1998). Heterogeneity of formation waters within and between oil fields by halogen isotopes. In: *Water-Rock Interaction*. G.B. Arehart and J.R. Hulston (Eds.). Balkema, Rotterdam, pp. 309–312.
84. Gee, G.W., Dhanpat, R., and Seme, R.J. (1983). Mobility of radionuclides in soils. In: *Chemical Mobility & Reactivity in Soil Systems*. pp. 208–227.
85. Mazor, E. et al. (1981). Sodium exchange in a NaCl waste disposal case (Lobatse, Botswana): implications to mineral water studies. *Environ. Geol.* **3**: 195–199.
86. Song, H., Song, Z., and Xiao, Z. (1990). The stable isotope geochemistry of fresh water and brine in Sichuan Basin. *Proc. National Seminar on Isotope Methods in Environmental Studies, Hydrology and Geochemistry*. Beijing Research. Inst. Uranium Geology, Beijing, pp. 88–96.
87. Wassenaar, L. (1995). Evaluation of the origin and fate of nitrate in the abbotsford aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^-. *Applied Geochemistry* **10**: 391–405.
88. Auge, M.P. and Nagy, M.I. (1996). Origen y evolución de los nitratos en el suelo y el agua subterránea de la Plata, Provincia de Buenos Aires, Argentina. In: *Tercer Congreso Latinoamericano de Hidrología Subterránea, Noviembre*. San Luis Potosí, México, pp. 1–13.
89. Tandia, A.A., Gaye, C.B., and Faye, A. (1998). Origin, process and migration of nitrate compounds in the aquifers of Dakar region, Senegal. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA TECDOC-1046. IAEA, Vienna, pp. 67–80.
90. Aggarwal, J., Sheppard, D.S., and Robinson, B.W. (1998). Analytical developments and measurements of boron, nitrate, phosphate and sulphate and case examples of discrimination of nitrogen and sulphur sources in pollution studies. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA TECDOC-1046, IAEA, Vienna, pp. 3–15.
91. Shivanna, K., Navada, S.V., Kulkarni, K.M., Sinha, U.K., and Sharma, S. (1998). Application of isotope techniques to investigate groundwater pollution in India. In: *Application of Isotope Techniques to Investigate Groundwater Pollution. IAEA TECDOC-1046*. IAEA, Vienna, pp. 167–184.
92. Halas, S. and Trembaczowski, A. (1998). The influence of brown coal exploitation in Poland on the groundwater pollution as determined by isotopic analysis of sulphate. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA TECDOC-1046. IAEA, Vienna, pp. 81–93.
93. Liu, F., Liu, P., Zhu, W., Wu, X., and Zeng, Y. (1998). Application of isotope techniques to groundwater pollution research for Xiangshan uranium ore field, China. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA TECDOC-1046. IAEA, Vienna, pp. 107–116.
94. Qureshi, R.M., Mashiatullah, A., and Javed, T. (1998). The application of stable carbon isotope ratios as water quality indicators in coastal areas of Karachi, Pakistan. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA TECDOC-1046. IAEA, Vienna, pp. 185–207.
95. De Vito, K.J., Fitzgerald, D., Hill, A.R., and Aravena, R. (2000). Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality* **29**: 1075–1084.
96. Poulsen, S.R., and Drever, J.I. (1999). Stable isotope (C, Cl, and H) fractionation during vaporization of trichloroethylene. *Environ. Sc. Technol*. **33**: 3689–3694.
97. Harrington, R.R., Poulsen, S.R., Drever, J.L., Colberg, P.J.S. and Kelley, E.F. (1999). Carbon isotope systematics of monoaromatic hydrocarbons: vaporization and adsorption Experiments. *Organic Geochemistry* **30**: 765–775.
98. Meckenstock, R.U., Morasch, B., Warthmann, R., Schink, B., Annweiler, E., Michaelis, W., and Richnow, H.H. (1999). $^{13}C/^{12}C$ isotope fractionation of aromatic hydrocarbons during microbial degradation. *Environm. Microbiol.* **1**: 409–414.
99. Ahad, J.M.E., Sherwood Lollar, B., Edwards, E.A., Slater, G.F., and Sleep, B.E. (2000). Carbon isotope fractionation during anaerobic biodegradation of toluene. Implication for intrinsic bioremediation. *Environ. Sci. Technol.* **34**: 892–896.

ENVIRONMENTAL ISOTOPES IN HYDROGEOLOGY

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In the last three to four decades, environmental isotopes have contributed immensely to studies and investigations in hydrogeology, complementing physical and chemical hydrogeology. Many hydrogeologic studies use stable isotopes of the water molecule to determine groundwater quality, origin, recharge mechanism, and rock–water interaction. A good number of the applications of environmental isotopes in hydrogeology have been in the arid and semiarid areas of the world, where water scarcity is most acute and poses constraints on economic development. A substantial amount of basic data (1–3) and results of applied field investigations have already been published (4–15) on applications of different isotopes for hydrologic purposes.

Environmental isotopes provide indications of groundwater age and serve as natural tracers for groundwater provenance. Stable isotopes of carbon, boron, nitrogen, and sulphur (i.e., $^{13}C/^{12}C$, $^{11}B/^{10}B$, $^{15}N/^{14}N$, and $^{34}S/^{32}S$) can give valuable information about reactions involving these elements and can also serve as pollution tracers. On the other hand, radioactive isotopes of some of these elements decay, providing us with a measure of the circulation time and, invariably, groundwater renewability. The most common of the radioisotopes, carbon-14, is used to estimate groundwater residence time. Isotopes of the uranium series (^{234}U, ^{238}U, ^{226}Ra, and ^{222}Rn) are also useful tracers in isotope hydrogeology but are often not

precise enough to establish the age of groundwater due to mineral–water interactions

HISTORICAL BACKGROUND

The history of isotopes dates back to the formation of matter by nucleosynthesis during the birth of our solar system more than 5 billion years ago. This process produced most of the stable and unstable (radioactive) isotopes that naturally exist today (16).

The term "isotope" was first used in 1913 by Soddy Frederick to describe nuclides that occupy the same position in the periodic table but differ in their nuclear properties. Thomson (1913) later showed that the element neon is made up of more than one isotope. In 1919, Francis Aston constructed a mass spectrograph that could be used in discovering virtually all elements. But it was not until 1925 that the existence of oxygen of mass 17 was first observed (32). Later on, oxygen-18 and 17 were discovered in natural material (18). In 1931, Urey discovered the hydrogen isotope of mass 2 (called deuterium) and estimated its natural concentration (19 a, b).

This achievement made it obvious that the isotopic compositions of oxygen and hydrogen were highly variable. As more precise measurements of isotopic ratios continued, it became evident that almost all D_2O and H_2O depleted in deuterium could be prepared by electrolytic decomposition of water. Much later, the concentration of pure ^{18}O was achieved in Switzerland using a thermal diffusion method (20). The work of Urey in 1946 formed the basis of isotopic fractionation (21).

Significant achievement in measuring of natural isotope abundances came with the advent of the Nier/McKinney mass spectrometer (22,23) designed for measuring small differences in isotopic abundance. The discovery of isotopes of water molecules stirred up the several earlier investigations on isotopic hydrology, as reviewed in the work of Rankama (24). Ever since then, investigations using the natural isotopic abundances of all lighter elements have continued to increase and many of them have been published in several texts, journals, and edited specialist volumes (16,25–33).

FUNDAMENTALS OF ISOTOPES IN HYDROGEOLOGY

Isotope derived its name from the Greek word, "*isos*," meaning equal, and "*topos*," which means place (referring to the place in the periodic table). Generally, isotopes of an element are atoms or nuclides that have the same number of protons in the nucleus and thus the same atomic number but differ in the number of neutrons and hence in their atomic mass. There are 92 naturally occurring elements comprising more than 1000 isotopes. Most of these occur in terrestrial compounds in trace amounts, but some are sufficiently abundant to be determined quantitatively through routine analysis. Hydrogen, for example, is known to have three isotopes with the following names and symbols:

1. H—common hydrogen (one proton)
2. D—deuterium, heavy and stable Hydrogen (two protons + one neutron)
3. T—tritium, radioactive hydrogen (one proton + two neutrons).

These isotopes can also be described by adding the number of particles in the nucleus of each (i.e., proton + neutron) and placing this at the upper left corner of the symbol for the element. In this way the hydrogen isotopes above may be written as ^1H, ^2H, and ^3H, respectively. For details on elements, nuclei, and valences, see Ref. 30.

There are two classes of isotopes:

(1) Stable isotopes, that do not change with time, even though their concentrations are affected by other physicochemical processes (such as evaporation or condensation).

(2) Unstable isotopes, that decay with time. The products of this decay are said to be radiogenic if they do not themselves decay. An alternative grouping of isotopes exists: (a) environmental isotopes and (b) artificial isotopes.

Environmental isotopes occur naturally, and investigators have no direct control on the variations of their concentrations: artificial isotopes are those whose variations in the environment are created by humans.

The environmental isotopes most commonly used in hydrogeology are the stable isotopes deuterium (^2H) and oxygen-18 (^{18}O) as well as the radioisotopic molecules tritium (^2H), carbon-14 (^{14}C) (see Tables 1 and 2).

The characteristics of isotopes useful to hydrogeologists are isotopic 'signature' and 'decay.' Once water reaches

Table 1. Stable Environmental Isotopes[a]

Isotope	Ratio	% Natural Abundance	Reference (abundance ratio)	Commonly Measured Phases
^2H	$^2H/^1H$	0.015	VSMOW (1.5575×10^{-4})	H_2O, CH_2O, CH_4, H_2, OH^- minerals
^3H	$^3He/^4He$	0.000138	Atmospheric He (1.3×10^{-6})	He in water or gas, crustal fluids
^6Li	$^6Li/^7Li$	7.5	L-SVEC (8.32×10^{-2})	Saline waters, rocks
^{11}B	$^{11}B/^{10}B$	80.1	NBS 951 (4.04362)	Saline waters, clays, borate, rocks
^{13}C	$^{13}C/^{12}C$	1.11	VPDB (1.1237×10^{-2})	CO_2, $CaCO_3$, DIC, CH_2, organics
^{15}N	$^{15}N/^{14}N$	0.366	Air N_2 (3.677×10^{-3})	N_2, NH_4^+, NO_3^-, N-organics
^{18}O	$^{18}O/^{16}O$	0.204	VSMOW (2.0672×10^{-2})	H_2O, CH_2O, CO_2, NO_3^-, sulfates
			VPDB (2.0672×10^{-3})	Carbonates, silicates, OH^- minerals
^{34}S	$^{34}S/^{32}S$	4.21	CDT (4.5005×10^{-2})	Sulfates, sulfides, H_2S, S-
^{37}Cl	$^{37}Cl/^{35}Cl$	24.23	SMOC (0.324)	Saline waters, rocks, evaporites,
^{81}Br	$^{81}Br/^{79}Br$	49.31	SMOB	Developmental for saline waters
^{87}Sr	$^{87}Sr/^{86}Sr$	^{87}Sr = 7.0 ^{86}Sr = 9.86	Absolute ratio measured	Water, carbonates, sulfates, feldspar

[a]Ref. 16.

Table 2. Environmental Radioisotopes[a]

Isotope	Half-life (years)	Decay mode[a]	Principal sources	Commonly Measured Phases
^{3}H	12.43	β^-	Cosmogenic, weapons testing	H_2O, CH_2O
^{14}C	5730	β^-	Cosmogenic, weapons testing, nuclear reactors	DIC, DOC, CO_2, $CaCO_3$, CH_2O
^{36}Cl	301,000	β^-	Cosmogenic and subsurface	Cl^-, surface Cl salts
^{39}Ar	269	β^-	Cosmogenic and subsurface	Ar
^{85}Kr	10.72	β^-	Nuclear fuel processing	Kr
^{81}Kr	210,000	ec	Cosmogenic and subsurface	Kr
^{129}I	1.6×10^7	β^-	Cosmogenic, subsurface, nuclear reactors	I^- and I in organics
^{222}Rn	3.8 days	α	Daughter of ^{226}Ra in ^{238}U series	Rn gas
^{226}Ra	1600	α	Daughter of ^{230}Th in ^{238}U series	Ra^{2+}, carbonate, clays
^{230}Th	75,400	α	Daughter of ^{234}U in ^{238}U series	Carbonates, organics
^{234}U	246,000	α	Daughter of ^{234}Pa in ^{238}U series	UO_2^{2+}, carbonate, organics
^{238}U	4.47×10^9	α	Primordial	UO_2^{2+}, carbonate, organics

[a]Ref. 16. β^-—beta emission; α—alpha emission, ec—electron capture.

the water table, it retains its isotopic content, as long as isotopic exchange with the reservoir at high temperature does not occur (34).

THE ISOTOPES: ^{2}H, ^{18}O, ^{3}H, ^{13}C AND ^{14}C

Stable Isotopes of the Water Molecule (^{2}H, ^{18}O)

Water is composed of hydrogen and oxygen and therefore occurs with different isotopic combinations in its molecules. As discussed in the previous section, the isotopes of hydrogen are ^{1}H, ^{2}H, ^{3}H, and those of oxygen are ^{16}O, ^{17}O, ^{18}O. Therefore, the possible stable isotopes of water species are $H_2^{16}O$, $HD^{16}O$, $D_2^{16}O$, $H_2^{17}O$, $HD^{17}O$, $D_2^{17}O$, $H_2^{18}O$, $HD^{18}O$, and $D_2^{18}O$.

Significant among these in geochemistry (based on the natural abundance of the isotopes) are $^{1}H_2^{16}O$, $HD^{16}O$, $H_2^{17}O$, and $H_2^{18}O$. The slight variations in their abundance are caused by small differences in the reactivity of the isotopes due to mass differences. Usually, $H_2^{16}O$ is about 10% lighter than $H_2^{18}O$ and therefore more reactive. Under closed conditions and without further reactions, the concentrations of isotopes of the water molecule remain stable over time.

Generally, stable environmental isotopes are measured as ratios of the two most abundant isotopes of a given element. The absolute abundance ratio of isotopes is not usually measured in natural waters because it requires a sophisticated mass spectrometric technique. Due to the low differences, the ratio of the stable isotopes R is given in a delta notation (in per mil units, i.e., parts per thousand) as a deviation from a standard. The mean isotopic composition of seawater, generally known as "SMOW" (Standard mean ocean water), is used for reference (35). However, the reference now commonly adopted for stable oxygen and hydrogen isotopic variation in natural water is V-SMOW (Vienna standard mean ocean water), which is isotopically identical to SMOW (9,36). This difference between samples and the reference standard is expressed in the following relation:

$$\text{Delta}(\delta) = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}} \times 1000 \quad \text{(per mil or ‰)} \tag{1}$$

(R = ratio of the heavy isotope to the light one, for example, $[^{1}H^{2}H^{16}O]/[^{1}H_2{}^{16}O]$).

By definition, the seawater standard has $\delta^{2}H$ and $\delta^{18}O$ values equal to 0‰. Negative values characterize water isotopically depleted ("lighter"), whereas positive values correspond to water samples isotopically enriched ("heavier") with respect to the standard. The measuring accuracy is 0.15‰ for $\delta^{18}O$ and 1‰ for delta $\delta^{2}H$ (37). For details of the measuring technique, refer to IAEA (9,29).

Isotopic Fractionation. Environmental isotopes of the same element can be partitioned or separated in a thermodynamic reaction due to differences in the rates of reaction of different molecular species. Fractionation is a fundamental process common to stable isotopes of H, B, C, O, N, S, and Cl and can occur under equilibrium or nonequilibrium (kinetic) conditions. Fractionation can also result from molecular diffusion. The different isotopic water molecules have various vapor pressures and freezing points. The changes in the isotopic ratio during evaporation, condensation, and chemical and biological processes—caused by these differences—are termed "isotopic fractionation."

Vapor derived from seawater is isotopically depleted compared to SMOW. One of the reasons for the depletion is the lower vapor pressure of the heavy water (e.g., $^{2}H_2^{18}O$). The fractionation or separation occurs at the transition between gaseous, liquid, or solid phases, and this is usually expressed by fractionation factor, α, which is defined as

$$\alpha = R_{\text{reactant}}/R_{\text{product}} \tag{2}$$

For example, the exchange between isotopes of the water molecule and the associated fractionation is defined as follows:

$$H_2O_{\text{liquid}} \Leftrightarrow H_2O_{\text{vapor}} \tag{3}$$

$$\alpha_{\text{liquid-vapor}} = (^{2}H/^{1}H)_{\text{liquid}}/(^{2}H/^{1}H)_{\text{vapor}} \tag{4}$$

$$\text{or } \alpha_{\text{liquid-vapor}} = (^{18}O/^{16}O)_{\text{liquid}}/(^{18}O/^{16}O)_{\text{vapor}}$$

Details of the theory and applications of stable isotopic fractionation exist in publications (16,30,34,38–40).

Of major importance in isotope fractionation is "kinetic" separation, which occurs when there is a deficit of moisture in the vapor phase. Kinetic separation results from the differing diffusion constants for the heavy (e.g., $^2H_2^{18}O$) and the light (e.g., $^1H_2^{16}O$) water molecules: during evaporation the light molecules diffuse faster than the heavy ones through the boundary layer between the water body and the atmosphere (41,42).

Isotopic fractionation is more efficient if the vapor produced in condensation is constantly removed. This leads to the concept of "Rayleigh fractionation," a process in which ^{18}O or ^2H is selectively removed from the vapor phase, so that rain becomes progressively lighter in $\delta^{18}O$ and δ^2H, as it falls farther from the ocean. Rayleight fractionation (or distillation, as it is now called) is an exponential function expressed by the relation:

$$R/R_0 = f^{(\alpha-1)} \tag{5}$$

where $R = {}^{18}O/{}^{16}O$ of residual vapor
$f =$ fraction of residual vapor
$\alpha =$ fractionation factor (= 1.009)

For details on Rayleigh processes in hydrogeological applications, see Reference 16. Isotope fractionation can be used to interpret isotopic data from natural settings and is also a useful tool for elucidating and quantifying processes as well as reactions in a hydrogeologic system.

Dependencies of the Isotopic Composition. In environmental isotopic studies, ^{18}O and ^2H concentrations in precipitation provide a characteristic input signal that varies regionally and over time. The isotopic signatures encountered in precipitation depend on parameters like temperature, deficit of moisture in the air, and the isotopic ratio of the water vapor source. When these parameters are taken into consideration, the isotopic signatures give information about the origin of vapor, precipitation, and groundwater—and partly about climatic conditions during recharge processes in the past. Based on these interrelations, some generally valid dependencies of the isotopic composition of a groundwater sample can be deduced (41).

The Elevation Effect. During the rise of humid air due to orographic obstacles and successive precipitation, the concentration of heavy isotopes in the precipitation decreases with elevation. The depletion also results from the general decrease of cloud temperatures with elevation. For the elevation effect, the depletion is -1 to $-4‰$ and -0.15 to $-0.5‰$ for δ^2H and $\delta^{18}O$ per 100 m rise. The elevation correction (also known as the altitude or alpine effect) distinguishes groundwater recharged at high altitudes from that of low altitude. Therefore, it turns out to be a useful tool in hydrogeologic studies.

The Continental Effect. During the condensation of atmospheric vapor, the liquid phase (i.e., rain droplets) is isotopically enriched, and the vapor phase is isotopically depleted. However, the amount of vapor in a cloud is limited. As this process continues, the isotopic signature of the vapor and consequently, of the condensed water is continuously changing, which, invariably, leads to a situation in which both the precipitation and groundwater are found depleted with respect to heavy isotopes, as the distance away from the coast increases.

The Effect of Precipitation Rate. This is otherwise known as the amount effect that shows the dependence of the isotopic composition on the amount of rainfall: Heavier rain or greater precipitation amounts result in more negative δ^2H and $\delta^{18}O$ values. As the amount of precipitation increases, depletion in the rain can be observed. During one precipitation, of a significant difference in the isotopic signature is found due to (1) progressive condensation and (2) variations in the intensity of the rain.

The Temperature Effect. The isotopic composition of precipitation depends on the temperature at which oceanic water is evaporated into the air. Seasonal fluctuations of the isotopic composition in local precipitation are influenced by fluctuations in temperature. Rain during winter is isotopically lighter than rain during the summer. In the past, when the climate was significantly different from that of today, then the isotopic signature of groundwater formed in the past differed strongly from that of modern precipitation and modern groundwater.

Moreover, the dependence of isotopic fractionation on temperature and moisture causes an annual fluctuation (seasonal effect) and depletion with latitude (latitude effect). In arid and semiarid zones of low moisture saturation and precipitation amounts, an enrichment of the heavy isotopes in raindrops occurs while they are falling (evaporation effect). Also due to evaporation, surface water in rivers and lakes is isotopically enriched.

Meteoric Water Line. Precipitation in rivers and lakes measured worldwide (35) showed that the delta values of the stable isotopes fit along a straight line on a δ^2H–$\delta^{18}O$ plot. This line, termed the "global meteoric water line" is characterized by the relation:

$$\delta^2H = 8\delta^{18}O + 10(‰) \tag{6}$$

Craig's global line was later refined from more than a decade of worldwide monitoring of the stable isotopic composition of precipitation [IAEA Global Network of Isotopes in Precipitation—GNIP, reported in (43)] as

$$\delta^2H = 8.13\delta^{18}O + 10.8(‰) \tag{7}$$

From Equation 6, the gradient (s) of the GMWL line is 8, and "d," the intercept on the y axis is 10‰. The value of d, first used by Dansgaard (34) to characterize the deuterium excess in global precipitation, is defined from Equation 6 as

$$d = \delta^2H - 8\delta^{18}O(‰) \tag{8}$$

Evaporation during precipitation changes in the gradient of the straight line to values <8 causes (see Table 3).

Table 3. Examples of Regional Meteoric Lines[a]

Region	Meteoric line (‰)
'Global' (meteoric line)	$\delta^2H = 8\delta^{18}O + 10$
Northern Hemisphere (continental)	$\delta^2H = (8.1 \pm 1)\delta^{18}O + (11 \pm 1)$
Mediterranean (or Middle East)	$\delta^2H = 8\delta^{18}O + 22$
Maritime Alps (April 1976)	$\delta^2H = (8.0 \pm 0.1)\delta^{18}O + (12.1 \pm 1.3)$
Maritime Alps (October 1976)	$\delta^2H = (7.9 \pm 0.2)\delta^{18}O + (13.4 \pm 2.6)$
Northeastern Brazil	$\delta^2H = 6.4\delta^{18}O + 5.5$
Northern Chile	$\delta^2H = 7.9\delta^{18}O + 9.5$
Tropical Islands	$\delta^2H = (4.6 \pm 0.4)\delta^{18}O + (0.1 \pm 1.6)$

[a]Ref. 30.

Tritium (^3H)

Tritium, the radioactive isotope of hydrogen, is produced naturally in the upper atmospheric strata by the influence of cosmic radiation on nitrogen atoms:

$$^{14}N + n \Rightarrow {}^{15}N \Rightarrow {}^{12}C + {}^{3}H \quad (9)$$

Tritium, which combines in the atmosphere with oxygen to form water, may precipitate on the earth as rain and thus reach the groundwater. Tritium is usually symbolized as T or simply ^3H. Its concentration in water is expressed in tritium units (TU): 1 TU corresponds to 1 atom ^3H per 10^{18} atoms ^1H. Details of measuring techniques and procedure are fully discussed in Ref. 44.

Tritium decays with a half-life of about 12.35 years to form ^3He. The atmospheric concentration of tritium prior to 1953 was about 3–5 TU. Due to nuclear weapon tests, the concentrations in precipitation up to 1963 reached several thousand TU. Hence, since the early 1960s, the anthropogenic tritium from bombs was used as tracer to study young groundwater. In the meanwhile, however, in Europe, the concentrations have decreased to values <10 TU (45). Measurable tritium in groundwater usually signifies modern recharge. High tritium (>30 TU) indicates recharge in the 1960s, and low values (<1 TU) usually signify paleogroundwater (older groundwater) that has mixed with shallow modern groundwater.

Although, qualitative and quantitative approaches to dating groundwater are also possible for tritium (16), the direct age determination of groundwater accurate to a year is somewhat uncertain partly due to the unknown extent of mixing of each year's recharge with that of the previous year's and partly because of high local and temporal variability of input values in precipitation. However, by measuring ^3H together with its daughter ^3He, true age determination is possible by calculations not based on the complicated tritium input function.

Carbon-14 and Carbon-13

There are three isotopes of carbon in nature: common and stable carbon (^{12}C), rare and stable carbon (^{13}C), and very rare and radioactive carbon (^{14}C). ^{14}C is formed, like tritium, in the upper atmosphere from the impact of neutrons produced by cosmic radiation on nitrogen atoms:

$$^{14}N + n- \Rightarrow {}^{14}C + p \quad (10)$$

where n = neutron and p = proton.

The half-life ($t_{1/2}$) of carbon-14 is $5{,}730 \pm 30$ years. The natural ^{14}C-level in the atmosphere corresponds to a ratio $^{14}C/^{12}C$ of 1.18×10^{-12}. The ^{14}C concentration of a sample is given in pmc units (percent modern carbon) as share of the atmosphere value in 1950, which was fixed at 100 pmc. ^{14}C values >100 pmc in the atmosphere and in shallow aquifers document nuclear weapon tests during the 1950s.

The stable isotope ^{13}C is often used to determine the initial content of ^{14}C. The processes of fractionation can reflect themselves in the ratio $^{13}C/^{12}C$. The^{13}C concentration of a sample is given as deviation in ‰ from a standard. As standard, the ^{13}C value of a marine limestone (Peedee belemnite = PDB) that has the delta value of 0‰ is used. Within the atmosphere, δ values range from −7 to −8‰. Isotopic fractionation is stronger during biological processes. Hence, biological CO_2 has values of about −25 to −15‰ depending on the predominant photosynthesis cycle.

Carbon Dating: Principles and Problems. There are two methods of sampling for ^{14}C: The first is by precipitation of approximately 60 millimoles of total carbon as barium or strontium carbonate at a pH > 9. The second method involves acidification of a water sample, gas stripping the CO_2 with nitrogen, and trapping the evolved CO_2 in a solution of CO_3^{-2}-free NaOH. ^{14}C is measured by beta counting either in gas or liquid phase or by a more recent method using accelerator mass spectrometry of a graphite target. Radiocarbon activities expressed as percent "modern" carbon (pmc) represent the activity of carbon prior to the dilution by postindustrial 'dead' fossil fuel carbonate. For example, a carbon sample that has 0 pmc is deemed dead or has an age beyond the limit detectable by radiocarbon dating. The age of a given water sample can be calculated from the relation,

$$t = 1/\lambda \ln C/C_0 \quad (11)$$

where t = age (in years), λ = decay constant of ^{14}C, C = measured ^{14}C activity, and C_0 = initial ^{14}C activity.

The age dating of groundwater that contains dissolved, inorganic radioactive carbon (^{14}C) may be used for ages up to 60,000 years, although poor preservation and subsequent contamination of old material now makes the effective dating range shorter. For organic material, the effective range is <50,000 years; for groundwater, the range is limited to 30,000 years or less. The main problems associated with ^{14}C dating are (1) determination of the initial C-14 value, (2) mixtures of waters of different ages, (3) a diffusive admixture of CO_2 from the atmosphere, and (4) dissolution of carbonates. Despite these problems, ^{14}C -age dating is widespread and yields good results in simple situations (16,46).

Correction of the Carbon-14 Age. By various interactions of recent and fossil carbon, an initial ^{14}C value between 50 and 100 pmc results. Other, partly bacterial processes can also influence the isotopic composition of groundwater. During the development of the ^{14}C method, several correction models were set up that reduce the

initial activity of samples below 100 pmc. The result is a corrected age. Several correction models exist (46–51). The resulting ages are often compared with conventional ages, which are obtained with initial values of 100 pmc.

OTHER NATURALLY OCCURRING ISOTOPES

Chlorine-36 (^{36}Cl)

Chlorine-36 is a radioactive isotope of chlorine whose application to hydrology has attracted much interest in the last decade. It is naturally produced by cosmic rays interacting with atmospheric argon (^{40}Ar) and finds its way into the hydrologic cycle either as dry fallout or in precipitation. The thermonuclear bomb testing of the 1960s contributed a significant amount of ^{36}Cl, thus elevating its concentrations above the natural atmospheric abundance. ^{36}Cl behaves conservatively in most hydrologic environments, and like bomb tritium, it is useful in delineating recharge rates. However, unlike tritium, its use for dating modern groundwater is unrealistic. But its half-life of 301,000 years makes ^{36}Cl a useful tool in groundwater age determination in the range of 10^5–10^6 years.

Chlorofluorocarbons (CFCs)

Chlorofluorocarbons exist in the atmosphere as CCl_3F and CCl_2F_2 (simply referred to as CFC-11 and CFC-12, respectively). The production of Freons for use as solvents, refrigerants, and propellants has released large quantities of these compounds into the atmosphere. The source of CFCs is mainly anthropogenic, and studies have shown that their concentration in the atmosphere is steadily increasing since the production of Freons started in the mid-1940s. Hydrogeologists have found a use for CFCs, which have accumulated as contaminants in the atmosphere, as tracers like tritium. The analysis of CFC compounds is less complicated than that of tritium. This advantage, coupled with the decreasing concentration of bomb tritium (since the 1990s), is responsible for its increasing applications in hydrogeologic studies. CFC-11 and CFC-12, whose atmospheric residence times are 60 and 120 years, respectively, are not isotopes in themselves but equilibrate with water to form a dating tool for groundwater (<50 years old). They are equally applicable as tracers of groundwater and of sewage contamination in water (16,33).

Uranium Series Isotopes

The radioactive decay of uranium and thorium results in the formation of a series of isotopes, which are in themselves radiogenic. Significant among these are ^{234}U, ^{238}U, ^{226}Ra, and ^{222}Rn. The uranium series displays an enormous array of half-lives (10^5–10^9) and many geochemical distinctive characteristics that make them useful in hydrogeologic applications (16,33):

1. Evaluation of mixing between groundwater bodies can be achieved on a plot of excess ^{234}U versus ^{238}U concentration.
2. The wide range of half-lives is useful in tracing groundwater movement and investigating geochemical processes.
3. Measurement of groundwater–surface water interactions and recharge processes is made possible with ^{222}Rn (half-life $\approx$ 4 days).
4. Uranium activity ratios may provide additional information on the geochemistry of the groundwater system.

Boron Isotopes and Other Pollution Tracers

Natural boron has two stable isotopes, ^{11}B and ^{10}B. Boron is used as tracer in groundwater because of its high solubility in aqueous solution, natural abundance in all waters, and the lack of effects by evaporation, volatilization, and oxidation–reduction reactions. ^{11}B mixing curves enable identification, and in some cases, quantification of contaminants in groundwater (52).

A good number of other isotopes have been employed to trace groundwater pollution. The type of pollutant investigated governs the type of isotope used to trace groundwater pollution. For example, ^{15}N/^{14}N and ^{18}O/^{16}O are used for nitrates in groundwater, ^{34}S/^{32}S for dissolved sulfates, and ^{13}C/^{12}C for dissolved inorganic carbon. ^{11}B (with ^{18}O, ^{87}Sr/^{86}Sr, Br/Cl) is useful in tracing salinity, and ^{13}C/^{12}C, ^{2}H/^{1}H, and ^{37}Cl/^{35}Cl can be used to trace organic carbon pollutants.

SUMMARY OF APPLICATIONS OF ENVIRONMENTAL ISOTOPES

The environmental isotope technique in hydrogeology is based on the principles that stable isotopes and tritium data for groundwater correlate with local precipitation. ^{18}O and ^{2}H concentrations in precipitation provide a characteristic input signal that varies regionally and over time. The isotopic signatures encountered in precipitation depend on parameters like temperature, the deficit of moisture in the air, and the isotopic ratio of the water vapor source. When these parameters are taken into consideration, the isotopic signatures give information about the origin of vapor, precipitation, and groundwater—and partly about the climatic conditions during recharge processes in the past.

Although, qualitative and quantitative approaches to dating groundwater are possible using tritium, the accuracy of this age determination is in question due to the unknown extent of mixing of recharging water with that of the previous year and partly because of high local and temporal variability of input values in precipitation. However, by measuring ^{3}H together with its daughter ^{3}He, true age determination is possible by calculations not based on the complicated tritium input function. Age dating of groundwater with ^{14}C is also widespread in spite of the problems inherent in the method. Stable isotopes of carbon, boron, nitrogen, and sulfur (i.e., ^{13}C/^{12}C^{11}B/^{10}B, ^{15}N/^{14}N, and ^{34}S/^{32}S) can give valuable information about reactions involving these elements and can also serve as pollution tracers. On the other hand, radioactive isotopes of some of these elements decay, providing us with a

measure of circulation time and invariably groundwater renewability. In all, environmental isotopes have been applied to a wide spectrum of hydrogeologic problems.

BIBLIOGRAPHY

1. IAEA. (1976). *Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology*. TECDOC-Series, IAEA, Vienna, p. 228.
2. IAEA. (1981). *Statistical Treatment of Environmental Isotope Data in Precipitation*. TECDOC-Series, IAEA, Vienna, p. 276.
3. IAEA. (1990). *World Survey of Isotope Concentration in Precipitation (1953–1987)*. Vols. 1–9, IAEA, Vienna.
4. IAEA. (1962). *Applications of Techniques in Hydrology*. TECDOC-Series, IAEA, Vienna, p. 31.
5. IAEA. (1967). *Isotopes in Hydrology*. TECDOC-Series, IAEA, Vienna, p. 740.
6. IAEA. (1978). *Isotope Hydrology—Vol. I*. TECDOC-Series, IAEA, Vienna, p. 440.
7. IAEA. (1979). *Isotope Hydrology—Vol. II*. TECDOC-Series, IAEA, Vienna, p. 540.
8. IAEA. (1980). *Arid Zone Hydrology: Investigations with Isotope Techniques*. TECDOC-Series, IAEA, Vienna, p. 265.
9. Gat, J.R. and Gonfiantini, R. (1981). *Stable Isotope Hydrology, Deuterium and Oxygen-18 in the Water Cycle*. IAEA, Tech. Rept. Series No. 210, p. 337.
10. IAEA. (1983). *Isotope Techniques in Hydrological Assessment of Potential Sites for the Disposal of High-Level Radioactive Wastes*. TECDOC-Series, IAEA, Vienna, p. 164.
11. IAEA. (1984). *Isotope Hydrology*. TECDOC-Series, IAEA, Vienna, p. 874.
12. IAEA. (1986). *Isotope Techniques in the Study of the Hydrology of Fractured and Fissured Rocks*. TECDOC-Series, IAEA, Vienna, p. 306.
13. IAEA. (1994). *Mathematical Models and Their Applications to Isotope Studies in Groundwater Hydrology*. TECDOC-777, IAEA, Vienna, p. 283.
14. IAEA. (1996). *Isotope Field Applications for Groundwater Studies in the Middle East*. TECDOC-890, IAEA, Vienna, p. 250.
15. IAEA. (1998). *Applications of Isotope Techniques to Investigate Groundwater Pollution*. TECDOC-1046, IAEA, Vienna, p. 262.
16. Clark, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. Lewis, Boca Raton, FL, p. 328.
17. Blackett, P.M.S. (1925). Ejection of proton from nitrogen nuclei photographed by the Wilson method. *Proc. R. Soc. (London), Ser. A* **107**: 349.
18. Giauque, W.F. and Johnston, H.L. (1929). An isotope of oxygen, mass 18. *J. Am. Chem. Soc.* **51**: 1436.
19. Urey, H.C., Brickwedde, F.G., and Murphy, G.M. (1932a). A hydrogen isotope of mass 2. *Phys. Rev.* **39**: 1645;
(1932b). Hydrogen mass 2 and its concentration. *Phys. Rev.* **40**: 145.
20. Clusius, K., Dickel, G., and Becker, E. (1943). Reindarstellung des schweren Sauerstoff-isotopes $^{18}O_2$ und des Stickstoffs $^{14}N^{15}N$. *Naturwissenschaften*. **31**: 210.
21. Urey, H.C. (1947). Thermodynamic properties of isotopic substances. *J. Chem. Soc.* **1947**: 562–581.
22. Nier, A.O. (1947). A mass spectrometry for isotope and gas analysis. *Rev. Sci. Instrum.* **18**: 398.
23. McKinney, C.R., McCrea, J.M., Epstein, S., Allen, H.A., and Urey, H.C. (1950). Improvements in mass spectrometers for the measurements of small differences in isotope abundance ratios. *Rev. Sci. Instrum.* **21**: 724.
24. Rankama, K. (1954). *Isotope Geology*. Pergamon Press, Oxford, p. 490.
25. Dostrowsky, I. and Raviv, A. (1958). Separation of the Heavy Isotopes of Oxygen by Distillation. Isotope Separation. *Proc. Int. Symp*. Amsterdam, p. 336.
26. Fidel, R. (1976). *Bibliography of Hydrogen and Oxygen Stable Isotope Hydrology*. Hebrew University, Jerusalem.
27. Fritz, P. and Fontes, J.Ch. (1980). *Handbook of Environmental Isotope Geochemistry*. Vol. 1, Elsevier, Amsterdam, p. 545.
28. Fritz, P. and Fontes, J.Ch. (1986). *Handbook of Environmental Isotope Geochemistry*. Vol. 2, Elsevier, Amsterdam, p. 557.
29. IAEA. (1995). Reference and Intercomparison Materials for Stable Isotopes of Light Elements. *Proc. Consultants meeting held in Vienna*, December 1–3, 1993. IAEA-TECDOC-825, IAEA, Vienna, p. 165.
30. Mazor, E. (1997). *Chemical and Isotopic Groundwater Hydrology*. Marcel Dekker, New York, p. 413.
31. Kendall, C. and McDonnell, J.J. (1998). *Isotope Tracers in Catchment Hydrology*. Elsevier, New York, p. 839.
32. Cook, P.G. and Herczeg, A.L. (1999). *Environmental Tracers in Subsurface Hydrology*. Kluwer, Dordrecht, the Netherlands.
33. Herczeg, A.L. and Cook, P.G. (2002). *Environmental Isotope in Groundwater*. CGS Workshop presented at the International Groundwater Conference, Darwin, Australia, May 12–17.
34. Dansgaard, W. (1964). Stable isotopes in precipitation. *Tellus*. **16**: 436–469.
35. Craig, H. (1961). Isotopic variations in meteoric waters. *Science*. **133**: 1702–1703.
36. Gonfiantini, R. (1978). Standards for stable isotope measurements in natural compounds. *Nature*. **271**: 534–536.
37. IAEA. (1998). Analytical quality in the IAEA isotope hydrology laboratory: Some recent improvements. *Water Environ. News*, IAEA, No. 3, pp. 5–7.
38. Gat, J.R. (1981). Isotopic fractionation In: *Stable Isotope Hydrology, Deuterium and Oxygen-18 in the Water Cycle*. J.R. Gat and R. Gonfiantini (Eds.). IAEA, Tech. Rept. Series No. 210.
39. Hoefs, J. (1997). *Stable Isotope Geochemistry*, 4th Edn. Springer-Verlag, Heidelberg, p. 251.
40. Kendall, C. and Caldwell, E.A. (1998). Fundamentals of isotope geochemistry. In: *Isotope Tracers in Catchment Hydrology*. C. Kendall and J.J McDonnell (Eds.). Elsevier, New York, p. 839.
41. Moser, H. and Rauert, W. (1980). *Isotope Methods in Hydrogeology* (in Deutsch). Lehrbuch Hydrogeologie, 8, Stuttgart, p. 400.
42. Jacob, H. and Sonntag, C. (1991). An 8-year record of the seasonal variation of ^{2}H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany. *Tellus*. **43B**: 291–300.
43. Rozanski, K., Araguas-Araguas, L., and Gonfiantini, R. (1993). Isotopic Patterns in Modern Global Precipitation. In: *Continental Isotope Indicators of Climate*, American Geophysical. Union monograph 78, AGU, Washington, DC, pp. 1–36.
44. IAEA. (1981). *Low-level tritium measurement*. IAEA-TECDOC-246, p. 204.

45. Groning, M. (1994). *Noble Gases and Isotope Tracer in the Groundwater: Paleo-climatic Changes and Dynamics of Regional Groundwater Systems (in Deutsch)*. Ph.D. Thesis. University of Heidelberg, p. 136.
46. Vogel, J.C. and Ehhalt, D. (1963). The Use of Carbon Isotopes in Groundwater Studies. *Radioisotopes in Hydrology*. IAEA, Vienna, pp. 383–395.
47. Vogel, J.C. (1970). Carbon-14 Dating of Groundwater. In: *Isotope Hydrology, IAEA Symposium 129*, pp. 225–239.
48. Tamers, M.A. (1975). The validity of radiocarbon dates on groundwater. *Geophy. Surv.* **2**: 217–239.
49. Fontes, J.Ch. and Garnier, J.M. (1979). Determination of the initial ^{14}C activity of total dissolved carbon: A review of existing models and a new approach. *Water Resour. Res.* **15**: 399–413.
50. Maloszewski, P. and Zuber, A. (1991). Influence matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. *Water Resour. Res*. **27**: 1937–1945.
51. Kalin, R. (1999). ^{14}C in Groundwater. In: P.G. Cook and A.L. Herczeg (Eds.). *Environmental Tracers in Subsurface Hydrology*. Kluwer, Dordrecht, the Netherlands.
52. Vengosh, A. (1998). Boron Isotopes and Groundwater Pollution. *Water Environment News*, IAEA, No. 3, pp. 15–16.

WATER-JETTING DRILLING TECHNOLOGIES FOR WELL INSTALLATION AND *IN SITU* REMEDIATION OF HYDROCARBONS, SOLVENTS, AND METALS

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Water-jet drilling or jetting has been used as a drilling method in both the developing world for water supply projects and in the United States for in situ remediation of hydrocarbons, chlorinated solvents, and metals.

Jetting has been documented for installing water supply wells in coarse materials such as boulders in glacial till deposits where the water pressure nozzle can move coarse gravels. This method uses a high-velocity stream of water to advance the borehole. The jet-percussion system is limited to drilling 7 to 10 cm diameter wells to depths of about 60 meters. Drilling tools consist of a chisel-shaped bit attached to the lower end of a piping string. Nozzles on each side of the bit shoot water out at moderate to high pressures. The water keeps the bit clean and lubricated and carries the pulverized drill cuttings in suspension up the annulus. The cuttings settle out by gravity in suspension pits. The water is then picked up by the suction of the mud pump and recirculated through the drill pipe to the nozzles at the bottom of the borehole (1).

As a source of clean water wells for the developing world, such as Africa, well jetting has been successfully designed for the resources, tools, and skills of even the poorest farmers. In the 1980s, George and Richard Cansdale of SWS Filtration developed jetting as a drilling technique that could be used by the developing world to obtain economical and safe supplies of water. The hand pump, called a Rower Pump, is a suction piston pump made by SWS Filtration. The Rower Pump has the entire main pump components such as a foot valve, piston valve, and pump cylinder. The operator holds the T-handle, pulls and pushes directly on the piston rod as the water pours out the top of the well. The manually operated pump pulls water from the 1 to 5 cm diameter wells at a rate of several liters per minute.

Well jetting is particularly suited to unconsolidated sediments such as sandy riverbeds or riverbanks, where water is generally found close to the surface (1 to 5 meters). The jetting technique, which generally does not penetrate more than 10 meters, can be used to drive a pipe and filter into the sandy riverbed of a dry river or wadi, so that subsurface water, close to the surface, can be pumped from below the surface. The jet of water is pushed from a tank through a pump and into a PVC or steel rod, which makes the sand fluid and allows the pipe to slide into the subsurface. On some floodplains, it is possible to jet through more than 30 meters of silt before reaching an underlying sandy aquifer. Small-diameter jetted wells, called "washbores" by local farmers, are used worldwide to irrigate crops during the dry season. Some small-bore jetted wells are used for domestic water supplies. More details are described in Power (2).

Case studies of the jetted wells have been documented in Zambia, Sudan, Nigeria, and Zaire, as well as other countries. For their efforts, the Cansdales were awarded a 1990 IBM Award for Sustainable Development for their well jetting and the muscle-powered Rower Pump. Other low-technology methods for bringing water to the surface through the jetted well include a check ball valve connected to plastic tubing.

Jetting technology can also be used to install small diameter piezometers or well points in sand. The small diameter (1 to 2.5 cm diameter) well pipe with pressure nozzles on the bottom is pushed downward as the water jets advance the borehole in front of the pipe. The well pipe is left in place at the target depth, and the well point is sealed in place at the surface with neat cement grout.

For environmental cleanup projects, jetting technology has been used successfully as a delivery method for treatment chemicals for remediating hydrocarbons, solvents, and metals. Remediation jetting using high-pressure, low to high volume injection of liquids into the subsurface through a small-diameter wand or lance driven into the subsurface has been widely used for several decades. Jetting technology uses tree root feeder systems to inject liquids into the ground. The remediation injection process (RIP®), an updated and more powerful, versatile and adaptable jetting delivery system, has been used efficiently to implement or augment a variety of environmental remediation processes, including chemical oxidation, bioremediation, pH adjustment, and metal stabilization. Handheld RIP® lances have been designed to use high-pressure liquid pumps to increase flow at the tip of the wand at pressures from 20,000–35,000 kilopascals (kPa). High-pressure injection of remediation treatment chemicals can be done in sensitive areas (Fig. 1).

At these pressures, the lances are driven downward at velocities up to 1/3 meter per second. High-pressure



Figure 1. Handheld lances used to perform remediation by jetting technology in a limited-access site (FAST-TEK).

injection points placed on close spacing, such as 0.6 to 1.5 meter centers, allow complete in situ coverage, vertically and laterally. The radius of influence around injection ports exceeds 3 meters (3). Injection port spacing includes overlapping areas (Fig. 2).

Jetting technology is used to remediate areas of limited access such as underneath slabs, railways, and buildings; around tanks, pipelines, and subsurface utilities; and into hillsides, excavation pits, and stockpiles. The flexibility and accuracy of this injection delivery system provides distinct advantages over both conventional in situ and ex situremediation systems. Hot spots can be effectively treated using this technology. As a result, jetting can provide appreciable savings in cost and time over traditional remediation technologies (4).

Jetting uses chemical oxidizers to treat soils rapidly that are contaminated by toxic and persistent organic wastes. The two most common liquid oxidizers used for jetting in soil and groundwater remediation are hydrogen peroxide and potassium permanganate.

Alkalinity, pH, and organic content must be evaluated prior to any in situ metal stabilization project. Injection ports are grouted with bentonite or neat cement.

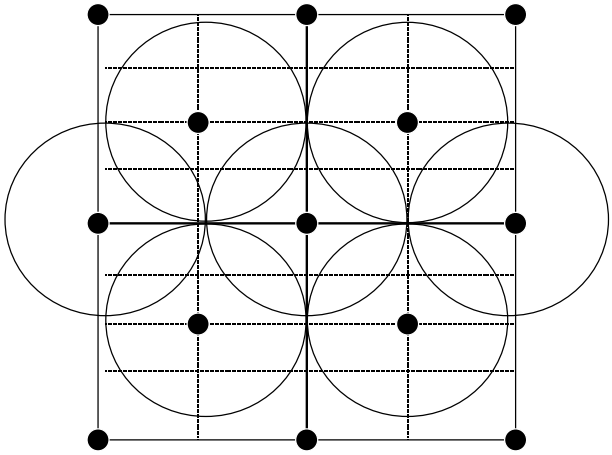


Figure 2. Plan view of overlapping injection zones, spread approximately 0.6 to 1.5 meters apart.

Documented jetting projects include oxidation using hydrogen peroxide and potassium permanganate for both chemical oxidation and aerobic bioremediation of a variety of hydrocarbon contaminants, including gasoline and diesel. Chlorinated solvents have been successfully remediated using chemical oxidation methods. Anaerobic biodegradation of chlorinated solvents combines jetting technology with the injection of carbon sources (molasses, cheese whey, lactic acid, or other chemicals). Metal stabilization uses chemical reductants such as sulfide-based treatments (calcium polysufide, sodium metabisulfite, or ferrous sulfate) with jetting equipment to stabilize various metals successfully, including arsenic, lead, and hexavalent chromium (5–9).

BIBLIOGRAPHY

1. Driscoll, F.G. (1986). *Groundwater and Wells*, 2nd Edn. Johnson Filtration Systems, St. Paul, MN, pp. 307–308.
2. Power, G. (1984). Bangladeshi Rover travels to Africa. *World Water Mag.*, June 2003. Available: http://dspace.dial.pipex.com/swsfilt/rower/rp5.htm.
3. Jacobs, J., Ruslen, D., MacLeod, S., and Taylor, T. (1999). *In-situ* high pressure remediation injection process. *Hydrovisions* Fall 1999, Groundwater Resources Association.
4. Jacobs, J. (2000). In-Situ Remediation of Hot Spots Using Jetting Technology. *52nd Annu. Natl. Ground Water Assoc. Meet.*, Las Vegas, NV, p. 24.
5. Jacobs, J. (2001). Optimization of Existing Soil Vapor Extraction and Pump and Treat Systems Using In-Situ Hydraulic Fracturing. *Groundwater Resourc. Assoc. Calif., 10th Annu. Meet.* and *23rd Biennial Groundwater Conf.*, Sacramento, CA, October 30, p. 65.
6. Jacobs, J. (2001). In-Situ Delivery Methods for Remediation of Hexavalent Chromium in Soil and Groundwater. *Natl. Joint Meet. Assoc. Eng. Geol. Am. Inst.* of *Prof. Geol.*, St. Louis, MO, October 5, p. 62.
7. Jacobs, J. (2001). Insights Into Remediation of Recalcitrant Compounds Using In-Situ Liquid Delivery Systems for Chemical Oxidation, Bioremediation, and Metals Stabilization. *Groundwater Resourc. Assoc. Calif., 2nd Symp.* in *Seri. Groundwater Contaminants: Characterization & Remediation of Emerging and Recalcitrant Contaminants*, June 14–15, 2001.
8. Jacobs, J. (2000). Applications of Jetting Technology for In-Situ Remediation. *Assoc. Eng. Geol. Groundwater Resourc. Assoc. 2000 Annu. Meet.*, San Jose, CA, p. 92.
9. Suthersan, S.S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL.

KARST HYDROLOGY

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The most interesting aspect of a karst landscape is its unique hydrologic system. Karst landscapes are primarily underlain by carbonate, primarily limestone and dolomite, where surface water and groundwater are interconnected to form one functional unit. The end result

of this hydrologically integrated flow system is the karst spring. Springs provide substantial quantities of water for human consumption and commercial enterprises. Because karst aquifers provide effective natural cleansing, it is imperative to understand the dynamic flow systems within these aquifers to protect these vulnerable water supplies from contamination.

Karst landscapes occupy 10–20% of the earth's land surface (1). The complex hydrology of karst aquifers has been studied for more than a century, and the understanding of flow patterns has advanced significantly in the last 30 years. Investigative methods used have included spring hydrographs and chemographs, groundwater dye tracing, cave mapping, and computer modeling. However, there is still more to learn about the complex nature of karst groundwater flow systems.

This synopsis includes the terms and concepts developed throughout the last 40 years to characterize the hydrology within karst landscapes. The simultaneous efforts by many researchers throughout Europe, North America, China, and Australia in different karst settings has shaped our understanding of the hydrology of karst landscapes. Excellent sources on karst hydrology are Milanovic (2), Bonacci (3), White (4), Ford and Williams (5), Quinlan et al. (6), and White (7).

GROUNDWATER RECHARGE TO KARST SYSTEMS

Several terms have been developed throughout the years that describe where and how meteoric water enters the subsurface to replenish or recharge underlying aquifers. The first two terms refer to where the recharge waters originate. Jakucs (8) and Pitty (9) recognized allogenic and autogenic recharge. Allogenic recharge is surface water that flows from adjacent nonkarst areas onto to karst. Autogenic recharge refers to water that fall directly onto the karst landscape from precipitation. Gunn (10) proposed four recharge types for conduit flow dominated karst aquifers that combined where and how the water entered the subsurface that included diffuse allogenic, concentrated allogenic, diffuse autogenic, and concentrated autogenic recharge.

The second two terms define how the water moves into the subsurface. Aley (11) used the terms diffuse and discrete recharge. Diffuse recharge falls directly onto the karst landscape and enters the subsurface at a large number of sites where inflow is small. Water infiltrates the soil zone or rock outcrop into the groundwater flow system through joints or fissures in the uppermost layer of the bedrock. Diffuse recharge is relatively slow and can be seen in caves as drip water emerging from cracks in the roof where it deposits secondary carbonates such as dripstone and flowstone (12).

Discrete recharge, also called concentrated recharge, enters the groundwater flow system through localized areas, such as sinking streams or sinkholes. Substantially greater quantities of water per unit area enter the groundwater flow system through discrete recharge areas than through diffuse recharge areas (11). Discrete recharge and diffuse recharge represent the maximum ends of a continuum, and most karst landscapes exhibit both types. Atkinson (13) preferred to use "quickflow" to describe water entering the subsurface through sinking streams and sinkholes, and "baseflow" refers to slow percolation of water into the subsurface through nonlocalized areas.

An argument can be made that the use of any of these eight terms is appropriate and depends on the objective of the study. However, it's the authors opinion that all these terms that have been used to define recharge to karst systems simply leads to confusing terminology for those entering the field of karst science. Palmer (14), Smart and Hobbs (15), and White (12) provide more detailed discussions about recharge in karst systems.

THE EPIKARSTIC ZONE

The epikarstic zone is the uppermost part of the carbonate rock that consists of an integrated system of intersecting dissolution-widened fissures, fractures, cavities, and shafts. The epikarstic zone can vary from zero to 98 feet (16) in thickness, and its development is controlled by such factors as bedrock structure, climate, time since the last glaciation, solubility, vegetal cover, and depth of groundwater circulation. The quantity and depth of solution within the epikarst depends on the quantity of rainfall, its distribution in time, the velocity of recharge water, its composition, and the thickness of the soil and rocks (3). The percentage of bedrock removed by dissolution can range from less than 1% to more than 50% (16). Fissures are considerably widened and observation shows that they decrease rapidly with depth (17) due to the decreased amount of CO^2 in solution as the groundwater approaches equilibrium (18).

Dissolution features in the epikarstic zone are organized to move infiltrating water laterally to localized zones where collector structures, such as shafts, conduct the water farther into the subsurface (19). Water storage in the epikarst generally depends on relief. Areas of gentle topography tend to have higher storage, whereas areas of steeper topography have lower storage. Due to the higher storage capacity in many epikarstic zones, the epikarst serves as a perched aquifer.

Aley (20) divided epikarstic zones into three hydrological types: rapidly draining, seasonally saturated, and perennially saturated. These hydrological types were conceptualized on the basis of dye recovery results where dye was introduced directly into locations of discrete recharge that passed through the epikarst and ultimately discharged at springs. Generally, groundwater travel rates vary in epikarstic systems, and two or more hydrological types may exist. The primary criteria used to distinguish these zones were based on their ability to store water.

Rapidly draining epikarsts are saturated with water for short periods of time especially after major storms that provide little water storage or detainment. Infiltration of fine textured sediment is negligible. Lands commonly characterized by rapidly draining epikarsts include areas of high topographic relief, carbonate bedrock with high solubility, and areas of thin soil and residuum.

Seasonally draining epikarsts store water after major storms lasting for weeks or months or store water on a seasonal basis. Sediment infiltration in voids is greater than that in rapidly draining epikarst. Seasonally saturated epikarsts typically develop in humid areas of moderate relief, appreciable soil and residuum thickness, and at elevations greater than those of local perennial streams. Dye recovery results range from 1–10% for seasonally saturated zones.

Perennially draining epikarsts occur in humid areas of low to moderate relief along perennial streams and are mostly saturated with water. Dye recovery rates are commonly from 0.1–1% for permanently saturated epikarstic zones.

GROUNDWATER TRANSPORT IN KARST SYSTEMS

Before conceptual models of aquifer flow are discussed, one must first define the karst aquifer. The textbook definition of an aquifer does not apply to karst landscapes. Freeze and Cherry (21) define an aquifer as a saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients, which means that most or the entire host rock in the aquifer must be saturated, which is typical in clastic rocks. However, this is not the case in karst areas. Drilling can intercept a water filled conduit that has significant quantities of water in one place, whereas another well drilled 20 feet in any direction may come up dry or provide an inadequate source of water. Furthermore, this definition considers the rock adjacent to a cave stream perched above the water table as an aquifer, even though the rock is not saturated (22), which presents a problem because the entire bedrock unit in karst is not completely saturated, as stated by the textbook definition. Therefore, a more precise definition to satisfy the unique hydrology of karst landscapes was required.

A karst aquifer is an aquifer that contains soluble rocks whose permeability structure is dominated by interconnected conduits dissolved from the host rock which are organized to facilitate the circulation of fluid in a downgradient direction wherein the permeability structure evolved as a consequence of dissolution by the fluid (19). Dissolution of the bedrock increases the permeability of karst aquifers through time. The permeability and preferential pathways created within the karst aquifer are dictated by the hydrodynamic characteristics of the flow system, not the inherited geologic fabric (23). The permeability and hydraulic gradient are the dominant forces that determine the location of conduits where driving force that governs conduit localization is the hydraulic gradient (19,24).

Several terms and analytical methods have been used to conceptualize water movement through karst aquifers. Burdon and Papakis (25) applied the terms diffuse circulation, flow through pores and fractures, and concentrated circulation, flow through larger openings to characterize aquifer flow. Ashton (26) used flood pulse analysis to study the behavior within a karst drainage system. Pitty (9) recognized that karst water exists in discrete systems of fissures. Atkinson (27) separated aquifer flow into three components, diffuse, fissure, and conduit flow. Quinlan and Ewers (28) proposed granular, diffuse, fracture, and conduit flow.

White (29) was the first to develop an oversimplified series of conceptual models for carbonate aquifer flow based on hydrogeology. He proposed two end member aquifer types: conduit flow and diffuse flow. Conduit flow systems form in areas of mature karst and have well-integrated solution channels ranging in size from small pipes to large caves (30). Response to storms is rapid, causes turbulent flow; water can reach velocities of 10^{-3} to 10^{-1} meters per second (22) and has an almost insignificant low-flow hydraulic gradient (31). However, conduit flow represents only a small portion of the aquifer porosity. It has been demonstrated from case studies that enhancement of porosity by dissolution in unconfined carbonate aquifers is relatively minor whereas enhancement of permeability is considerable because dissolution has created an efficient dendritic network of interconnecting channels that can convey 94% or more of the flow in the aquifer (32). Aquifer storage is relatively low in conduit flow systems.

Diffuse flow systems commonly occur in areas of less mature karst. Diffuse flow can occur as fracture flow in dense limestones or intergranular flow in porous limestones. These systems exhibit laminar to slightly turbulent flow through a system of small discrete pathways (widened joints or bedding planes) that are being dissolutionally enlarged extremely slowly (33). Velocities can reach 10^{-8} to 10^{-2} meters per second (22), and response to storms is less than that of conduit flow aquifers. Aquifer storage is higher in diffuse flow systems.

White (34) revised his conceptual model from 1969 to consider the effect of relief, geologic structure, and the aerial extent of the aquifer on its development. The most important conclusion from the study was that recharge was a key factor to differentiate between conduit and diffuse flow aquifers. However, White's conceptual model did not quantify the amount of diffuse and conduit flow in the aquifer. In recognition of this, Atkinson (13) studied the Cheddar Spring catchment within the carboniferous limestone of the Mendip Hills in Great Britain to determine the proportions of conduit flow and diffuse flow within an aquifer. Results indicated that the majority of true groundwater occurs within narrow fissures (diffuse flow), whereas most of the water is transported through the conduits. Recharge to the conduits is derived from quick flow as well as water draining from the diffuse portion of the aquifer. Conduit flow probably accounts for 60–80% of the water transmitted in the aquifer (13).

Quinlan et al. (6) developed a conceptual model that recognized recharge, flow, and storage as the primary components of the classification. They proposed four dominant aquifer types: hypersensitive aquifers, very sensitive aquifers, moderately sensitive aquifers, and slightly sensitive nonkarst aquifers. Each aquifer type describes the aquifer's sensitivity to contamination.

Worthington (35) reported that the threshold passage diameter for conduit flow in a karst aquifer is about 10 mm and that maximum diffuse flow velocities are $<10^{-2}$ m s^{-1} and $<10^{-6}$ m^3 s^{-1} of diffuse flow in a fissure. Because the mean discharges of most karst springs are greater

than 10^{-4} $m^3 s^{-1}$, this indicates that these springs are discharging from conduits, that the term diffuse karstic aquifer is a contradiction in terms, and that all karst springs are conduit springs. White (36) agreed with Worthington that the term "diffuse" as applied to spring flow may not be appropriate.

There is agreement among investigators today that karst aquifers consist of a combination of highly anisotropic flow routes and should be classified as triple porosity aquifers (7,37–40). Porosity exists within the rock matrix, in fractures, and in conduits. Matrix porosity refers to water that moves through the intergranular pores in the bedrock. Fracture porosity refers to water movement through fractures and bedding plane partings with the bedrock. Dissolution may or may not have taken place. Conduit or channel porosity refers to the movement of water through dissolutionally widened pathways that commonly have greater flow velocities than those of fracture porosity. Water moving through cave streams is an example of channel porosity.

Worthington et al. (32,38) provided credible support for a triple porosity model in unconfined carbonate aquifers. Case studies were examined in four contrasting carbonate aquifers in the Lower Paleozoic dolostone of Ontario, Canada; the Upper Paleozoic limestone of the Mammoth Cave area in Kentucky in the United States; the English chalk of Great Britain; and the Cenozoic limestone of the Yucatan Peninsula in Mexico. Results demonstrated that at least 96% of the storage in all four aquifers was in the matrix portion of the rock (32) and 94% or more of the flow was through the interconnected network of channels (conduits) within the aquifers.

GROUNDWATER STORAGE IN KARST SYSTEMS

The volume of water within a karst aquifer is commonly defined as storage. Because the karst aquifer is considered to have triple porosity, water in storage can be found in the rock matrix, within fractures that have undergone limited dissolution, and in larger channels where significant dissolution has occurred. Storage depends primarily on such factors as hydraulic gradient, bedrock composition, and the degree of karstification within the flow system. Just like recharge and flow, aquifer storage falls within a continuum. The following studies represent the various conceptual models proposed to characterize karst aquifer storage.

Aley (11) developed a predictive hydrologic model to evaluate the effects of land use and management on the quantity and quality of water from Ozark springs. The model was the result of a study conducted in the Hurricane Creek topographic basin in southern Missouri. Aley stressed that groundwater movement in karst areas cannot be compared to water movement in nonkarst areas. Typical groundwater movement in nonkarst areas is less that 10 feet per year and under such conditions it seems proper to view groundwater as water in storage (11). However, water movement in karst, as substantiated by numerous dye traces, can be several orders of magnitude greater than that in nonkarst areas; flow rates are up to 1 mile per day through conduits and cave streams. As a result, Aley divided groundwater movement into two components within a continuum. Water moving at rates greater than 1 foot per hour was considered "water in transit," while water moving less than 1 foot per hour was "water in storage."

Gunn (41) summarized the work of previous researchers that characterized karst aquifer storage. All studies relied on the importance of storage in the unsaturated zone and recognized four major areas of storage or stores: the soil and superficial deposits, the epikarst, water filled conduits in the phreatic zone along with associated solutionally enlarged fissures and bedding planes, and the saturated rock mass.

Smart and Hobbs (15) proposed that storage, just like recharge and flow type, fell within a continuum that has two end members: unsaturated storage and permanently saturated storage, where a seasonally saturated storage component is the central zone. The model was developed to conceptualize aquifer flow within the unsaturated and saturated zones. Two dominant types of storage were recognized in the saturated zone: dynamic storage and perennial storage. Dynamic storage occurs above base level in unconfined aquifers and flows under gravity to provide discharge at springs; storage is relatively low due to steeper hydraulic gradients. Perennial storage occurs below base level in unconfined aquifers and has a greater volume of water than dynamic storage. Due to the lower hydraulic gradients in this portion of the aquifer, storage is generally higher.

Quinlan et al. (6) modified the Smart and Hobbs model and proposed three distinct zones of storage within the karst aquifer system. The zone of limited storage, the low-end member, is confined to the soil and epikarstic zone, predominately the unsaturated zone. The second zone is identical to the zone of limited storage but a seasonally saturated zone is added. The high-end member comprises aquifers that have an unsaturated zone, a seasonally inundated saturated zone, and either perennial storage in a confined aquifer or a water table aquifer that extends well below spring level (6).

GROUNDWATER DISCHARGE FROM KARST SYSTEMS

Springs represent the pulse of a karst aquifer. For many years, investigators wrestled to find the mechanism that causes variations in spring chemistry. Analysis of spring flow and water chemistry have been the primary techniques used for karst aquifer characterization. Jakucs (8) suggested that recharge type was an important factor that influenced spring chemistry variation; springs that had high chemical variation were related to autogenic percolation recharge, whereas springs that had low chemical variation were associated with concentrated allogenic recharge. Pitty (9) stressed that the percentage of different recharge waters (allogenic recharge via sinking streams and autogenic recharge via percolation) influenced spring chemistry variation. Newson (42) recognized a linear correlation between the percentage of allogenic recharge in a spring's catchment to the coefficient of variation (COV) of hardness at springs; as the percentage of allogenic recharge increased, so did the COV of hardness

at the springs. Additionally, Newson found that spring total hardness could be expressed in terms of a simple two-component mixing model (35). From the study of total hardness of springs, cave streams, and percolation water in the Mendip Hills of England, he determined the percentage of allogenic and autogenic recharge received at local springs.

Shuster and White (33) conducted a study within the folded Ordovician dolomites and limestones of central Pennsylvania using 14 springs. They suggested that flow type within the aquifer controlled the chemical character of the springs and used the COV of hardness as the principal statistical parameter. The first group of springs that discharged from fractured dolomites had a constant hardness and a COV of less than 5%, displayed a nearly constant chemical character regardless of season or storm, was recharged by diffuse infiltration, and they called them diffuse flow springs. The second group of springs discharged from karstic limestones with internal recharge from sinkholes. Hardness was very variable throughout the year and had a COV greater than 10%; they called these conduit flow springs. Jacobson and Langmuir (43) produced similar results for chemical variation at carbonate springs.

The conduit flow springs were generally undersaturated with respect to calcite. Springs that discharge from conduit flow systems are flashy based on the high ratios between maximum discharge and base flow discharge. Flow is turbulent, whereas water hardness is low at a mean of 100 ppm, but highly variable. The COV of hardness ranges from 10 to 25% or more (28,44). Groundwater flow velocities are commonly rapid, and water can travel up to a mile per day. Conduit flow springs were considered outlets from conduit flow systems and are described by pipe and channel equations (45).

The diffuse flow springs were generally saturated with respect to calcite. Turbidity is low, but water hardness may exceed 300 ppm; the COV of hardness is typically less than 5% (28). Discharge is nonflashy, groundwater flow is much slower, and water can take months to travel short distances. Diffuse flow springs were considered outlets from diffuse flow systems.

The use of hardness variation to distinguish between flow types appeared to work well for the study conducted by White for small drainage basins in temperate climates. However, larger drainage basins show less variation when springs are fed by conduits (4). It is likely that this is due to longer residence times and the contribution of other waters whose chemistry is different from that of other parts of the basin. Subsequent studies found that the binary classification developed by Shuster and White (33) was not applicable to all karst settings.

Aley (11) applied different terms to Missouri springs. As previously discussed, he divided groundwater in storage into transit water and storage water, which resulted in two spring classifications: high transit springs and high storage springs. High transit springs are similar to conduit flow springs; water is derived from areas of discrete recharge. High storage springs are similar to diffuse flow springs; water is derived from areas of diffuse recharge.

Smart and Hobbs (15) recognized that flow type alone is not responsible for the chemical variation at springs and incorporated recharge and storage components into a simple conceptual model. From this model, it is possible to map the different types of carbonate aquifers. Scanlon and Thrailkill (46) conducted a study in the relatively flat limestones and shales of the Inner Bluegrass karst region of central Kentucky. The physical and chemical characteristics of springs from the Inner Bluegrass were compared with those from the study conducted by Schuster and White (33). Results from their study showed that seasonal water chemistry variation in major low level springs and local high level springs did not correspond with the physical characteristics of the springs over time. Chemical similarities were attributed to the mode of recharge. The difference in bedrock types and structure between the two studies was considered a control factor for the relationships between the physical and chemical attributes of the springs.

Worthington et al. (47) performed a statistical analysis using data from 39 springs in six countries using temperate climates taken from the literature. Results from their study demonstrated no evidence that hardness variation was an indicator of flow conditions within an aquifer, as suggested by Schuster and White, and that greater than 75% of hardness variation was explained by recharge type. Currently, it is recognized that recharge type and storage both play an integral role in the chemical variations at karst springs.

SPRING HYDROGRAPHS AND CHEMOGRAPHS

Spring hydrograph and chemograph analysis have been widely used in concert to gain insight into the hydraulics of the karst groundwater system. A hydrograph is a time series plot of spring discharge versus time. Discharge is plotted on the vertical axis and time on the horizontal axis. The shape of the hydrograph recorded at a spring is a unique reflection of the response of the aquifer to recharge (3,5). A spring hydrograph is divided into three main responses to a discharge event: lag time, the rising limb, and the falling limb. Each of these three components is shown in Fig. 1. The lag time shows the spring discharge before the recharge reaches the spring. The rising limb represents the first arrival and increase of discharge at the spring. The peak of the graph indicates the maximum amount of spring discharge from the storm. The water that flows at the spring at this time does not reflect recharge water; it is older water in the most downstream part of the aquifer that is displaced from storage (49), which represents the pulse-through event, the arrival of energy at the spring from the storm. The falling limb, more commonly called the recession curve, shows the spring discharge as it returns to prestorm conditions.

The recession limb typically consists of a fast response segment and a slow response segment, as shown when the recession limb is plotted on semilogarithmic paper. The fast response segment can be assigned to the conduit portion of the aquifer that drains rapidly when the storm input ceases; the slow response segment can be assigned

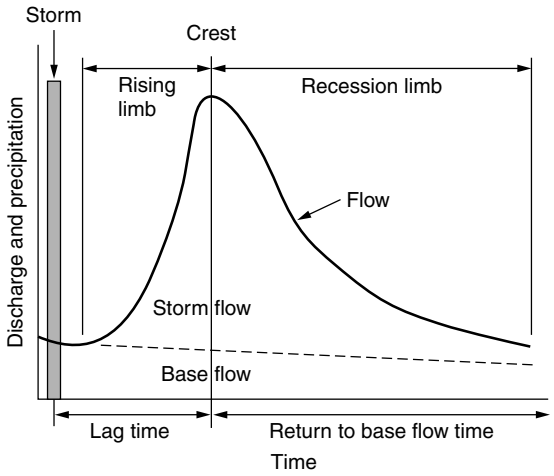


Figure 1. Example of a hypothetical hydrograph (taken from Ref. 48).

to the draining of the fracture system into the conduit after the conduit has emptied (7).

Chemographs show measured concentrations of dissolved chemical parameters in spring water over time. Although many parameters can be used to characterize the chemistry at karst springs, common parameters include turbidity, dissolved oxygen, hardness, stable isotopes, specific conductance, and temperature (5). Figure 2 shows a hydrograph and chemograph from Komlos spring in Hungary. The graph generally shows the increase in parameter concentration after the arrival of the storm pulse wave. Thus, spring hydrographs show a pattern composed of sequential and sometimes superimposed pulses of water of different quality and quantity from different stores and tributary inputs (5).

GROUNDWATER TRACING THROUGH KARST SYSTEMS

Water tracing in karst landscapes has proven to be an effective tool for aquifer characterization. A variety of tracing agents have been used throughout the years to trace and estimate groundwater flow velocities from discrete recharge areas to springs. Tracing agents used include bacteria, surfactants (wetting agents), salts, ions in solution, radioactive isotopes, environmental isotopes, club moss spores, nonfluorescent dyes, and fluorescent dyes (50). Although all agents have been widely used to trace water through karst systems, the following discussion focuses on the use of fluorescent dyes.

Tracing groundwater flow routes with fluorescent dyes is highly successful because the dyes are easily detected in concentrations that are one to three orders of magnitude less than those at which nonfluorescent dyes can be measured spectrometrically (6). Furthermore, fluorescent dyes perform well in different hydrogeologic settings and can be used effectively to trace water from subsurface to surface water bodies.

Dye tracing has been employed extensively in karst areas for a wide variety of purposes. Some of the uses of dye tracing include delineation of spring recharge areas and subsurface basins, determination of site-specific hydrology, estimation of groundwater flow velocities, detection of leakage from residential sewage disposal systems and dam sites, and identification of sources of potential pollution from hazardous waste sites. Dye tracing has also been used successfully during highway corridor studies to identify areas sensitive to accidental spills (51).

Selection of dye introduction points, the manner in which the dyes are introduced, the sampling strategy employed, and the analytical approach used must be tailored to the hydrogeologic setting and the issues of

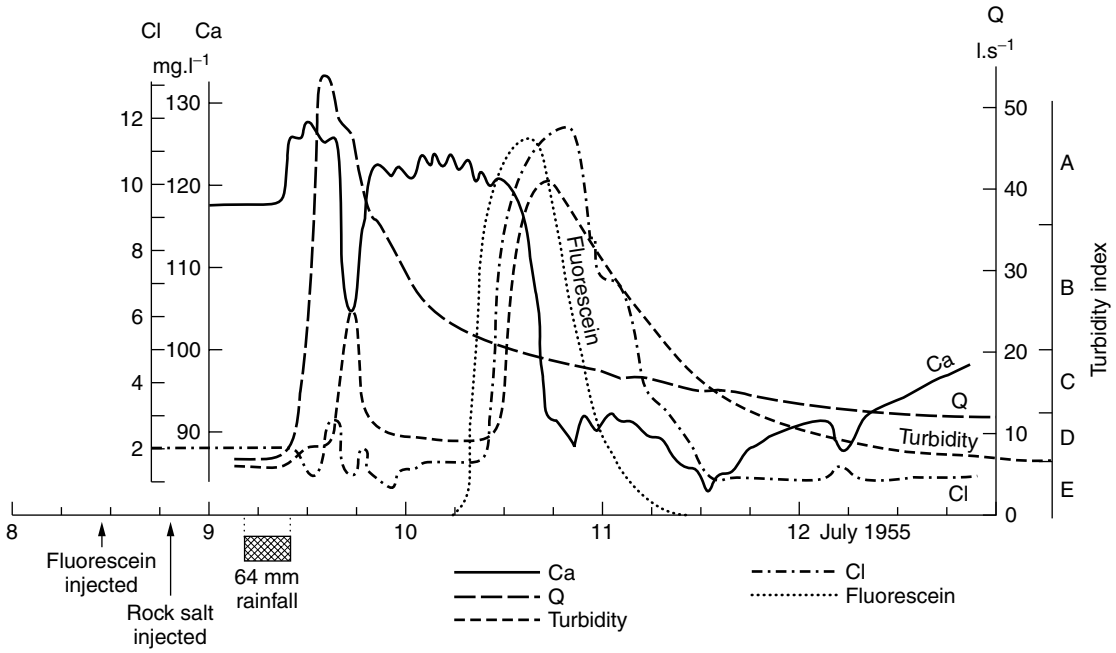


Figure 2. Hydrograph and chemograph of Komlos spring, Hungary (taken from Ref. 8).

concern (52). The amount of dye used for tracing studies is usually based on professional experience because there is no credible standard equation for estimating the dye quantities needed for groundwater tracing. One well-designed dye trace, properly done and correctly interpreted, is worth 1000 expert opinions or 100 computer simulations of groundwater flow (53). Some excellent sources for discussions of groundwater tracing in karst systems include Aley (20,52,54), Smart and Laidlaw (55), Mull et al. (56), Alexander and Quinlan (57), and Kass (50).

VULNERABILITY OF KARST LANDSCAPES

An old adage is that whatever goes up comes down. In karst areas, whatever goes down comes up through a cave, a spring or a well (58). In areas of localized recharge in karst areas, surface water is directly connected to the groundwater flow system. Karst aquifers are highly vulnerable to contamination because they commonly transport water at rates several orders of magnitude greater than those encountered in nonkarst groundwater systems, provide minimum adsorption or other natural cleansing processes, commonly support flow in the turbulent regime, and are too large to provide effective filtration for most pathogens (16). Another concern regarding contamination in karst landscapes is that contamination can enter the subsurface through one location and discharge at multiple spring locations miles apart from each other. Improved adaptation to karst conditions requires that land use and land management decisions simultaneously consider both surface and subsurface resources and conditions (59). Unfortunately, development on karst will continue, but with the implementation of proper land use strategies impacts to this vulnerable landscape can be avoided or at best minimized.

Spores can be dyed various colors and injected into different discrete recharge areas at the same time. Once collected, samples are detected with a microscope. Analysis and preparation techniques require skilled personnel and considerable care (59). An advantage to using spores rather than dyes is that they can be injected in up to six input sites and traced simultaneously, whereas only three sites can be used using during fluorescent dye traces (5).

KARST MODELING

Karst modeling involves developing of methods for reproducing karst processes in the laboratory, so that the natural phenomena can be understood better (60). Karst modeling can include interpretation of several aspects of the karst environment; some of them include groundwater geochemistry and flow patterns, distribution of porosity and permeability in the karst aquifer, fate and transport of contaminants, and groundwater monitoring and remediation strategies. Conceptual, analytical, digital, statistical, and scale models have been used to understand the nature of karst processes better.

Conceptual models are built on ideas based on field observation along with an understanding of relevant physical and chemical characteristics of the system. For a conceptual model to be sound, it must stand alone without quantitative support (60). Analytical models use mathematical equations based on physical laws to model natural phenomena. Equations of fluid flow, chemical kinetics, and conservation of mass are commonly used. When analytical models begin to approach the complexity of real systems, the only way to solve them quantitatively is to break the model into discrete space and time increments so that each increment can then be solved simultaneously (60).

Digital models come in two formats: commercial software for interpreting groundwater flow patterns and chemical equilibria and specialized numerical models designed to investigate complex physical relationships, for example, in the evolution of karst conduits (1). Statistical models are based on measured field data. A hypothesis is developed, and a statistical analysis is conducted to use the model to predict or extrapolate the occurrence of karst features or processes. Scale modeling refers to the actual construction of a model to evaluate physical processes. Sources that discuss karst modeling include White (29), Curl (61), Mangin (62,63), Gunn (64), Clemens et al. (65), and Palmer (60).

BIBLIOGRAPHY

1. Palmer, A.N. (1991). Origin and morphology of limestone caves. *Geological Society of America. Bulletin* **103**(1): 1–21.
2. Milanovic, P.T. (1981). *Karst Hydrogeology*. Water Resources Publications, p. 434.
3. Bonacci, O. (1987). *Karst Hydrology, With Specific Reference to the Dianric Karst*. Springer-Verlag, New York, p. 184.
4. White, W. (1988). *Geomorphology and Hydrology of Karst Terrains*. Oxford University Press, Oxford, UK, p. 464.
5. Ford, D. and Williams., P. (1989). *Karst Geomorphology and Hydrology*. Chapman and Hall, London, p. 701
6. Quinlan, J.F. et al. (1992). Recommended administrative/regulatory definition of karst aquifer, principles for classification of carbonate aquifers, practical evaluation of vulnerability of karst aquifers, and determination of optimal sampling frequency at springs. In: *Conference on Hydrogeology, Ecology, Monitoring, and Management of Groundwater in Karst Terranes Proceedings*. J. Quinlan and A. Stanley (Eds.). National Groundwater Association, pp. 573–635.
7. White, W. (1999). Groundwater flow in karstic aquifers. In: *The Handbook of Groundwater Engineering*. J. Delleur (Ed.). CRC Press, Boca Raton, FL.
8. Jakucs, L. (1959). Neue methoden der hohlenforchung in ungarnund ihre ergebnisse. *Die Hohle* **10**(4): 88–98.
9. Pitty, A.F. (1966). *An approach to the study of karst water, illustrated by results from Poole's Cavern, Buxton*. University of Hull, Occasional Paper in Geography No. 5.
10. Gunn, J.A. (1983). Point recharge of limestone aquifers—a model from New Zealand karst. *Journal of Hydrology* **61**: 19–29.
11. Aley, T. (1978). Ozark hydrology: a predictive model. Missouri Speleology. *Journal of the Missouri Speleological Survey* **18**: 185.
12. White, W. (1990). Surface and near-surface karst landforms. In: *Groundwater Geomorphology: The Role of Subsurface Water in Earth-Surface Processes and Landforms*.

C.G. Higgins and D.R. Coates. (Eds.). Geological Society of America Special Paper 252, pp. 157–175.

13. Atkinson, T.C. (1977). Diffuse flow and conduit flow in limestone terrain in mendip hills, somerset (Great Britain). *Journal of Hydrology* **35**: 93–110.
14. Palmer, A.N. (1984). Geomorphic interpretation of karst features. In: *Groundwater as a Geomorphic Agent*. R.G. Lafleur (Ed.). Allen and Unwin, p. 37.
15. Smart, P.L. and Hobbs, S.L. (1986). Characteristics of carbonate aquifers: a conceptual model. In: *Environmental Problems in Karst and Their Solutions Conference Proceedings*. National Water Well Association, pp. 1–14.
16. Aley, T. (2000). Karst systems. In: *The Standard Handbook of Environmental Science, Health, and Technology*. H. Jay and J.K. Lehr (Eds.). McGraw-Hill, New York, pp. 19.1–19.10.
17. Williams, P.W. (1985). *Subcutaneous Hydrology and the Development of Doline and Cockpit Karst*. Zeitschrift fur Geomorphologie, pp. 463–482.
18. Williams, P.W. (1983). The role of the subcutaneous zone in karst hydrology. *Journal of Hydrology* **61**: 45–67.
19. Huntoon, P. (1994). Is it appropriate to apply porous media groundwater circulation models to karstic aquifers? In: *Assessment of Models for Groundwater resources Analysis and Management Conference Proceedings*. Lewis, Boca Raton, FL, pp. 1–16.
20. Aley, T. (1997). Groundwater tracing in the epikarst. In: *The Engineering Geology and Hydrogeology of Karst Terranes*. Beck and Stephenson (Eds.). Balkema, Rotterdam, pp. 207–211.
21. Freeze, R.A. and J.A. Cherry. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ, p. 604.
22. Quinlan et al. (1992). *Rationale for the Design of Cost-Effective Groundwater Monitoring Systems in Limestone and Dolomite Terranes: Cost Effective as Conceived is Not Cost Effective as Built if the System Design and Sampling Frequency Inadequately Consider Site Hydrogeology*. U.S. Environmental Protection Agency, pp. 552–570.
23. Huntoon, P. (1995). Gradient controlled caves: trapper-medicine lodge area, bighorn basin, Wyoming. *Groundwater* **23**: 443–448.
24. Huntoon, P. (1999). Karstic permeability: organized flow pathways created by circulation. In: *Karst Modeling*. Karst Water Institute Special Publication 5, pp. 79–81.
25. Burdon, D.J. and Papakis, N. (1963). *Handbook of Karst Hydrogeology*. Institute for Geology and Subsurface Research/ United Nations Food and Agricultural Organization, Athens, p. 276.
26. Ashton, K. (1966). The analysis of flow data from karst drainage systems. *Transactions of the Cave Research Group of Great Britain* **7**(2): 163–203.
27. Atkinson, T.C. (1985). Present and future directions in karst hydrogeology. *Annales de la Societe Geologique de Belgigue* **108**: 293–296.
28. Quinlan, J.F. and Ewers, R.O. (1985). Groundwater flow in limestone terranes: strategy rationale and procedure for reliable, efficient monitoring of groundwater quality in karst areas. *National Symposium and Exposition on Aquifer Restoration and Groundwater Monitoring, Proceedings*. National Water Well Association, pp. 197–234.
29. White, W. (1969). *Conceptual Models for Carbonate Aquifers. Groundwater* **7**, (3).
30. Crowther, J. (1983). Hydrology of autogenic percolation systems in some tropical karst outcrops, West Malaysia. *Journal of Hydrology* **60**: 227–242.
31. Field, M. (1992). Karst hydrology and chemical contamination. *Journal of Environmental Systems* **22**(1): 1–26.
32. Worthington, S. et al. (2001). Characteristics of porosity and permeability enhancement in unconfined carbonate aquifers due to the development of dissolutional channel systems. In: *Present State and Future Trends of Karst Studies Proceedings*. G. Gunay, K. Johnson, D. Ford, and A.I. Johnson (Eds.). Technical Documents in Hydrology, Vol. 1, No. 49, UNESCO, pp. 13–29.
33. Shuster, E.T. and White, W. (1971). Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate springs. *Journal of Hydrology* **14**: 93–128.
34. White, W. (1977). Conceptual models for carbonate aquifers: revisited. In: *Hydrologic Problems in Karst Regions*. R.R. Dilamarter and S.C. Csallany (Eds.). Western Kentucky University, pp. 176–187.
35. Worthington, S. (1991). *Karst Hydrology of the Canadian Rocky Mountains*. Unpublished Ph.D. Dissertation. Department of Geography, McMaster University, Hamilton, Ontario, Canada.
36. White, W. (1999). Karst hydrology: Recent developments and open questions. In: *Hydrogeology and Engineering Geology of Sinkholes and Karst Proceedings*. Rotterdam, Balkema, pp. 3–21.
37. Worthington, S. (1999). A comprehensive strategy for understanding flow in carbonate aquifers. In: *Karst Modeling*. A.N. Palmer, M.V. Palmer, and I.D. Sasowsky (Eds.). Karst Waters Institute, Special Publication No. 5, pp. 30–37.
38. Worthington et al. (2000). Porosity and permeability enhancement in unconfined carbonate aquifers as a result of solution. In: *Speleogenesis: Evolution of Karst Aquifers*. Klimchock et al. (Eds.). National Speleological Society, Inc., pp. 463–471.
39. White, W. and White, E. (2000–2001). Conduit fragmentation, cave patterns, and the localization of karst groundwater basins: the appalachians as a test case. *Theoretical and Applied Karstology* **13–14**: 9–23.
40. Martin, J.B. and Screaton, E.J. (2001). Exchange of matrix and conduit water with examples from the floridian aquifer. In: *U.S. Geological Survey Karst Interest Group Proceedings*. Water Resources Investigations Report 01–4011, pp. 38–44.
41. Gunn, J.A. (1986). A conceptual model for conduit flow dominated karst aquifers. In: *Karst Water Resources Proceedings*. International Association of Hydrological Sciences, Publication No. 161, pp. 587–596.
42. Newson, M.D. (1971). A model of subterranean limestone erosion in the british isles based on hydrology. *Institute of British Geographers, Transactions* **54**: 51–70.
43. Jacobson, R.L. and Langmuir, D.L. (1974). Controls on the quality variations of some carbonate spring waters. *Journal of Hydrology* **23**: 247–265.
44. Quinlan, J. (1989). *Groundwater Monitoring in Karst Terranes, Recommended Protocols and Implicit Assumptions*. US Environmental Protection Agency.
45. Gale, S.J. (1984). The hydraulics of conduit flow in carbonate aquifers. *Journal of Hydrology* **70**: 309–327.
46. Scanlon, B.R. and Thrailkill, J. (1987). Chemical similarities among physically distinct spring types in a karst terrain. *Journal of Hydrology* **89**: 259–279.
47. Worthington et al. (1992). Geochemistry of springs in temperate carbonate aquifers: recharge type explains most of the variation. In: *Colloque d'Hydrologie en pays Calcaire et en Millieu Fissure (5th Neuchatel Switzerland), Proceedings*.

Annales Scientifiques de l'Universitie de Besancon, Geologie—Memoires Hors Series, No. 11, pp. 341–347.

48. Jones, W.K. (1997). *Karst Hydrology Atlas of West Virginia*. Karst Waters Institute, Special Publication 4, p. 111.
49. Huntoon, P.W. (2000). Variability of karstic permeability between unconfined and confined aquifers, Grand Canyon region, Arizona. *Environmental and Engineering Geoscience* **6**(2): 155–170.
50. Kass, W. (1998). *Tracing Technique in Geohydrology*. A.A. Balkema, Rotterdam, p. 581.
51. Bednar, D., Jr. and Aley, T., (2001). Groundwater dye tracing: an effective tool to use during the highway development process to avoid or minimize impacts to karst groundwater resources. In: *Geotechnical and Environmental Applications of Karst Geology and Hydrology, Proceedings*. B.F. Beck and J.G. Herring (Eds.). A.A. Balkema, Rotterdam, pp. 201–207.
52. Aley, T. (1999). *The Ozark Underground Laboratory's Groundwater Tracing Handbook*. The Ozark Underground Laboratory, p. 35.
53. Quinlan et al. (1988). How to Use Groundwater Tracing to "Prove" that Leakage of Harmful Materials From a Site in a Karst Terrane Will Not Occur. In: *Environmental Problems in Karst Terranes and Their Solutions Conference Proceedings*. National Water Well Association, pp. 289–301.
54. Aley, T. (1976). The water tracer's cookbook. *Journal of the Missouri Speleological Survey* **16**(6).
55. Smart, P.L. and Laidlaw, I.M.S. (1977). An evaluation of some fluorescent dyes for water tracing. *Water Resources Research* **131**: 15–33.
56. Mull, D.S., Liebermann, T.D., Smoot J.L., and Woosley, L.H., Jr. (1988). *Application of Dye Tracing Techniques for Determining Solute-Transport Characteristics of Ground Water in Karst Terranes*. EPA 904/6-88-001, United States Environmental Protection Agency.
57. Alexander, C.E. and Quinlan, J.F. (1992). *Practical Tracing of Groundwater, with Emphasis on Karst Terranes*. Geological Society of America.
58. Aley, T. (2000). Karst Groundwater. *Missouri Conservationist*, **61**, (3): 8–11.
59. Aley, T. (2000). Water and Land-Use Problems in areas of Conduit Aquifers. In: *Speleogenesis: Evolution of Karst Aquifers*. A.B. Klimchouk et al. (Eds.). National Speleological Society. pp. 481–484.
60. Palmer, A.N. (1999). Introduction. In: *Karst Modeling*. Karst Waters Institute Special Publication No. 5. A.N. Palmer, M.V. Palmer, and I.D. Sasowsky (Eds.). Karst Waters Institute, pp. 1–9.
61. Curl, R.L. (1974). Deducing flow velocity in cave conduits from scallops. *National Speleological Society Bulletin* **36**: 1–5.
62. Mangin, A. (1974–1975). Contribution a l etude hydrodynamique des aquifers kartiques. *Ann Speleol* **29**(3/4): 283–601; **30**(1): 21–124.
63. Mangin, A. (1994). Basic and applied hydrogeological research in french karstic areas. In: *COST 65 ACTION, Hydrogeological Aspects of Groundwater Protection in Karstic Area*. N. Crampon and M. Bakalowicz (Eds.). p. 11–24.
64. Gunn, J.A. (1985). Conceptual model for conduit flow dominate aquifers. In: *Karst Water Resources Proceedings. International Association of Hydrological Science*. Publication No. 161, pp. 587–596.
65. Clemens, T. et al. (1999). Simulation of the development of karst aquifers: role of the epikarst. *International Journal of Earth Science* **88**(1): 157–162.

KARST TOPOGRAPHY

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Karst is an irregularly shaped area of land where underground drainage dominates and has resulted in dissolving the bedrock to form distinctive surface and subsurface features. Karst predominately develops on lands underlain by soluble bedrock such as limestone and dolomite, but can also form in marble, gypsum, and halite. Due to differences in climate, cover, rock type, hydrology, and geologic structure, some areas show significant expression of karst development at the surface, and others show no obvious signs at all. Chemical solution of the bedrock by groundwater leads to the formation of open passageways into and through the subsurface. The degree of development of these features varies greatly from one region to another (1).

The term karst is derived from a plateau region located along the northeastern shore of the Adriatic Sea between Slovenia and Italy. Karst topography, it is estimated, covers about 20% of the earth's surface and can be found in the United States, Russia, the Baltic Republics, Great Britain, Japan, China, Vietnam, Australia, Brazil, and Europe. About 25% of the United States is karst, and it is estimated that 40% of the land east of the Mississippi River is karst. Karst topography occurs in areas of Kentucky, Tennessee, southern Indiana, and central and northern Florida.

BEDROCK DISSOLUTION

The development of karst topography begins with the first drop of precipitation from the atmosphere. Water falls through the atmosphere and reacts with carbon dioxide to produce carbonic acid. As the water infiltrates through the soil horizon, the amount of carbonic acid increases due to reactions with organic matter. Water enters the soluble rock through bedding plains and joints and slowly breaks down and transports dissolved mineral matter into the epikarst.

The epikarst or epikarstic zone (sometimes called the subcutaneous zone) is the dissolutionally weathered upper portion of the bedrock that can vary in thickness from zero to about 100 feet or more (2). Groundwater typically moves horizontally in multiple directions untill it reaches enlarged vertical fissures or shafts where the water moves into deeper portions of the karst aquifer system. Depending on topography, the epikarst can store appreciable amounts of water or transmit water quickly. Water storage is greater in gentle topography as opposed to rapid flow in steeper areas. The intensity of epikarstic development, which can be expressed as a percentage of the bedrock that has been removed by dissolution, is highly variable. This percentage can range from 1 to more than 50% (3). However, many epikarstic zones contain some degree of sedimentation. This can range anywhere from 5 to more than 95%.

Based on the results of about 1,000 positive groundwater trace, Aley (3) divided the epikarst into three hydrological types based on water storage capability. Rapid draining epikarsts are characterized by low water storage and voids that are relatively free of fine textured sediment. These areas typically occur in areas of high relief and where the soluble purity of the bedrock is high. Water that is stored seasonally and after major storms is stored in a seasonally saturated epikarst. In these areas, voids are commonly partially or completely filled with fine textured sediment, occur in humid climate or moderate relief, and the elevation of the epikarst is greater than the elevation of the local perennial streams. Perennial saturated epikarsts contain constant water storage, occur in humid climates and areas of low to moderate relief, and are located along perennial streams. However, all epikarstic zones would more than likely contain a combination of the above.

SURFACE FEATURES IN KARST

Dissolution of the bedrock underground can sometimes produce features that are visible at the surface. Sinkholes are the most common surface features in karst areas. However, the lack of sinkholes at the surface does not indicate a lack of karstification in the subsurface. Sinkholes are bowl-shaped depressions on the surface of the earth that vary in size up to 100 meters deep and 1000 meters in diameter. Subsidence sinkholes form from the gradual movement of soil into the bedrock through solutionally enlarged preferential flow routes in the bedrock (Figs. 1a, 1b, and 1c). As soil moves into the bedrock over time, a circular depression forms at the surface. Collapse sinkholes form when the roof of underlying cavities in the bedrock becomes weak from the weight of the overburden and collapses (Figs. 2a, 2b, and 2c). Caprock protected sinks occur when a sandstone unit located immediately above limestone collapses into the cavernous limestone. The rim of the depression is protected by the sandstone, so that these sinkholes tend to be very deep and steep-sided. Compound sinks form as individual sinkholes grow to form a larger sinkhole that has multiple drainage points.

Karren is another distinctive surface feature. As water flows over soluble rocks on the surface, small-scale dissolution grooves, pits, or channels form. Karren comes in many different patterns and is described in detail by Ford and Williams (4). Additionally, karren can form in the subsurface on bedrock beneath a soil cover.

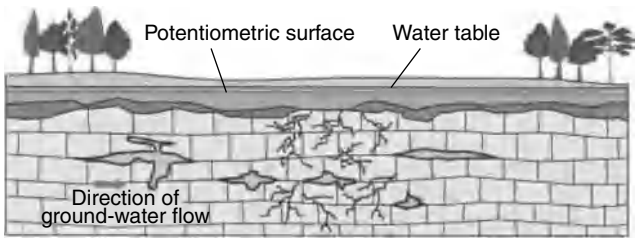


Figure 1(a). Formation of a subsidence sinkhole. From U.S. Geological Survery Report by Galloway et al. (1999).

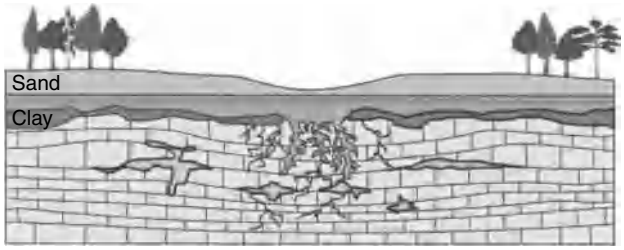


Figure 1(b).

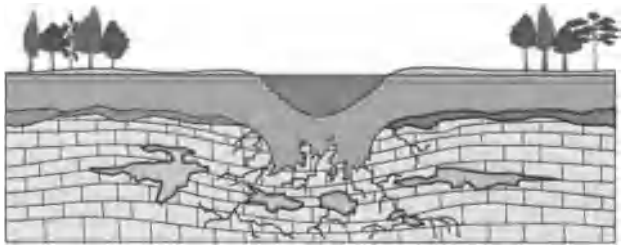


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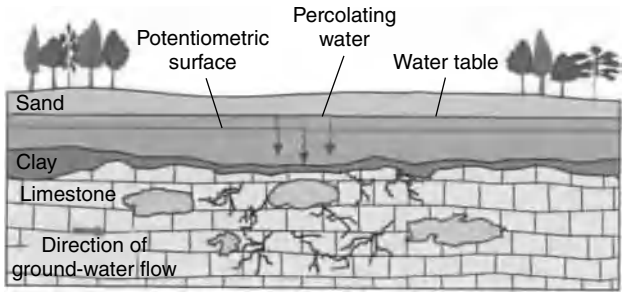


Figure 2(a). Formation of a collapse sinkhole. Form U.S. Gelogical Survery Report by Galloway et al. (1999).

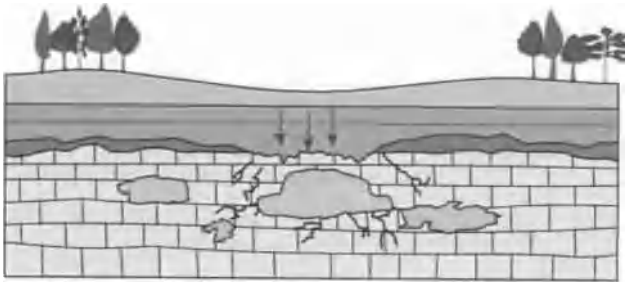


Figure 2(b).

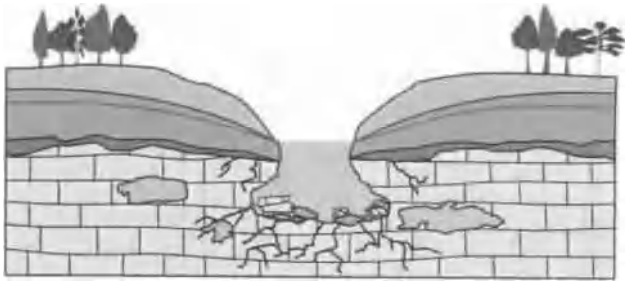


Figure 2(c).

KARST VALLEYS

Three types of distinctive valleys exist in karst areas. Some areas of karst were originally overlain by nonsoluble rocks in topographic valleys. Through time, the overlying rock erodes away by stream action to expose the underlying soluble bedrock in the stream channel. Surface water begins to recharge the groundwater flow system, and the capacity of the groundwater flow system increases to a point where it can handle the entire base flow of the stream. The valley maintains its shape, gradient, and channel, but the discharge from the basin is lost to the groundwater flow system, and it is called a dry valley. Overland flow will occur only during floods. "In some karst river valleys, rivers flow for greater distances before all water is lost to the subsurface at one location. River valleys that end abruptly in this instance are known as blind valleys. The most favorable conditions for the formation of blind valleys are hilly areas of heavy rainfall with well developed streams on impermeable rocks upstream of areas of massive limestone (5)."

Poljes represent another type of karst valley. Meaning "field" in Slovene, poljes are large closed depressions that have well-developed underground drainage systems bounded by steep-sided uplands. Runoff from the surrounding uplands discharges at springs in the polje and forms alluvial streams. These streams sink into caves or swallow holes on the opposite side during periods of low to moderate flow and discharge from them when the groundwater system is at full capacity during periods of high flow.

SPRINGS

Water that disappears into the subsurface in karst areas reappears at the surface at springs. Springs typically discharge along valley floors. Springs can discharge from the contact between two geologic strata, from a solutionally widened opening in the bedrock, or at cave entrances. Quinlan (6) stressed that springs are the pulse of karst aquifers and provide important information about flow regimes. There are two general types of springs in karst areas. Springs that exhibit turbulent flow, respond rapidly to rainfall, and have a highly variable discharge rate are known as diffuse flow springs. Springs that are less turbulent, respond slower to precipitation, and have a low variable discharge rate are called conduit flow springs. However, flow type largely depends on the type of recharge and storage in the karst aquifer as well as the size of the groundwater basin. It must be emphasized that diffuse and conduit flow springs are end members of a continuum and that most springs fall somewhere in the middle (7).

SUBSURFACE FEATURES

Caves and speleothems represent subsurface features in karst areas. A cave is a naturally occurring void in the subsurface that can be easily entered by humans. Caves are formed by the dissolution of the rock along bedding planes and fractures from the circulation of groundwater. Cave formation is affected by such parameters as water quality, tectonics, lithology, topography, geologic structure, climate, and hydrogeologic factors. Additionally, the mode of groundwater recharge helps to enhance cave development.

The shape of cave passageways is dictated by structure and stratigraphy. White (1) placed cave passageways into two broad classes, single conduit and maze passages; each has three distinct geometries. Single conduit caves are classified as those that have linear, angulate, and sinuous passageways. Linear passages are straight without any bends, and the structure of the bedrock controls the path of flow. Angulate passages are characterized by sharp bends and straight segments. Sinuous passages take the pattern of meandering streams, as seen on the surface, that have many curves and few straight segments. Cave patterns found in karst aquifers include branchwork and maze patterns. Sinkholes supply the necessary water flow to form a branchwork (single conduit caves) cave network. In this case, recharge enters the groundwater flow system through several small catchment areas into the subsurface.

Maze-type passages fall into three categories that include network, anastomatic, and spongework mazes. Network mazes consist of intersecting passageways in a uniform grid orientation that are developed by floodwater recharge. This situation is typical where runoff from large areas of insoluble rocks can flow directly into adjacent soluble rocks. The water enters the karst aquifer through a small number of sinking streams each having variable flow. This limited number of input points results in the development of mazes and blind fissures (8). Anastomatic passages look like braided streams on the surface. Spongelike passages are random, interconnected passageways that vary in size and consist of-three-dimensional patterns. The geometry of the cave passage is further dictated by the type of openings through which the water flows, including fractures, bedding plane partings, and intergranular pores.

Speleothems, formerly known as cave formations, form from carbon dioxide rich water that enters the cave atmosphere. Excess carbon dioxide in solution is lost as the groundwater enters the cave atmosphere, and carbonate minerals begin to precipitate out onto the ceiling, walls, or across the floor of the cave. Speleothems are dominantly composed of crystals of calcite and aragonite. Magnesium carbonate deposits are found to a lesser degree. Speleothems are rarely composed of dolomite.

Speleothems are divided into two broad categories, dripstone and flowstone. The common types of dripstones are called stalactites and stalagmites. Stalactites grow as water enters the cave ceiling through joints and bedding-plane partings and slowly drips to the cave floor. Drop by drop, a ring of calcite is deposited to form a hollow tube. Young stalagmites are called soda straws (Fig. 3). Excess water drops onto the floor of the cave and begins to form a mound of calcite known as a stalagmite. Stalagmites form from the cave floor, and successive layers of calcite accumulate upward with time. Sometimes, stalactites and stalagmites come together and form a column. However, this is not always the case. Figure 4 shows an example of a stalactite, stalagmite, and a column.

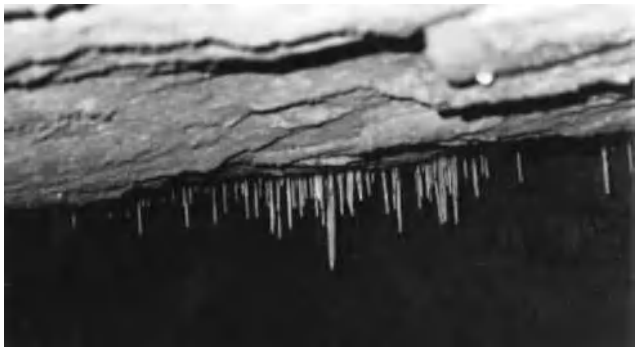


Figure 3. Soda straws at Mystic Caverns, north central Arkansas.



Figure 4. Stalactite, stalagmites, and a column at Mystic Caverns, north central Arkansas.

Flowstone forms as sheet flows across the cave floor or down the walls of the cave. Draperies (Fig. 5), the most spectacular forms of flowstone, are deposited as water flows over a surface on a cave wall that has an abrupt overhang and deposits in thin trails. Other speleothems within the cave environment include moonmilk, cave coral, rimstone dams, and helictites. Moonmilk is a white unconsolidated deposit of carbonate minerals that resembles cottage cheese when wet (1). Cave coral forms in cave pools when the water becomes oversaturated with calcite and the crystals drop out of solution. Rimstone dams (Fig. 6) are found along the cave floor. These features deposit along the edges of water flowing along the cave floor or at the edges of pools of water where carbon dioxide is lost. Helictites (Fig. 7) are known as eccentric speleothems that defy the law of gravity and grow in any direction from solutions fed along tiny capillaries. They are commonly very short and have a sinuous to curvilinear appearance.



Figure 5. Massive draperies at Mammoth Cave Kentucky.



Figure 6. A rimstone dam at Hidden River Cave in north central Arkansas.



Figure 7. Helictites—Mystic Caverns, north central Arkansas.

GROUNDWATER RECHARGE

Four dominant types of groundwater recharge are recognized in karst areas. Diffuse recharge enters the groundwater flow system across a broad area. Discrete recharge, also called concentrated recharge, is restricted to small areas, especially through sinkholes or losing streams. Substantially greater quantities of water per unit area enter the groundwater flow system through discrete recharge areas than through diffuse recharge (9). Usually there are several sinking points, or swallow holes, along the course of sinking streams. Surface water is continually lost to the groundwater flow system throughout the year during periods of moderate and high flow. This occurs because the groundwater flow system has reached full capacity and cannot transmit all surface water flow. However, during the summer months, overland flow decreases, and a portion of the stream becomes lost. This water loss through swallow holes or openings in the underlying bedrock eventually reappears at the surface at springs or multiple springs. Surface water that flows from adjacent non-karst areas onto karst is called allogenic recharge. Precipitation that falls directly on the karst that enters the groundwater flow system is known as autogenic recharge. The former two recharge types describe how the water enters the subsurface while the latter two types refer to the where the water originated.

TYPES OF KARST SETTINGS

Quinlan (10,11) noticed that karst settings vary greatly in appearance and classified them into two major types based on cover type. Covered karsts are areas where the bedrock is covered by some material and not exposed at the surface. Four subcategories of covered karst include mantled karst, buried karst, interstratal karst, and subaqueous karst. Mantled karst occurs when a thick layer of unconsolidated sediments partially or wholly covers the bedrock. Buried karst, also know as paleokarst, is an ancient karst landscape that was completely buried by younger rocks. In some instances, soluble rocks are buried beneath less soluble or insoluble bedrock. However, due to circulating groundwater, these rocks are eventually dissolved and are defined as interstratal karst. Karst that forms beneath bodies of water such as river, lakes, or within tidal zones is called subaqueous karst.

Exposed karsts are areas where sediment cover is absent and the rock is exposed at the surface. Four subcategories of exposed karst include naked karst, denuded karst, exhumed karst, and relict karst. Naked karst occurs primarily in alpine regions where soils are poorly developed (1). Denuded karst is interstratal karst that has been exposed at the surface. Karst that was buried by sediment and then later exposed by erosion is called exhumed karst. Relict karst refers to areas where the bedrock has been removed by erosion without any trace of topographic expression.

Additional karst settings identified include deep-seated karst, subjacent karst, and entrenched karst. Deep-seated karst is found buried beneath younger rocks. There is no evidence at the surface, and the soluble rocks are not exposed. Subjacent karst occurs when a portion of the soluble rocks is exposed and surface features are evident. Entrenched karst occurs where the entire thickness of the soluble rock is entrenched along valleys, but the insoluble cap remains over most of the interfluves (7).

VULNERABILITY OF KARST TO CONTAMINATION AND POLLUTION

Karst areas are highly vulnerable to groundwater contamination. Spills that occur on karst can enter the groundwater flow system through discrete recharge zones and travel miles within days or weeks to springs and wells used as sources of water. The high permeability of a karst aquifer provides ineffective natural cleansing of any contaminants transported through it. Contaminated soils have the potential to be washed into the groundwater flow system in diffuse recharge zones without any biological interaction with the soil horizon. Water in storage is more subject to long-term contamination than water in transit (9). Groundwater moves slower under low gradient conditions, and cleanup of contaminated aquifers can last for years.

Keeping vulnerable karst aquifers free of contaminants for water supplies is essential during proper land use planning to minimize impacts to the karst groundwater flow system. In recent years, groundwater dye tracing has proven to be a useful tool for characterizing groundwater flow systems in karst. The delineation of recharge areas for important springs is essential during land use planning.

BIBLIOGRAPHY

1. White, W. (1988). *Geomorphology and Hydrology of Karst Terrains*. Oxford University Press, New York.
2. Aley, T. (2000). Karst systems. In: *Standard Handbook of Environmental Science, Health, and Technology*. J.H. Lehr and J.K. Lehr. (Eds.). McGraw-Hill, New York, p. 1600.
3. Aley, T. (1997). Groundwater tracing in the epikarst. In: *The Engineering Geology and Hydrogeology of Karst Terranes*. Beck and Stephenson (Eds.). Balkema, Rotterdam, pp. 207–211.
4. Ford, D.C. and Williams, P.W. (1989). *Karst Geomorphology and Hydrology*. Chapman and Hall, London.
5. Sweeting, M.M. (1973). Columbia University Press.
6. Quinlan, J. et al. (1992). Recommended administrative/regulatory definition of karst aquifer, principles for classification of carbonate aquifers, practical evaluation of vulnerability of karst aquifers, and determination of optimum frequency at springs. In: *Conference on Hydrogeology, Ecology, Monitoring, and Management of Groundwater in Karst Terranes*. Quinlan and Stanley, A. (Eds.). National Groundwater Association, pp. 573–635.
7. Klimchouk et al. (2000). Speleogenesis. *Evolution of Karst Aquifers*. National Speleological Society, Inc., p. 527.
8. Palmer, A.N. (2000). Hydrogeologic control of cave patterns. In: *Speleogenesis: Evolution of Karst Aquifers*. Klimchouk et al. (Eds.) National Speleological Survey, Inc., pp. 77–90.
9. Aley, T. (1978). Ozark hydrology: a predictive model. *Journal of the Missouri Speleological Survey* **18**: 185 pages.
10. Quinlan, J. (1967). Classification of Karst Types: A review and synthesis emphasizing the North American Literature,

1941–1966. *National Speleological Society Bulletin* **29**: 107–109.

11. Quinlan, J. (1978). *Types of Karst, with emphasis on cover beds in their classification and development*. PhD Thesis, Geology, University of Texas, Austin, TX.

READING LIST

Jennings, J.N. (1971). *Karst*. MIT Press, Cambridge, MA.

DETECTING MODERN GROUNDWATERS WITH ^{85}Kr

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NATURAL PRODUCTION MECHANISMS AND DECAY BEHAVIOR OF ^{85}Kr

Krypton-85 (^{85}Kr) is a relatively short-lived radioactive isotope of the noble gas krypton (Kr) that is produced naturally in very minor amounts in the atmosphere by spallation reactions (n, γ) with the stable Kr isotope ^{84}Kr. ^{85}Kr decays to rubidium-85 (^{85}Rb) by beta release:

$$^{85}\mathrm{Kr} \longrightarrow {}^{85}\mathrm{Rb} + \beta^- \qquad (1)$$

The decay of ^{85}Kr follows a first-order decay rate given by

$$^{85}\mathrm{Kr}_t = {}^{85}\mathrm{Kr}_0 e^{-\lambda t} \qquad (2)$$

where $^{85}\mathrm{Kr}_t$ is the ^{85}Kr concentration at time t (the elapsed time), $^{85}\mathrm{Kr}_0$ is the initial ^{85}Kr concentration, and λ is the ^{85}Kr decay constant (0.06442/yr). The ^{85}Kr half-life ($t_{1/2}$, 10.76 yr) is the time it takes for half of the initial ^{85}Kr to decay to ^{85}Rb and is related to the decay constant by

$$\lambda = \frac{\ln 2}{t_{1/2}} \qquad (3)$$

Krypton is chemically inert, and the only significant sink for atmospheric ^{85}Kr is radioactive decay.

ANTHROPOGENIC SOURCES AND ATMOSPHERIC DISTRIBUTION OF ^{85}Kr

Since the 1950s, anthropogenic contributions of ^{85}Kr to the atmosphere (primarily the result of nuclear weapons testing and nuclear fuel rod reprocessing) have completely overwhelmed natural background concentrations. Worldwide release of ^{85}Kr increased from less than 5 petabecquerels (PBq) per year in 1950 to more than 350 PBq per year in 1986 (1). Although atmospheric ^{85}Kr concentrations vary spatially with strong latitudinal correlation (higher concentrations occur in the Northern Hemisphere due to minimal ^{85}Kr releases in the Southern Hemisphere), the most significant characteristic is the nearly linear increase in concentration (Fig. 1). In contrast with the declining input signal for the tritium groundwater dating method, the increasing ^{85}Kr input signal will facilitate robust apparent age calculations well into the foreseeable future.

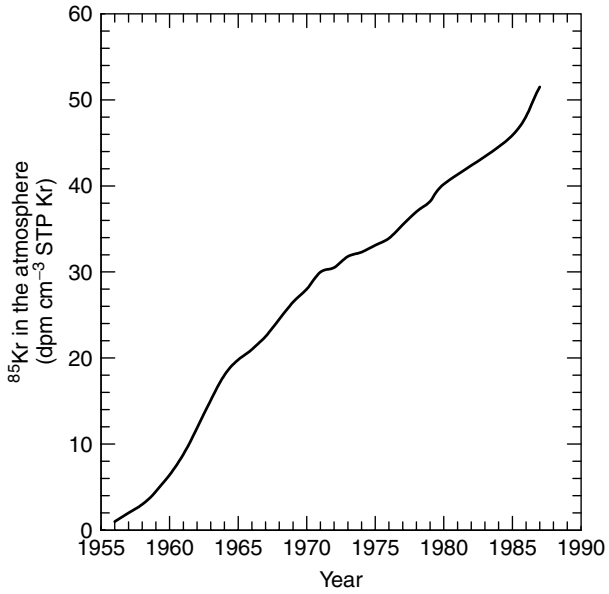


Figure 1. Activity of ^{85}Kr in the atmosphere of the Northern Hemisphere (after Reference 2).

PRINCIPLES, ADVANTAGES, AND DISADVANTAGES OF THE ^{85}Kr DATING METHOD

Anthropogenically related ^{85}Kr overwhelmingly dominates natural background activity in the atmosphere; therefore, the presence of ^{85}Kr in groundwater clearly indicates that the water is relatively young (i.e., recharged after 1950). Furthermore, the relatively simple behavior of the atmospheric concentration history permits estimating exact recharge dates to approximately 1960 by measuring the amount of ^{85}Kr activity in groundwater and accounting for radioactive decay. If dispersion is negligible, an age can be estimated by plotting the measured ^{85}Kr activity in groundwater samples back to an intercept point on the atmospheric ^{85}Kr activity curve (3). Alternatively, a decay-corrected ^{85}Kr activity curve can be plotted for the sample collection date directly relating measured activity to an apparent groundwater age (Fig. 2). For the ^{85}Kr method, the "clock" begins at the seasonal high water table because it is assumed that the ^{85}Kr concentration in the groundwater is in equilibrium with soil gas and the atmosphere (4).

A primary advantage of ^{85}Kr is that it is chemically inert in groundwater and is therefore affected only by the hydraulic properties of the aquifer and radioactive decay (5). Furthermore, age calculations do not require recharge temperature and krypton solubility information because the ^{85}Kr activity is normalized to the total ^{85}Kr present, which also implies that errors from excess air trapped in the aquifer or sample loss are negligible.

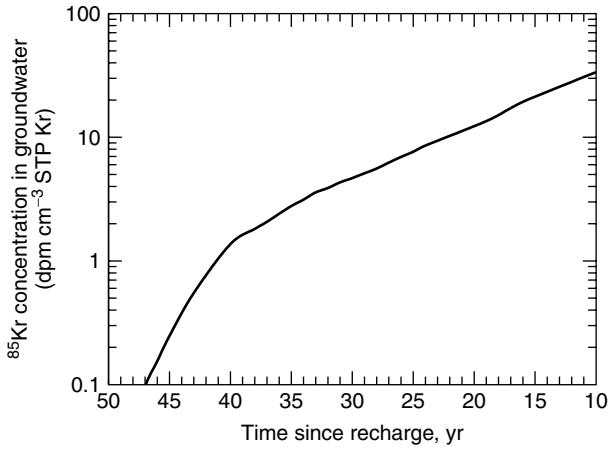


Figure 2. Relationship between apparent age (time since recharge) decay-corrected ^{85}Kr activity for samples collected in 2004 based on the activity of ^{85}Kr in the atmosphere of the Northern Hemisphere (Fig. 1).

However, because of the high current ^{85}Kr activity in the atmosphere, care must be taken to prevent sample contamination during well installation and sample collection. Note that the ^{85}Kr method may overestimate the groundwater age for deep-water tables (greater than 10 meters) due to a time lag through the unsaturated zone (3).

A significant disadvantage of the ^{85}Kr method is the large volume of groundwater required for analysis ($\sim$100 L) due to its relatively low aqueous solubility. Furthermore, analytical costs are relatively high: typically \$500–1,500 per sample (4). Water samples must be degassed in the field by vacuum extraction and isolated from the atmosphere. Sampling and analytical methods are discussed by Smethie and Mathieu (6). Ekwurzel et al. (5) report an analytical precision for ^{85}Kr of $\pm$2.9 disintegrations per minute per cubic centimeters of total Kr (dpm cm^{-3} STP Kr).

CASE STUDY: COMPARISON OF THE ^{85}Kr METHOD TO THE ^{3}H–^{3}HE AND CFC DATING METHODS

Ekwurzel et al. (5) compared apparent groundwater ages for several different tracer dating methods, including the ^{85}Kr method, in a study on the Delmarva Peninsula located on the east coast of the United States. The hydrogeology of the area is relatively simple and consists of highly permeable surficial materials and shallow water tables with assumed vertical flow velocities near the water table interface. Discrete groundwater samples were collected in support of tritium–helium (^{3}H–^{3}He) and chlorofluorocarbon (CFC, specifically CFC-11 and CFC-12) dating methods at approximately 30 wells throughout the Delmarva Peninsula. Most wells were screened across less than 1 m of the aquifer and therefore represent relatively discrete intervals of the aquifer. Four ^{85}Kr samples were collected in addition to the other tracers at a local well-characterized flow system within the Delmarva Peninsula (Locust Grove).

The ^{85}Kr method yielded apparent ages that agreed closely (generally within $\sim$30%) with the results of the other dating methods (Table 1). The effect of dispersion on apparent ages was modeled and was relatively insignificant for the ^{85}Kr method for ages younger than 25 years based on site conditions. The investigators also demonstrate that use of multiple methods for groundwater age dating may be advantageous because tracers are affected differently by potential error sources, such as diffusion, dispersion, sorption, degradation, gas entrapment, excess air, recharge temperature, and sampling errors. For additional discussion and case studies on the ^{85}Kr groundwater dating method, see Loosli et al. (7), Loosli (2), Smethie et al. (8), Cook and Solomon (3), Clark and Fritz (9), and Cook and Solomon (4).

Table 1. Comparison of Apparent Groundwater Ages (in years) at Locust Grove, Delmarva Peninsula for Various Dating Methods[a]

	Dating Method			
Well Name	^{85}Kr	^{3}H–^{3}He	CFC-11	CFC-12
KE Be 52	7.7	7.1	8.1	8.4
KE Be 61[b]	14.4	16.7	19.7	20.3
KE Be 62	5.4	3.1	3.2	3.6
KE Be 163	5.7	7.8	9.3	9.2

[a] Reference 5.
[b] Apparent ages are averaged for well KE Be 61 with multiple sampling for the ^{3}H–^{3}He and CFC methods.

BIBLIOGRAPHY

1. Weiss, W., Sartorius, H., and Stockburger, H. (1992). Global distribution of atmospheric ^{85}Kr. In: *Isotopes of Noble Gases as Tracers in Environmental Studies: IAEA Proc. Consultants Meet.*, May 29–June 2, 1989, Vienna, pp. 29–62.
2. Loosli, H.H. (1992). Applications of ^{37}Ar, ^{39}Ar, and ^{85}Kr in hydrology, oceanography, and atmospheric studies. In: *Isotopes of Noble Gases as Tracers in Environmental Studies: IAEA Proc. Consultants Meet.*, May 29–June 2, 1989, Vienna, pp. 29–62.
3. Cook, P.G. and Solomon, D.K. (1995). Transport of atmospheric trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and krypton 85. *Water Resour. Res.* **31**: 263–270.
4. Cook, P.G. and Solomon, D.K. (1997). Recent advances in dating young groundwater: Chlorofluorocarbons, ^{3}H/^{3}He and ^{85}Kr. *J. Hydrol.* **191**: 245–265.
5. Ekwurzel, B. et al. (1994). Dating of shallow groundwater: Comparison of the transient tracers ^{3}H/^{3}He, chlorofluorocarbons, and ^{85}Kr. *Water Resour. Res.* **30**: 1693–1707.
6. Smethie, W.M. and Mathieu, G. (1986). Measurement of krypton-85 in the ocean. *Mar. Chem.* **18**: 17–33.
7. Loosli, H.H., Lehmann, B.E., and Dappen, G. (1991). Dating by radionuclides. In: *Applied Isotope Hydrology. A Case Study in Northern Switzerland. Studies in Environmental Science*. J. Pearson et al. (Eds.). Elsevier, Amsterdam, **43**: 153–174.
8. Smethie, W.M., Solomon, D.K., Schiff, S.L., and Mathieu, G.G. (1992). Tracing groundwater flow in the Bordon aquifer using krypton-85. *J. Hydrol.* **130**: 279–297.
9. Clarke, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. CRC Press, New York, pp. 20, 174–188.

LAND USE IMPACTS ON GROUNDWATER QUALITY

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The manner in which humans use land has important consequences for groundwater quality. Using land for waste disposal, recreation, agriculture, residential development, and industry releases different types and quantities of chemicals to the environment. These chemicals often end up in shallow groundwater, where they may impair water quality.

Groundwater impacts from point sources, such as landfills and hazardous waste sites, are well understood. Impacts from "routine" land use, such as residential, commercial, industrial, or agricultural use, are not fully understood or readily apparent. Sources of chemicals from these land uses are called nonpoint or areawide sources. Examples include fertilized urban lawns or all feedlots in an area. This discussion focuses on water quality impacts in shallow groundwater resulting from routine land use.

To assess water quality, we compare chemical concentrations in water to a standard. Most standards are designed to protect human or ecosystem health, but standards also include ambient or natural concentrations of a chemical. For example, a nitrate concentration of 2 mg/L in groundwater under an urban subdivision is well below the drinking water standard of 10 mg/L but may be more than twice the concentration found in areas not impacted by humans.

Resource managers are increasingly concerned about impacts of human activity on groundwater quality. Between 1982 and 1997, the United States population grew about 15%. During that same period, the percentage of developed land, which includes urban land and land used for transportation, increased 34% to just over 98 million acres, which represents 6.6% of the nonfederal land in the United States (1). Urban development is only one of several land use changes that have the potential to impact groundwater quality. Others include changes in agricultural fertilizer and herbicide use, changes in the number of acres under irrigation, and changes in atmospheric deposition resulting from automobile and industrial air emissions. Groundwater impacts from land use are greatest where aquifers are sensitive to contamination. Examples include fractured bedrock or glacial aquifers that are close to the land surface and overlain by permeable geologic material.

UNDEVELOPED AREAS

Undeveloped areas include forested lands, grasslands, wetlands, and other areas not used for urban or agricultural development. These areas are minimally impacted by humans. Water quality from undeveloped areas serves as a benchmark for comparison with other land uses. Typically, pesticides and volatile organic compounds (VOCs) are absent, and concentrations of inorganic chemicals are low unless local geologic deposits are enriched in a particular element (Table 1) (2–5). Variability in chemical concentrations under undeveloped land use is low compared with that of other land uses (6).

Synthetic organic chemicals are occasionally found in undeveloped areas. Chloroform is the most commonly found VOC, atrazine and its primary metabolite, deethylatrazine, are the most common herbicides. These chemicals may be the result of atmospheric deposition (3,7). Chlorinated insecticides, such as dieldrin and DDE, are sometimes detected in groundwater under undeveloped areas and represent historic use of these persistent chemicals (3).

URBAN LAND USE

Urban areas include residential, commercial, and industrial land use. Distinctions between urban land uses are not always clear. Residential areas often include commercial development and may include small tracts of industrial or agricultural land. Residential areas served by municipal sewers (sewered) and septic systems (nonsewered) may be mixed. This intermingling of land uses makes it difficult to associate groundwater quality with a specific land use.

Studies of water quality in urban areas rarely distinguish between different types of urban land use. Consequently, Table 1 shows a wide range in chemical concentrations. Concentrations of major ions, trace elements, pesticides, and VOCs exceed concentrations found in undeveloped areas. Prometon, simazine, dicamba, bromacil, and 2,4-D are the most commonly detected herbicides (7). Prometon, bromacil, and simazine are applied for weed control in rights-of-way, and dicamba and 2,4-D are applied to urban lawns (8). These chemicals are found primarily during the growing season. The organochlorine insecticides, dieldrin and chlordane, are often observed in groundwater beneath urban areas (7,9). Atrazine and deethylatrazine are frequently observed in urban areas (10). Although used on agricultural crops, atrazine is present in precipitation in many areas of the United States (8,11,12). Concentrations of pesticides in urban ground water are typically well below drinking water standards, although standards do not exist for many of the compounds detected (13).

The widespread occurrence of VOCs is the most conspicuous difference between undeveloped and urban areas. Chlorinated hydrocarbons, particularly 1,1,2-trichloroethene (TCE), 1,1,2,2-tetrachloroethene (PCE), and 1,1,1-trichloroethane (TCA), account for the majority of VOC detections. These persistent chemicals were used as degreasers, in dry cleaning, or in septic systems (3,6). Trihalomethanes, particularly chloroform, also occur within urban areas. They are byproducts of disinfection, but other sources include atmospheric deposition and lawn watering with chlorinated water (14). Nonchlorinated hydrocarbons, such as benzene and substituted benzenes, occur in areas where underground fuel tanks have contaminated the groundwater (13).

Table 1. Summary of Median Chemical Concentration, Range in Concentration, and Number of Data Points for Three Land Uses

Chemical[a]	Median			Range			Number of Data Points		
	Und.[b]	Urb.	Agr.	Und.	Urb.	Agr.	Und.	Urb.	Agr.
Major Ions (mg/L)									
Calcium	9	89	60	5–63	20–123	16–92	3	5	5
Chloride	2.4	63	20	1.8–3.0	22–83	10–41	2	4	4
Magnesium	22	26	23	22	18.7–29	22–25	1	3	3
Nitrate	0.6	2.4	4.1	0.5–1.0	1.4–6.1	1.3–15	3	10	11
Potassium	1.1	2.6	2.0	1.1	1–3.2	1.3–5	1	3	3
Sodium	3.3	22	7.4	1–5.6	12–63	4.3–35	2	4	4
Sulfate	8	17	13	3–13	7.1–72	6.3–40	2	4	4
Synthetic Organic Chemicals (% of Samples Detected)									
Total PAHs	0	0	0	0	0–33	0	1	2	2
Total pesticide	4.4	32	86	0–35	0–70	29–100	4	9	8
Total VOCs	4	66	7	0–15	3–100	0–9	3	7	5
Trace Elements (ug/L)									
Arsenic	0.7	1.4	2.9	0.7	0.7–2	0.7–5	1	5	4
Boron	16	56	39	15–17	41–71	21–80	2	3	3
Cadmium	0.1	0.09	2.0	0.1	0.04–1.5	0.04–4	1	5	4
Chromium	1.1	3.1	3.4	1.1	1.1–6	0.59–6	1	5	4
Copper	<5.4	2	5.4	<5.4	2– < 5.4	5.4	1	6	2
Iron	10	34	4.3	10	5.6–63	3.6–4.9	1	3	2
Lead	0.04	0.06	0.027	0.04	0.05–0.07	0.027	1	5	2
Manganese	0.6	5.0	1.7	0.6	0.5–440	0.5–2.6	1	4	2
Zinc	5.9	5.5	6.6	5.9	5.1–9.1	6–7.1	1	4	2

[a] Data are compiled from many sources cited in references.
[b] Und. = undeveloped, urb. = urban, agr. = agriculture.

There are water quality differences between the three urban land uses (Table 2). Nitrate, phosphorus, and boron concentrations are higher in nonsewered areas than in sewered areas (5,15,16). In nonsewered subdivisions that are more than 10 years old and have lot sizes of 1 acre or less, nitrate concentrations often exceed the Maximum Contaminant Level (MCL) in 10% or more of sampled wells (17–20). Manganese concentrations are higher, and VOCs occur more frequently in sewered areas (5). Concentrations of TCE and PCE may exceed drinking water standards in older sewered areas where industries used these chemicals (7).

AGRICULTURAL AREAS

Agriculture includes cropland, pasture, rangeland, and areas managed for silviculture. Cropland can be divided into different cropping types and irrigated or dryland agriculture.

Nitrate concentrations and frequency of herbicide detection in agricultural areas are higher than in undeveloped and urban areas. Concentrations of most other chemicals are higher than concentrations in undeveloped areas but lower than concentrations in urban areas. VOCs are detected less frequently than in urban areas, whereas organochlorine insecticides occur at similar frequencies. DDT, DDE, dieldrin, and heptachlor epoxide are the organochlorine chemicals found most frequently.

Table 2. Summary of Median Chemical Concentrations for Different Urban Land Uses

Chemical[a]	Sewered Residential	Nonsewered Residential	Commercial-Industrial
Major Ions (mg/L)			
Calcium	105	73	74
Chloride	79	83	42
Magnesium	29	19	28
Nitrate	2.4	6.1	2.0
Potassium	2.9	1.0	3.2
Sodium	26	63	17
Sulfate	18	7.1	12
Synthetic Organic Chemicals (% of Samples Detected)			
Total PAHs	0	0	33
Total pesticide	10	0	7.5
Total VOCs	52	3.0	73
Trace Elements (ug/L)			
Arsenic	0.70	0.70	0.49
Boron	41	71	57
Cadmium	0.09	0.04	0.07
Chromium	1.2	1.1	0.81
Copper	<5.4	<5.4	<5.4
Iron	5.6	<3.1	9.3
Lead	0.07	0.05	0.06
Manganese	8.0	0.45	20
Phosphorus	0.027	0.035	0.020
Zinc	9.1	5.1	7.9

[a] Data from Ref. 5.

Carbamate insecticides occur in areas where they are applied (Table 1) (3,6).

Atrazine, deethylatrazine, and metolachlor are the most commonly observed herbicides in agricultural areas (7,10,21). The presence of other herbicides relates to regional use and includes metribuzin, EPTC, bentazon, diuron, 2,4-D, and dicamba (14,21,22). Recent studies suggest that herbicide metabolites occur at much greater frequency than parent compounds (5). Prometon, simazine, and tebuthiuron are used in road rights-of-way and occur in groundwater from agricultural areas, but at frequencies lower than those in urban areas.

Concentrations of both nitrate and herbicide are directly proportional to the amount of these chemicals applied to cropland (23). Nitrate concentrations are about 1 mg/L under noncropland, 1–3 mg/L under small grains and soybeans, 3–7 mg/L under nonirrigated row crop agriculture, and more than 10 mg/L under irrigated agriculture (5,22,24,25). Nitrate concentrations tend to be lower in areas that have extensive feedlots due to denitrification associated with organic carbon released from the feedlots. Total nitrogen concentrations in these areas, however, may exceed concentrations in areas lacking feedlots (5,24). Herbicides are generally absent under rangeland and forestland used for silviculture; concentrations under irrigated agriculture are about double those under nonirrigated agriculture. Pesticide concentrations typically are lower than drinking water standards, although standards do not exist for many chemicals.

GEOGRAPHIC AND DEPTH RELATIONSHIPS

The land use relationships discussed before are independent of geographic location, except that the chemicals differ locally (6,26). For example,

- Methyl tert-butyl ether (MtBE) is a VOC frequently found in groundwater but only in areas where the chemical is used as an additive in gasoline (7,13).
- Very densely populated urban areas have concentrations of major ions higher than those in less densely populated urban areas (6).
- Local pumping of surficial aquifers induces flow of water from different areas, resulting in a groundwater chemical signature that may not reflect the overlying land use (6).
- Specific synthetic organic compounds are often found in areas where specialty crops are grown. For example, 1,2-dichloropropane was frequently used as a fumigant for potatoes, berries, and other specialty crops. It is found in trace quantities in areas where it was applied to crops (13,22).

Impacts in shallow groundwater do not necessarily relate to water quality deeper in an aquifer. Many aquifers are protected by confining geologic layers or favorable geochemical conditions. Many aquifers, however, do not have adequate protection. Sensitive fractured bedrock aquifers, in particular, are affected by land use.

INFORMATION NEEDS

There are few studies that compare water quality beneath different land uses. Land use studies are complicated by concerns about where in an aquifer to collect samples, well spacing, defining discrete land uses, historical land use, and selection of a parameter list. Data for trace elements are generally lacking, although land use affects concentrations of arsenic, boron, lead, and manganese in ground water (3,5). Recent studies suggest that groundwater may contain chemicals not previously sampled, such as pesticide degradates; chemical additives such as tetrahydrofuran and MtBE; urban insecticides such as diazinon, carbaryl, chlorpyrifos, and malathion; pharmaceuticals; growth hormones; and antibiotics (3,5).

There is also a need for trend information. We do not understand rates of water quality change associated with land use changes. For example, nitrate loss from newly installed lawns is high the first year after establishment, particularly if the lawns are seeded. Other studies show that nitrate loss under established turfgrass is very low (5,27). Rates of change from these two conditions are not known, however. Some trend studies exist for the occurrence of nitrate in groundwater in agricultural and nonsewered residential areas (10,22,28–30). Concentrations of VOCs in urban areas should be decreasing in response to aggressive cleanup and control programs in the last 20 years, but there is limited data to support this assumption.

Finally, we need to understand the effectiveness of management strategies in protecting groundwater quality. For example, studies show that converting land to CRP improves water quality (5). There is less information on the effects of other agricultural BMPs, such as conservation tillage, crop rotation, and nutrient management. In nonsewered urban areas, increasing lot size results in lower nitrate concentrations in groundwater, but increased use of pesticides and fertilizers on larger urban lawns may offset this. In industrial areas, regulatory programs such as the Superfund have resulted in cleanup of soils and groundwater at contaminated sites, but there is limited information on the effectiveness of these cleanups in protecting water quality in aquifers.

SUMMARY

Research consistently shows that chemical concentrations in groundwater increase as the quantity used increases. The type and intensity of land use are thus the most important factors affecting groundwater quality in an area. Water resource managers need to be aware of the potential impacts of different land uses on groundwater quality.

BIBLIOGRAPHY

1. United States Department of Agriculture. (2000). *Summary Report—1997 National Resources Inventory*. Natural Resources Conservation Service, Iowa State University Statistical Laboratory, Ames, IA.

2. Clawges, R.M. and Vowinkel, E.F. (1996). Variables indicating nitrate contamination in bedrock aquifers, Newark basin, New Jersey. *Water Resources Bulletin* **32**: 1055–1066.
3. Eckhardt, D.A.V. and Stackelberg, P.E. (1995). Relation of ground-water quality to land use on long island, New York. *Ground Water* **33**(6): 1019–1033.
4. Taraba, J.L. and Dinger, J.S. (1998). Land use impacts on water quality in small karst agricultural watersheds. *University of Kentucky Waterworks Newsletter* **4**(2): 1–5.
5. Trojan, M.D. et al. (2002). Effects of land use on ground water quality in the anoka sand plain aquifer of Minnesota. Accepted for publication in Ground Water.
6. Cain, D., Helsel, D.R., and Ragone, S.E. (1989). Preliminary evaluations of regional ground-water quality in relation to land use. *Ground Water* **27**(2): 230–244.
7. Ayers, M.A., Kennen, J.G., and Stackelberg, P.E. (2000). *Water Quality in the Long Island-New Jersey Coastal Drainages*. New York and New Jersey, 1996–98. United States Geological Survey Circular 1201.
8. Andrews, W.J., Fong, A.L., Herrod, L., and Dittes, M.E. (1997). *Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-Water Quality in an Urban Part of the Twin Cities Metropolitan Area*. Minnesota, 1996. United States Geological Survey Water-Resources Investigations Report 97–4248.
9. Frick, E.A., Hippe, D.J., Buell, G.R., Couch, C.A., Hopkins, E.H., Wangsness, D.J., and Garrett, J.W. (1998). *Water Quality in the Appalachicola-Chattahoochee-Flint River Basin, Georgia, Alabama, and Florida, 1992–95*. U.S. Geological Survey Circular 1164.
10. U.S. Geological Survey. (1999). *The Quality of Our Nation's Waters—Nutrients and Pesticides*: U.S. Geological Survey Circular 1225.
11. Capel, P.D., Lin, M., and Wotzka, P.J. (1998). *Wet atmospheric deposition of pesticides in Minnesota. 1989–94*. U.S. Geological Survey Water Resources Investigations Report 97–4026, p. 43.
12. Ligocki, M.P., Leuenberger, C., and Pankow, J.F. (1985). Trace organic compounds in rain. II. Gas scavenging of neutral organic compounds. *Atmospheric Environment* **19**(10): 1609–1617.
13. Ebbert, J.C., Embrey, S.S., Black, R.W., Tesoriero, A.J., and Haggland, A.L. (2000). *Water Quality in the Puget Sound Basin, Washington and British Columbia, 1996–98*. United States Geological Survey Circular 1216.
14. Domagalski, J.L., Knifong, D.L., Dileanis, P.D., Brown, L.R., May, J.T., Connor, V., and Alpers, C.N. (2000). *Water Quality in the Sacramento River Basin, California, 1994–98*. United States Geological Survey Circular 1215, p. 37.
15. Hinkle, S.R. (1997). *Quality of Shallow Ground Water in Alluvial Aquifers of the Williamette Basin, 1993–95*. United States Geological Survey Water Resources Investigation Report 97–4082.
16. Lichtenberg, E. and Shapiro, L.K. (1997). Agriculture and nitrate concentrations in Maryland community water system wells. *Journal of Environmental Quality* **26**(1): 145–153.
17. Anderson, D.L., Rice, J.M., Voorhees, M.L., Kirkner, R.A., and Sherman, K.M. (1987). Ground water modeling with uncertainty analysis to assess the contamination potential from onsite sewage disposal systems (OSDS) in Florida. *Proceedings from the National Symposium on Individual and Small Community Sewage Systems*. December 14–15. Chicago, IL, p. 411.
18. Bauman, B.J. and Schafer, W.M. (1984). Estimating groundwater quality impacts from on-site sewage treatment systems. *Proceedings of the Fourth National Home Sewage Treatment Symposium*. ASAE, pp. 285–294.
19. Hantzsche, N.N. and Finnemore, E.J. (1992). Predicting ground-water nitrate-nitrogen impacts. *Ground Water* **30**: 490–499.
20. Quan, E.L., Sweet, H.R. and Illian, J.R. (1974). Subsurface Sewage Disposal and Contaminantion of Ground Water in East Portland, Oregon. *Ground Water* **12**: 356–366.
21. Anderson, H.W. (1993). *Effects of Agriculture and Residential Land Use on Ground-Water Quality, Anoka Sand Plain Aquifer, East-Central Minnesota*. United States Geological Survey Water-Investigations Report 93–4074.
22. Clark, G.M., Maret, T.R., Rupert, M.G., Maupin, M.A., Low, W.H., and Ott, D.S. (1998). *Water Quality in the Upper Snake River Basin, Idaho and Wyoming 1992–95*. U.S. Geological Survey Circular 1160.
23. Barbash, J.E., Thelin, G.P., Kolpin, D.W., and Gilliom, R.J. (1998). *Distribution of Major Herbicides in Ground Water of the United States*. Water-Resources Investigations Report 98–4245 8056–61.
24. Burkart, M.R. and Kolpin, D.W. (1993). Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. *Journal of Environmental Quality* **22**(4): 646–656.
25. Frenzel, S.A., Swanson, R.B., Huntzinger, T.L., Stamer, J.K., Emmons, P.J., and Zelt, R.B. (1998). *Water Quality in the Central Nebraska Basins, Nebraska, 1992–95*. U.S. Geological Survey Circular 1163.
26. Hamilton, P.A. and Helsel, D.R. (1995). Effects of agriculture on ground-water quality in five regions of the United States. *Ground Water* **33**(2): 217–226.
27. Geron, C.A. et al. (1993). The effects of establishment methods and fertilization practices on nitrate leaching from turfgrass. *JEQ*. **22**: 119–125.
28. Keeney, D.R. and DeLuca, T.H. (1993). Des moines river nitrate in relation to watershed agricultural practices: 1945 versus 1980s. *JEQ*. **22**: 267–272.
29. Kitchen, N.R., Blanchard, P.E., Hughes, D.F., and Lerch, R.N. (1997). Impact of historical and current farming systems on groundwater nitrate in Northern Missouri. *Journal of Soil and Water Conservation* **52**(4): 272–277.
30. Miller, J.C. (1975). Nitrate contamination of the water-table aquifer by septic tank systems in the coastal plain of Delaware. In: *Water Pollution Control in Low Density Areas*. W.S. Jewell and R. Swan. (Eds.). *Proc. Rural Environ. Eng. Conf.* Hanover, NH, September, 1973. Univ. Press of New England, Hanover, NH, pp. 121–133.

GROUNDWATER CONTAMINATION FROM MUNICIPAL LANDFILLS IN THE USA

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Groundwater contamination has been a significant environmental impact associated with landfills. Landfilling can affect groundwater quality through leachate releases, landfill gas migration, and runoff. Leachate releases are the most common and serious cause of impacts. Plume chemistry often limits extensive contamination to salts,

ammonia, and redox-sensitive metals. Liners and gas control systems are effective in preventing pollution at modern facilities.

INTRODUCTION

Groundwater contamination is often cited as the greatest environmental problem associated with landfills. Municipal solid waste (MSW) landfills are often said to release contaminants such as metals, volatile organic compounds (VOCs) (such as solvents and gasoline constituents), pesticides and herbicides, polychlorinated biphenyls (PCBs), and dioxins and furans to groundwater, often at concentrations associated with human health concerns (1). Additional impacts would occur where contaminated groundwater discharges to surface waters.

Landfilling proponents acknowledge that earlier operational practices at disposal sites caused impacts to ground water (2). Most are now convinced that modern landfill engineering has ended these impacts (3).

Historically, design choices have affected the degree and kind of groundwater contamination. The most important is site location. In addition, the use of active controls can limit groundwater impacts.

Landfills impact groundwater in three ways. The primary concern is leachate releases. Leachate forms within the landfill as a result of precipitation. Precipitation percolates through the fill and dissolves matter from wastes and materials such as cover soils. These liquids foster chemical and biological reactions that liberate various substances. Landfill biota are further known to alter the composition of leachate (4). All of these elements of leachate may react with each other and with landfill features, including the containment liners and associated piping. Leachates undergo alteration in the environment, react with sediments, groundwater, or vadose zone liquids, and undergo additional biological reactions (5).

Contaminants also reach groundwater through gas migration (6). Waste decomposition gases produced within the fill may migrate away, typically through the vadose zone. There, gas may dissolve in recharge to reach groundwater; gas may diffuse at the phreatic zone directly; or, if the pressures from the gas are large, it may bubble into shallow groundwater (enhancing contaminant dissolution). The principal constituents of landfill gas are methane and carbon dioxide, and they are often approximately 50% each by volume. However, chemicals that have high vapor pressures and reactive gases generated by waste reactions also are commonly found in landfill gas (7). VOCs are thus typical gas-generated groundwater contaminants; as metals are not typically found in landfill gas, landfill gas rarely causes any metal contamination of groundwater.

Runoff that was in contact with wastes is another pathway to contaminate ground water (8). Runoff differs from leachate in that liquids do not pass through the waste but have contact with surface or shallow subsurface wastes. The chemistry and biology affecting runoff are different from those generating leachate. The surfaces of landfills tend to be aerobic, whereas fills are anaerobic. Photodegradation is a surface phenomenon, and volatilization is enhanced by wind (albeit interior volatilization is promoted by elevated temperatures). Runoff flowing away from a landfill can percolate through the vadose zone to ground water and may be altered along this pathway.

HISTORICAL FACTORS REGARDING GROUNDWATER CONTAMINATION FROM LANDFILLS

Land disposal has been the most common means of waste management, other than random discards. As municipalities organized waste disposal, locations for discards burial were identified. Lands of little value (such as swamps) or areas needing improvement by fills (quarries, depressions, or shorelines) were used (9).

Early landfills may not have impacted groundwater to the extent that mid twentieth century landfills did. It is clear that cities cause deterioration of underlying groundwater resources through waste disposal. Much of Manhattan's groundwater was unpotable by 1799, for example (10). However, the primary pollutant there and for large third-world cities today appears to be septic wastes (9).

There are few reports of landfill groundwater impacts before the 1960s (11). Many early studies report plume sizes consonant with contamination initiation that coincided with the start of sanitary landfilling (12,13). However, the development of sanitary landfilling occurred when groundwater research became more widespread and as waste disposal rates greatly increased. Sanitary landfills replaced open dumps. Most dumps had small footprints and accepted low volumes of wastes; therefore, relatively small releases of contaminants would be expected. Many dumps were at groundwater discharge zones (shorelines, wetlands, depressions), minimizing impacts to regional resources. In addition, many dumps were managed by burning garbage (a source of noxious air pollution), which reduced labile carbon and formed ashes (14), which may have reduced biological and chemical activity and supported reactions with the remaining wastes or sediment matrices to minimize solubilities.

GEOGRAPHICAL FACTORS REGARDING GROUNDWATER CONTAMINATION FROM LANDFILLS

Three geographical parameters help determine if landfill groundwater contamination may occur and its seriousness. First, there must be groundwater present. Not all of the United States is underlain by aquifers. The absence of significant groundwater resources means there is no resource to impact. Secondly, the resources must be hydraulically connected to the surface. If there is an impermeable barrier (either natural or artificial) between the fill and resource or the distance to the aquifer is too far for the quantity of generated recharge to reach it, then the potential for contamination is very small (4).

Thus, local geology is paramount. In areas of unconsolidated sediments of high permeability, landfill-derived contaminants can reach and impact groundwater but may not in other geological settings (13).

Finally, landfill contamination is driven by precipitation. In desert areas, less leachate, landfill gas, and runoff are generated, compared with landfills in more humid, temperate zones. Therefore, the risk of groundwater impacts from landfills is high on the eastern coastal plain. Rainfall is plentiful, and local geology leads to high-yielding aquifers found near the surface. In the southwest, greater aridity, bedrock outcrops, and large distances to water tables tend to minimize concerns (15).

LEACHATE RELEASES

An early evaluation of landfill leachate contamination of ground water by the U.S. Geological Survey (USGS) occurred on Long Island. Plumes from two, unlined landfills were characterized as extremely salty and enriched in iron and manganese. Other trace metals (except for zinc) were not detectable. The plumes had very low dispersion constants (especially laterally) and tended to sink in the aquifer (13).

The USGS characterized landfill plume chemistry in Delaware, where the plume was delineated by redox zonation. Closest to the landfill was a methanogenic zone. Further from the fill, successive zones marked by iron reduction, manganese reduction, and nitrate reduction (for carbon oxidation by microbes) were observed—the absence of sulfate eliminated sulfate reduction. The work promoted predictions of differential chemical processes in the zones, resulting in differences in plume chemistry (16).

In 1983, a University of Waterloo landfill study was published (19) that established many basic methodologies for acquiring data and generating interpretations of leachate contamination. The discussion of plume geochemistry (18) reinforced the USGS findings and identified cation exchange and other sediment–plume interactions as major controls.

Early modeling efforts found that the leading edge of the plume moved as quickly as groundwater flowed (19), mostly because it was defined by unreactive chloride. Other plume constituents were slowed by reactions, as discussed by Nicholson et al. (18), but, generally, chlorides have defined leachate plumes.

Landfill leachate characterizations are marked by varying concentrations (Table 1), which is true across sites, and even for cells at one landfill. Two leachate samples from different cells of a Long Island landfill had chloride concentrations of 50 mg/L and 58,000 mg/L (8). These variations are generally explicable in terms of different wastes in the cells, but site-specific and time-specific leachate generation processes also cause differences. These variations make it difficult to predict impacts *a priori*, or to determine volumes of releases *post hoc*.

Commonly, it is assumed that the contaminating constituents directly represent disposed waste materials. At an extreme, this resulted in some reports stating that iron, chloride, calcium, and magnesium were dumped as discrete wastes because they were found in plumes at concentrations above drinking water standards (21). Organic compounds cause special problems in this regard. Complex molecules such as DDT or PCBs, if found in a contaminant plume, probably were disposed at the site. Benzene or toluene, however, could have been disposed of as particular solvents, released from petroleum products (22), or even generated as relatively refractory breakdown products as other organic compounds degraded. Once, chlorinated hydrocarbons found in the environment were all thought to be released as solvents. However, now it is known that particular microbes can degrade more complex chlorinated solvents to simpler compounds (23). Additionally, under certain conditions, chlorinated hydrocarbons can be generated *de novo* by environmental bacteria (25).

Table 1. Classic Definitions of Landfill Leachate Quality[a]

Parameter	Range of 20 Samples[b]	Representative Range[c]
Alkalinity	0–20,850	500–10,000
Ammonia	0–1,106	10–1,000
Biological oxygen demand	81–33,360	
Calcium	60–7,200	100–3,000
Chemical oxygen demand	40–89,250	1,000–90,000
Chloride	4.7–2,500	300–3,000
Copper	0–9.9	<10
Iron	0–2,820	1–1000
Lead	<0.1–2	<5
Magnesium	17–15,600	100–1,500
Manganese	0.06–125	0.01–100
Mercury		<0.2
Nickel		0.01–1
Nitrate		0.1–10
Organic nitrogen		10–1,000
Phosphorus as phosphate	0–130	1–100
Potassium	28–3,770	200–1,000
Sodium	0–7,700	200–1,200
Sulfate	1–1,558	10–1,000
Total dissolved solids	584–44,900	5,000–40,000
Total hardness	0–22,800	
Total organic carbon		200–30,000
Total suspended solids	10–26,500	
Zinc	0–370	0.1–100
pH	3.7–8.5	4–8

[a](in mg/L).
[b]USEPA, cited in Ref. 14.
[c]Compiled by Ref. 20.

Efforts to avoid groundwater contamination from landfills often begin by removing hazardous substances from the wastes (1). If landfills actually generate these kinds of compounds, these waste quality improvement programs might not achieve their goal.

A contaminant plume itself can control some pollutants. Research found that iron sulfide complex generation scavenged many free metal molecules, removing the immediate threat of trace metals migrating with the plume (25). In general, microbially mediated reactions together with groundwater–sediment interactions alter a plume substantially, biodegrade and chemically neutralize organic compounds in the near vicinity of many landfills, and limit their mobility in groundwater (26). Thus, leachate plumes at distances from the landfill often are no more than the more unreactive soluble salts (e.g., chloride, sodium, calcium, but not potassium), ammonia (if not nitrified), refractory carbon compounds, and dissolved iron.

LANDFILL GAS MIGRATION

Prior to sanitary landfilling, gas does not seem to have usually been generated in large quantities at most landfills. By the 1960s, landfill gas was a major problem. The most obvious dangers were explosions, especially at structures near landfills, which caused a number of deaths and injuries (27). Health concerns from exposure to the minor constituents of landfill gas also became a concern (28).

By the 1990s, it was becoming more widely known that landfill gas could directly cause groundwater contamination. VOC contamination from gas migration was the major concern (29). Some also noted that, analogous to natural gas impacts (30), redox-sensitive metals (iron and manganese, primarily) could be released from native sediments due to increased microbial activity and associated anoxic groundwater conditions. Methane can even increase alkalinity and therefore bicarbonate concentrations by increasing aqueous carbon (31).

Gas affects groundwater in three ways. It reacts with recharge as the gas migrates through the unsaturated zone away from the landfill (6). Second, as the gas fills the vadose zone, dispersion and surface film reactions can occur at the phreatic surface (32). Finally, if the landfill is producing large amounts of gas, it may increase the pressure gradient enough to infuse gas downward into the shallowest groundwater (33) (this is probably limited to directly beneath or adjacent to the fill), which can introduce gas below the immediate surface layer of the groundwater and allow more complete dissolution of contaminants.

Methane migration thus can cause VOCs and redox-sensitive metals contamination side-gradient and upgradient to overall groundwater flows and may enrich concentrations of these contaminants downgradient in the shallow aquifer. Methane migration cannot cause increases in soluble salts or nonnative metals, as gas cannot transport them. Methane impacts also tend to be restricted to the shallowest groundwater. Thus, impacts from landfill gas can be distinguished from leachate impacts (34).

UNCONTROLLED RUNOFF IMPACTS

There has been little research on runoff impacts from landfills. Modern landfill design intends to minimize and control runoff (35). Also, impacts from these surface flows off the landfill tend to occur very close to the fill, and so may be classed as leachate release impacts. However, where recharge basins are used to collect runoff from the landfill, concentrated impacts away from leachate plumes may occur.

Runoff may encounter only aerobic conditions on the fill, and its chemistry may be determined mostly by dissolution reactions (as is not necessarily so for leachate). Runoff may include high concentrations of particular salts if distinctive materials are found on the landfill surface. One Long Island landfill had unusually high concentrations of calcium and sulfate peripheral to its leachate plume. The landfill used ground construction and demolition debris, rich in gypsum ($CaSO_4$) from wallboard, as daily cover. In addition, organic pollutants (from solvents, for example) and easily dissolved metals may also become entrained in runoff (8).

POLLUTION PREVENTION

Many regulations governing landfills intend to prevent leachate releases. Much of the remaining regulatory effort prescribes extensive groundwater monitoring. Artificial liners evolved from simple sheets of plastics or clay beds pioneered in the 1970s to complex, engineered systems described by voluminous State and Federal regulations, and are required whenever groundwater impacts are possible (2). Early, simple liners had near 100% failure rates, and so now liners made of two separate materials and redundant systems are required in many jurisdictions. Regulations also limit hydraulic head buildup as leachate collects on the liner and require leachate removal off the liner and out of the landfill entirely. New York State, which requires redundant liner systems, has records showing that these modern liner systems can universally prevent all but environmentally unimportant releases to the environment (3). There is also some research that less complex systems, if managed properly, can be effective in controlling leachate releases (36).

Landfills are subject to complex closure procedures when operations cease. The intent is to create a “dry tomb” through continued removal of leachate and installation of an artificial cap on the wastes, so that precipitation cannot percolate in. Thus, the waste mass will be isolated from the environment—swaddled in plastics and/or clays—and leachate releases will be impossible (2). The system is also subject to continued maintenance and monitoring for 30 years, according to current regulations.

Controls on landfill gas migration, primarily through gas collection with combustion, are becoming more prevalent. These systems are usually installed for odor control, greenhouse gas reductions, and explosive gas control, not groundwater quality protection (37). However, the result is to limit groundwater impacts from gas migration directly and also to reduce VOC content in leachate, lessening impacts from leachate releases.

Runoff control for groundwater protection is also not a major concern. Runoff is controlled to reduce erosion and to minimize leachate (38). However, these ends may combine to direct liquids that have long waste contact times to management facilities outside of the leachate system. Most regulations, however, state that all water that comes in contact with wastes, no matter how long or brief the time, should be treated as contaminated leachate.

Tens of thousands of landfills have accepted wastes since 1970. Most have closed, and only approximately 2150 sites were operating in 2001 (39). However, probably all but several hundred of these landfills were at least partially constructed prior to 1993, and so are not engineered to the high standard required under the Federal Resource Conservation and Recovery Act Subtitle D (40 CFR Part 258) reauthorization. If the landfill is located in an area where impacts to groundwater can occur, a rigorous analysis of water quality near Subtitle D noncompliant sites is likely to find some impacts to groundwater

(although the pollution levels may not necessarily exceed water quality standards), which means that old generation landfills comprise one of the major sources of groundwater contamination in the United States.

GROUNDWATER REMEDIATION

Landfill plumes are difficult to clean up (40). They are not single constituent contaminations. Techniques appropriate for certain plume elements may be hindered by other plume constituents. Air stripping towers that work well with solvents are easily plugged by dissolved iron (which precipitates in contact with the atmosphere), for example (41). Ion exchangers do not collect nonpolar compounds such as most chlorinated organics. Many landfill remedial projects, as practical implementations, address only particular plume constituents rather than the entire range of contaminants affecting the groundwater. Source control (such as capping the landfill) remains the most common remediation for a landfill that is causing groundwater contamination.

BIOREACTORS AND THE POTENTIAL FOR GROUNDWATER IMPACTS

A popular, new concept in landfill design is the "bioreactor." It is a lined landfill where the degradation processes are enhanced through the controlled addition of liquids and/or the recirculation of leachates (42). An aim is to degrade labile carbon as quickly as possible, increasing settlement (making more air space available for disposal purposes), and causing biological stabilization of the waste mass. Recirculating leachate may also strip contaminants onto the wastes, decreasing treatment costs for the effluents (43). Bioreactor technology requires increasing the amount of liquids in the wastes and intentionally increasing gas generation (for capture and use for energy generation). Thus, the design seems to increase some of the factors that lead to landfill groundwater contamination. However, the approach relies on the documented success of modern liners to prevent leachate releases as well as active gas collection efforts to minimize environmental impacts.

SUMMARY

Landfills have historically caused extensive groundwater impacts in the United States, through leachate releases, methane migration, and uncontrolled runoff. These problems have been greatest in moist climates where aquifers have high conductivity potentials and are close to the ground surface.

Groundwater contaminated by a landfill is usually discolored and warm and smells bad. It contains high levels of salts, along with dissolved iron and often manganese. VOCs are a general concern in plumes but are not always found at significant concentrations or throughout the contamination. Many landfill plumes have much lower than expected dissolved trace metal levels because of scavenging by iron sulfides and hydroxides in low-redox, anoxic waters.

Modern engineering techniques have largely eliminated the major sources of contaminants. Modern artificial liner systems together with gas collection prevent landfill leachate and gas from carrying contaminants to groundwater. Dry tomb landfill closures isolate fills from the environment after waste disposal ceases.

However, the barriers and processes used to control access of water to wastes cannot be expected to function indefinitely. It is not clear exactly what the pollution potential of dry tomb landfills will be when the liners and caps decay and fail and the wastes are again exposed to the environment, which is an additional impetus for bioreactor research, as the material remaining in a stabilized landfill, it has been hypothesized, would be environmentally benign.

BIBLIOGRAPHY

1. Denison, R.A. (1996). Environmental life-cycle comparisons of recycling, landfilling, and incineration: a review of recent studies. *Annual Review of Energy and the Environment* **21**: 191–237.
2. Koerner, R.M. (1997). Design of Subtitle D and Subtitle C landfill containment systems. pp. 247–264. In: *Municipal Solid Wastes: Problems and Solutions*. R.E. Landruth and P.A. Rebers (Eds.). CRC Press, Lewis Publishing, New York.
3. Phaneuf, R.J. and Becker, D.A. (2001). Proper environmental containment system design and performance monitoring: can it lead to increased regulatory flexibility? *Presented at Federation of New York Solid Waste Associations Solid Waste and Recycling Conference and Trade Show*, Bolton Landing, NY, May 8.
4. Qasim, S.R. and Chiang, W. (1994). *Sanitary Landfill Leachate*. Technomic Publishing Co., Lancaster, PA.
5. Cozzarelli, I.M. et al. (2000). Geochemical and microbiological methods for evaluating anaerobic processes in an aquifer contaminated by landfill leachate. *Environmental Science and Technology* **34**(18): 4025–4033.
6. Clister, W., Brown, K., and Hibbs, S. (2001). Improvement of groundwater quality through management of landfill gas at MSW landfills. *MSW Management* **11**(3): 34–39.
7. Soltani-Ahmadi, H. (2002). A review of landfill gas components. *MSW Management* **12**(6): 120–123. (Expanded at *www.forester.net/mw_0209_nmoc.html*).
8. Tonjes, D.J. (1998). *Modified Normed Stiff Diagrams: A New Means of Interpreting Groundwater Sampling Results at Municipal Solid Landfills*. Dissertation, SUNY at Stony Brook.
9. Melosi, M.V. (2000). *The Sanitary City*. The Johns Hopkins University Press, Baltimore, MD.
10. Galusha, D. (1999). *Liquid Assets: A History of New York City's Water System*. Purple Mountain Press, Fleischmanns, NY.
11. Zanoni, A.E. (1972). Ground-water pollution and sanitary landfills: a critical review. *Ground Water* **10**(1): 3–13.
12. Apgar, M.A. and Langmuir, D. (1971). Ground-water pollution potential of a landfill above the water table. *Ground Water* **9**(6): 76–94.
13. Kimmel, G.E. and Braids, O.C. (1974). Leachate plumes in a highly permeable aquifer. *Ground Water* **12**(6): 388–392.
14. Office of Technology Assessment. (1988). *Facing America's Trash: What Next for Municipal Solid Waste?* United States Congress, Washington, DC.

15. Office of Technology Assessment. (1984). *Protecting the Nation's Groundwater from Contamination*. United States Congress, Washington, DC, Vol. 2.
16. Baedecker, M.J. and Back, W. (1979). Modern marine sediments as a natural analog to the chemically stressed environment of a landfill. *Journal of Hydrology* **43**: 393–414.
17. Cherry, J.A. (1983). Introduction. *Journal of Hydrology* **63**: vii–ix.
18. Nicholson, R.V., Cherry, J.A., and Reardon, E.J. (1983). Migration of contaminants in groundwater at a landfill: a case study, 6. Hydrogeochemistry. *Journal of Hydrology* **63**: 131–176.
19. Ostendorf, D.W., Noss, R.R., and Lederer, D.O. (1984). Landfill leachate migration through shallow unconfined aquifers. *Water Resources Research* **20**(2): 291–296.
20. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NJ.
21. NYSDEC. (1992). *Inactive Hazardous Wastes Disposal Sites in New York State, Annual Report: Appendix 1: List of Sites by County: Nassau, Suffolk*. New York State Department of Environmental Conservation, Albany, NY.
22. Lesage, S., Jackson, R.E., Priddle, M.W., and Riemann, P.G. (1990). Occurrence and fate of organic solvent residues in anoxic groundwater at the Gloucester Landfill, Canada. *Environmental Science and Technology* **24**(4): 559–566.
23. Leahy, J.G. and Colwell, R.R. (1990). Microbial degradation of hydrocarbons in the environment. *Microbiological Reviews* **54**(3): 305–315.
24. Myneni, S.C.B. (2002). Formation of stable chlorinated hydrocarbons in weathering plant materials. *Science* **295**: 1039–1041.
25. Kehew, A.E. and Passero, R.N. (1990). pH and redox buffering mechanisms in a glacial drift aquifer contaminated by landfill leachate. *Ground Water* **28**(5): 728–737.
26. Eganhouse, R.P., Cozzarelli, I.M., Scholl, M.A., and Matthews, L.A. (2001). Natural attenuation of volatile organic compounds (VOCs) in the leachate plume of a municipal landfill: using alkylbenzenes as process probes. *Ground Water* **39**(2): 192–202.
27. Hodgson, A.T., Garbesi, K., Sextro, R.G., and Daisey, J.M. (1992). Soil-gas contamination and entry of volatile organic compounds into a house near a landfill. *Journal of Air and Waste Management Association* **42**(3): 277–283.
28. NYSDOH. (1998). *Investigations of Cancer Incidence and Residence near 38 Landfills with Soil Gas Migration Conditions: New York State, 1980-1989*. Final Report to ATSDR. New York State Department of Health, Albany, NY.
29. Kerfoot, H.B. (1994). Landfill gas effects of groundwater samples at a municipal solid waste facility. *Journal of Air and Waste Management Association* **44**: 1293–1298.
30. Kelly, W.R., Matisoff, G., and Fisher, J.B. (1985). The effects of a gas well blow out on groundwater chemistry. *Environmental Geology Water Sciences* **7**(4): 205–213.
31. Fahrquahr, G.J. and Rovers, F.A. (1973). Gas production during refuse decomposition. *Water, Air, and Soil Pollution* **2**: 483–495.
32. O'Leary, P. and Walsh, P. (2002a). Landfill gas movement, control, and energy recovery. *Waste Age* **33**(3): 48–54.
33. Groseclose, M. et al. (2001). Hydraulic containment of landfill gas driven VOCs in groundwater using a state of the art computerized control system at the Los Reales Landfill. In: *Proceedings of the Fourth Annual Landfill Symposium*, Solid Waste Association of North America, Denver, CO, pp. 37–43.
34. Tonjes, D.J., Heil, J.H., and Black, J.A. (1995). Sliding Stiff diagrams: a sophisticated ground water analytical tool. *Ground Water Monitoring and Remediation* **15**(1): 134–139.
35. O'Leary, P. and Walsh, P. (2002b). Landfill cover and liner systems for water quality protection. *Waste Age* **33**(4): 124–129.
36. Othman, M.A., Bonaparte, R., and Gross, B.A. (1997). Preliminary results of study of composite liner field performance. In: *Proceedings of the GRI-10 Conference on Field Performance of Geosynthetics and Geosynthetic Related Systems*. R.M. Koerner, G.R. Koerner, and Y.G. Hsuan (Eds.). GSI Publications, Philadelphia, PA, pp. 115–142.
37. Guzzone, B. (2001). Landfill gas utilization: the future's so bright. *MSW Management* **11**(4): 46–51.
38. Reeves, T.S. (1999). Run-off/run-on management: observations of storm water management at landfills. In: *Proceedings of the Fourth Annual Landfill Symposium*, Solid Waste Association of North America, Denver, CO, pp. 145–154.
39. Goldstein, N. and Madtes, C. (2001). The state of garbage in America. *BioCycle* **42**(12): 42–54.
40. Christensen, T.H., Bjerg, P.L., and Kjeldsen., P. (2000). Natural attenuation: a feasible approach to remediation of ground water pollution at landfills?. *Ground Water Monitoring and Remediation* **Winter 2000**: 69–77.
41. Mackay, D.M. and Cherry, J.A. (1989). Groundwater contamination: pump-and-treat remediation. *Environmental Science and Technology* **23**(6): 630–636.
42. Campman, C. and Yates, A. (2002). Bioreactor landfills: an idea whose time has come. *MSW Management* **12**(6): 70–81.
43. Hull, P. (2000). Changing the schedule. *MSW Management* **10**(4): 40–45.

METAL ORGANIC INTERACTIONS IN SUBTITLE D LANDFILL LEACHATES AND ASSOCIATED GROUND WATERS

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INTRODUCTION

Organic compounds are one of the most important constituents of landfill leachate waters. Their nature and relative amount are dependent on landfill age and evolutionary stage (1). In the early stages of landfills, organic compounds present in the leachate are mostly species with molecular weight (MW) less than 1000 Da, although with a nonnegligible fraction of higher MW species. The leachate pH is typically around 5 in this stage because of the abundance of low molecular weight organic acids. This acidic stage can last for a few years or up to ten years depending on landfills. Gradually, landfill leachates evolve toward the methanogenic stage, attaining pH values around 8, where higher molecular weight organic acids develop, including fulvic- and humic-type compounds, together with the precipitation of sparingly soluble metal phases, which reduces their mobility (2). Organic compounds, with their abundant functional groups, are recognized important metal ligands in this system. Among the different types of compounds,

carboxylic acids and phenols are always the most abundant ones (3).

METAL—ORGANIC COMPLEX STABILITY

Metals do not constitute an important component of landfill waters. However, because they are persistent pollutants in the environment, knowing their fate is of utmost importance. Toxicity of metals to living creatures is a well-known issue. Despite such risk, not every chemical form is equally hazardous, one such example is Cr, being an essential component to glucose metabolism, it is also extremely poisonous in the chromate form (Cr(VI)). On the contrary, Cr(III) is not particularly toxic and forms insoluble solids, which reduces its bioavailability. Depending on the speciation and complex formation, metal cations may have different migration velocities in groundwater, which may increase with metal-organic ligand association, and eventually reduce their bioavailability.

Metal-organic interaction in landfill-contaminated waters depends on the stability of complex formation and metal concentration in solution. Classification of metals into hard-sphere (type A) or soft-sphere (type B) cations (4) is helpful in grouping them according to type of complex formation and stability. Hard-sphere cations have noble gas configurations with spherical symmetric orbitals, because of the low polarizability of the electron cloud. These cations form ionic bonds mostly with ligands that have oxygen as a donor atom. Alkali and earth-alkali metals and Al^{3+} are examples in this group. Soft-sphere cations have deformable electron clouds because of their greater polarizability. These metals predominantly form covalent bonds with ligands having S or N as donor atoms. Metal cations in this group include Cu^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, and Tl^{3+}. Besides, transition metal cations, such as V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}, also have similar properties (4).

For transition metal cations, a reasonably well-established rule for a sequence of complex stability indicates that the stability increases in the series (known as the Irving–Williams order) $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (4). For hard-sphere cations, complex stability is proportional to the charge/radius ratio of the cation.

Complexes with monodentate ligands are usually less stable than those with multidentate complexes (chelates). Normally, monodentate complexes are easily dissociated at dilute concentrations of the metal cation, which is well illustrated in experiments with monodentate, bidentate, and tertadentate Cu(II) amine complexes. At dilute metal concentrations ($<10^{-4}$ M), where the monodentate complex is fully dissociated, the tertadentate complex remains stable in solution. Thus, even at concentration levels that are likely to be found in leachate-contaminated waters, the complexing effect of monodentate ligands is expected to be negligible. This experimental evidence may justify the verification that the highly abundant monocarboxylic acids on leachate-derived waters had little influence on the adsorption of metals such as Cu and Zn onto solid phases (5,6). Recently, Schilling and Cooper (7) identified that carboxylic groups are the most important binding sites for Cu(II) cations in soil organic matter, and that phenol groups are less important. Increase on metal sorption capacity is also observed with the addition of carboxyl and amino groups to various types of biomass (8).

METAL-ORGANIC INTERACTION IN LANDFILL-POLLUTED ENVIRONMENTS

In spite of such general knowledge about metal-organic complexation stability, it must be stressed that a great deal of experimental studies do not reflect the environment of a landfill-polluted water. Thus, the expected behavior of metals may differ substantially from what may be previously known, and several factors may induce such a view: first, most experimental work deals with manipulated and treated organic compounds; second, very few reported investigations actually dealt with metal-organic complexation in landfill lechate or leachate-polluted groundwater systems; and third, the influence that a high ionic strength environment and the presence of multiple competing ligands has on the ability to form metal-organic complexes is not known. Specific studies on metal-organic complexation associated to landfill leachate waters or leachate-polluted groundwaters are restricted to a few metal cations, most notably Pb, Cd, Ni, Cu, Cr, and Zn (e.g., 9–12).

Despite how scarce and, ultimately, complex these studies may be, it has been possible to gather important knowledge on metal-organic compound interaction. Speciation studies on a landfill leachate based on an exchange procedure with Chelex 100 resin demonstrates that the free or labile complexed fraction is the most important for all the metals studied by Majone at al. (12), increasing from 50% to 80% in the order Cd < Pb < Ni < Cu (≈80%). The slowly enchangeable fraction represents 14% for Cu, 28% for Pb, and 47% for Cd. Ni has the higher relative percentage in the inert or stable complexed fraction (17%). In the case of Cu, this metal becomes complexed either with low molecular weight compounds (<1000 Da, around 47%) or with high molecular weight compounds (>12000 Da, around 45%), these latter corresponding probably to humic acids (12). Overall, these authors concluded that the high MW organic acids have an important influence on metal speciation, and bonding to these substances increases in the rank Ni < Cd < Cu. The work of Jensen and Christensen (11) and Jensen et al. (10) showed that a significant but highly variable fraction of heavy metals have affinity for dissolved or colloidal organic matter. It must also be stressed that the distribution of metals among the different groups considered (dissolved and colloidal forms, organic- or inorganic-associated) varied between samples and between metals within the same sample (10), which demonstrates the heterogeneity of these systems and difficulty in achieving general conclusions. However, in leachates, it has been possible to show that heavy metals, such as Cu, Pb, and Cd, are predominantly associated with organic matter, either in colloidal form or dissolved. A substantial fraction of dissolved metals, such as Zn and Ni, is mostly associated with dissolved inorganic complexes, the remaining are associated with colloidal fractions (either organic or inorganic). The importance that colloidal organic matter has on the speciation and

binding of Cu and Pb (10) seems to be the most plausible explanation for the differential partitioning of metals to sediments near the source of spilled landfill leachate to the surface environment (6). Besides, it has also been verified that metals such as Zn and Ni had much less affinity to organic compounds, preferentially forming insoluble sulfide phases, as in the case of Zn. Christensen et al. (9) also verified for Zn and Ni in leachate-contaminated groundwater that at the low concentrations usually observed in the natural system, complex stability decreases significantly.

BIBLIOGRAPHY

1. Christensen, T.H. et al. (2001). Biogeochemistry of landfill leachate plumes. *Appl. Geochem.* **16**: 659–718.
2. Pohland, F.G. and Kim, J.C. (2000). Microbially mediated attenuation potential of landfill bioreactor systems. *Water Sci. Technol.* **41**: 247–254.
3. Albaiges, J., Casado, F., and Ventura, F. (1986). Organic indicators of groundwater pollution by a sanitary landfill. *Water Res.* **20**: 1153–1159.
4. Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters*, 3rd Edn. John Wiley & Sons, New York.
5. Schroth, B.K. and Sposito, G. (1998). Effect of landfill leachate organic acids on trace metal adsorption by kaolinite. *Environment. Sci. Technol.* **32**: 1404–1408.
6. Gonçalves, M.A., Nogueira, J.M.F., Figueiras, J., Putnis, C.V., and Almeida, C. (2004). Base-metals and organic content in stream sediments in the vicinity of a landfill. *Appl. Geochem.* **19**: 137–151.
7. Schilling, M. and Cooper, W.T. (2004). Identification of copper binding sites in soil organic matter through chemical modifications and ^{13}C CP-MAS NMR Spectroscopy. *Environment. Sci. Technol.* **38**: 5059–5063.
8. Gardea-Torresdey, J.L., Tang, L., and Salvador, J.M. (1996). Copper adsorption by esterified and unesterified fractions of Sphagnum peat moss and its different humic substances. *J. Hazard. Mater.* **48**: 191–206.
9. Christensen, J.B., Jensen, D.L., and Christensen, T.H. (1996). Effect of dissolved organic carbon on the mobility of cadmium, nickel, and zinc in leachate polluted groundwater. *Water Res.* **30**: 3037–3049.
10. Jensen, D.L., Ledin, A., and Christensen, T.H. (1999). Speciation of heavy metals in landfill-leachate polluted groundwater. *Water Res.* **33**: 2642–2650.
11. Jensen, D.L. and Christensen, T.H. (1999). Colloidal and dissolved metals in leachates from four Danish landfills. *Water Res.* **33**: 2139–2147.
12. Majone, M., Papini, M.P., and Rolle, E. (1998). Influence of metal speciation in landfill leachates on kaolinite sorption. *Water Res.* **32**: 882–890.

LEACHING

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Leaching, sometimes referred to as eluviation, is the phenomenon whereby a liquid, usually water, moves through a matrix from one location to another, dissolving or suspending materials along the way. The matrix must be porous enough to allow fluid movement and is generally soil, but fractured bedrock or unconsolidated mineral or organic (humus) material can also leach liquids. Normally, this occurs under gravity and movement is downward. Occasionally, this movement is lateral when forces such as capillary action, soil matric potential, or confinement pressure draw the liquid to an area of high water tension or push the liquid from an area of high pressure. The liquid that migrates, generally referred to as leachate, contains a mix of dissolved and/or suspended ions or compounds. These materials, either present naturally in the environment or applied to the ground surface, include dissolved salts, fertilizers, soluble minerals, organic material such as humic or fulvic acids, plant nutrients, and natural or synthetic chemicals. Because water is a polar liquid, it can dissolve or transport a wide variety of substances from one location to another. Even nonpolar molecules can form micelles and be moved great distances by leaching.

Leaching is a function of several factors that affect the amount, rate, direction, and quality of the leachate: the hydraulic conductivity of the matrix, impeding layers (aquitards or aquicludes), partitioning coefficients of any chemicals present, antecedent soil water content (saturated vs. unsaturated flow), osmotic or matric potentials, the cation exchange capacity of the soil, the ionic makeup of the dissolved compounds in the percolating fluid, the water-holding capacity of the soil (largely attributable to soil texture), and the macropore flow (a function of soil porosity, structure, disturbance, burrowing animals, and root channels).

If water is applied at a rate slower than the ability of the soil surface to accept it (infiltration rate), water percolates downward once the water holding capacity of soil is exceeded. If water is applied at a faster rate, a portion of the applied water runs off the soil surface (potential erosion). See Table 1.

Most nonindustrial leaching occurs on agricultural land or under antiquated or modern landfills. Leaching rates are highest in humid regions or on land under irrigation and lowest in arid or permanently frozen regions. Leaching is governed by a few basic processes.

Table 1. Water-holding Capacity of Various Soils (Inches of Water Per Inch of Soil Depth)

Textural Class	Capacity
Sand	0.070
Loamy sand	0.065
Sandy loam	0.095
Sandy clay loam	0.150
Loam	0.165
Clay loam	0.185
Silt loam	0.20
Silt	0.23
Silty clay loam	0.25
Silty clay	0.22
Clay	0.20

Mass Flow

This is the dominant leaching process in most systems and accounts for the greatest movement of water and materials, often over large distances. When water infiltrates a dry, permeable soil, a discrete wetting front is formed that has a higher water content (lower tension) above than below. The depth of this wetting front depends on the amount of water added, the permeability of the surface (pore size, volume, and connectivity), and its initial wetness. To a lesser extent, wetting front migration is a response to the rate at which the water is applied. After water is no longer applied, the wetting front moves but at a slower rate due to reduced pressure from above.

Water infiltrating a dry soil can dissolve and transport salts or chemicals that are not strongly adsorbed on soil solids. Water can also dislodge and transport materials in suspension such as organic colloids or fine clays that are not readily soluble. This dissolved and/or suspended load is transported to depth via the percolating water, but only as far as the wetting front progresses. It can be moved more deeply by subsequent rainfall or irrigation, provided it is of sufficient volume to move percolating water past the previously established wetting front.

If a substance is loosely adsorbed onto solid surfaces in the soil, the depth to which the adsorbed chemical moves is reduced or the rate of movement slowed. This retardation factor, R, is related to the soil-water partition coefficient, K_d, of the particular substance being moved (Fig. 1):

$$R = 1 + \frac{\rho K_d}{\theta} \quad (1)$$

where ρ is the dry bulk density of the soil and θ is its volumetric water content. The retardation factor varies from a low of 1 for nonadsorbed chemicals to values in excess of 100 for some highly adsorbed ones. The depth to which a substance is leached largely depends on the adsorbent relationship between a substance and the matrix through which it percolates.

The wetting front in an initially dry soil corresponds to the leading edge of the infiltrating liquid. Surfaces that are not initially dry behave similarly except in some soils, where water entering a moist soil can displace water already present and push that water ahead of the front. In such cases, a dissolved or suspended substance would move only to the depth of the infiltrating water, not all the way to the wetting front. Alternatively, because macropore flow (preferential flow paths along cracks in structured soils or fractured rock) is usually present, some water at the wetting front may represent new water. Most likely the situation is a combination of these two mechanisms of water dispersal, which leads to uncertainty in the real location or concentration of a dissolved substance and also suggests that a dissolved chemical is not likely to be concentrated in a sharp pulse but will be more diluted or dispersed.

Dispersion

Water moving through soil pores travels at different rates due to porosity, tortuosity, and connectivity differences. A pulse of chemical traveling with the water has its leading and trailing edges spread out, a phenomenon called dispersion. Under natural conditions in the field, water rarely moves through a matrix at a constant rate at all times, even if its physical properties (texture, structure, ionic exchange capacity, etc.) are extremely uniform and water is applied at a constant rate.

Diffusion

Dissolved or suspended substances also move from regions of higher to lower concentration due to osmotic potential referred to as diffusion. Diffusion is usually much less significant than mass flow; it merely spreads the chemical out in an already wetted area. Its influence is generally small and its rate slow due to adsorption (on matrices high in clay and organic matter content).

Sorption

A chemical added to a soil partitions itself between a solution phase and an adsorbed solid phase. When the cation exchange capacity (CEC) of a soil is high (e.g., soils high in smectite clays or organic matter), this bonding is strong because cations are adsorbed to the negatively charged surfaces (Table 2). In other cases (soils with low-CEC clays or lacking clays and organic matter), bonding is quite weak.

Sorption or binding of dissolved chemicals on surfaces is significant because they are not free to move with percolating water. Although sorption retards the rate of

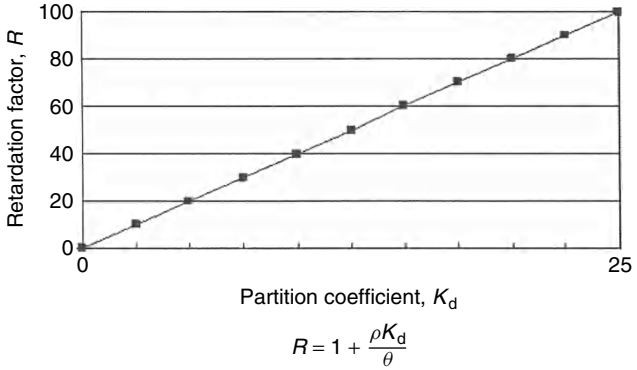


Figure 1.

Table 2. Normal Range of CEC Values for Common Soil Groups

Soil Groups	CEC in cmol(+)/kg
Light colored sands	3–5
Dark colored sands	10–20
Light colored loams and silt loams	10–20
Dark colored loams and silt loams	15–25
Dark colored silty clay loams and silty clays	30–40
Organic soils	50–100

chemical movement, it does not necessarily alter the rate of movement of the percolating solution itself.

Substances in a liquid–soil environment tend to establish a balance between the amount on solid surfaces and the amount in solution. Some chemicals exist primarily in the liquid phase; others are strongly adsorbed and exist primarily on solid surfaces. Molecules tend to move from one phase to another to maintain this balance. The manner in which the molecules are partitioned into solid and liquid phases depends on both matrix and chemical properties. These relationships, called sorption isotherms, can be determined experimentally. The center of the chemical pulse on a particular day is greater for substances that have smaller partition coefficients than for those that have larger ones because substances that have smaller partition coefficients are adsorbed less strongly to solid surfaces and can be dislodged and moved more readily by the percolating solution.

Degradation

Chemicals in the environment can undergo biological or chemical transformations, be absorbed by plants, volatilize into the atmosphere, be lost to surface water by surface water flow and erosion, or remain in the surface matrix and be available for leaching to groundwater. The importance of these different processes depends on the unique properties of the substance.

Many natural and synthetic chemicals break down or degrade over time from microbiological and chemical reactions. Substances with low persistence degrade quickly to other products, and highly persistent ones linger. Persistence is usually specified in terms of the degradation half-life, a measure of the time it takes for one-half of the original amount of a substance to be degraded (first-order degradation). Degradation rates are generally temperature and moisture dependent, and most biological breakdown occurs in the root zone of plants because more microbes exist there than elsewhere. Therefore, as compounds are leached to lower depths (below the root zone), they become more persistent and can leach to groundwater before surface organisms have had a chance to degrade them. Typically, root zones can vary from 1 to 6 feet below the surface, depending on the plant and its stage of development.

The chemical makeup of leachate can be altered or its volume reduced through several processes. Roots of actively photosynthesizing plants can scour out essential nutrients or absorb percolating water, denitrification and mineralization can remove or immobilize dissolved nitrogen, chemical alterations such as oxidation to less motile forms can occur (e.g., iron transformed in an oxidizing environment from a mobile, reduced ferrous Fe^{2+} state to an immobile, oxidized ferric Fe^{3+} state), cations (e.g., Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, etc.) can be adsorbed onto negatively charged surfaces, and shallow subsurface agricultural tile drains can siphon off leachate before it percolates more deeply (into groundwater).

The concern with leaching is that it accounts for the bulk of nonpoint source pollution of groundwater and subsequently to any surface water to which it is hydrologically connected. Any chemicals or suspended solids that are transported to groundwater may impair water quality for aquatic life or render it nonpotable or unfit for human contact (drinking, bathing, swimming). Lawn fertilizers, agricultural chemicals (pesticides, herbicides, fungicides, miticides, etc.), road salts, petrochemical spills, atmospheric particulate fallout (Hg, Pb, oxides of sulfur or nitrogen, etc.) can all end up in groundwater via leaching.

High-risk environments that are of primary concern include

- sandy soils
- shallow-rooted plants
- high rainfall areas or excess irrigation
- shallow unprotected groundwater
- wellhead protection zones
- homesteads with open wells

Leaching affects the receiving waterbody (e.g., a change in the trophic state of a lake receiving discharge from contaminated groundwater), and also in agricultural systems, represents a two-pronged economic loss: fertilizer purchases go wasted if nutrients end up in places other than the root zone, and plant nutrients made unavailable by leaching result in lower harvests. Essential plant nutrients, naturally occurring or supplemented by fertilizers, that are lost by leaching include

- *Calcium (Ca)*: ion generally in the largest concentration in leachate
- *Magnesium (Mg), Sulfur (S), Potassium (K)*: next highest concentrations, depending on soil composition and acidity of leachate
- *Nitrogen (N)*: ranges from high (recent fertilizer application on porous soil prior to intense rainfall) to low (natural systems with no disturbance or low precipitation), depending on plant growing conditions and natural soil fertility
- *Phosphorus (P)*: limited concentration in leachate due to low solubility and high affinity for sorption onto soil particles

The U.S. Environmental Protection Agency (EPA) regulates several pollutants that routinely make their way into drinking water supplies and pose health risks for consumers in the United States. For example, the EPA currently stipulates that drinking water cannot exceed 10 mg per liter (ppm) nitrate (NO_3^-); this poses significant problems for drinking water suppliers in rural areas that rely on aquifers under agricultural fields for their water source (Fig. 2). The EPA limits lead (Pb) in drinking water to 15 μg per liter (ppb), a challenge in older urban areas that still have lead service pipes as part of their underground water systems. Recently, the EPA issued guidelines for arsenic (Ar) in drinking water; the standard was lowered to a maximum of 10 ppb beginning January 23, 2006. In addition to these specific thresholds for drinking water, the EPA also regulates waterbodies (surface, groundwater, drinking water aquifers) for dissolved salts, fecal coliform

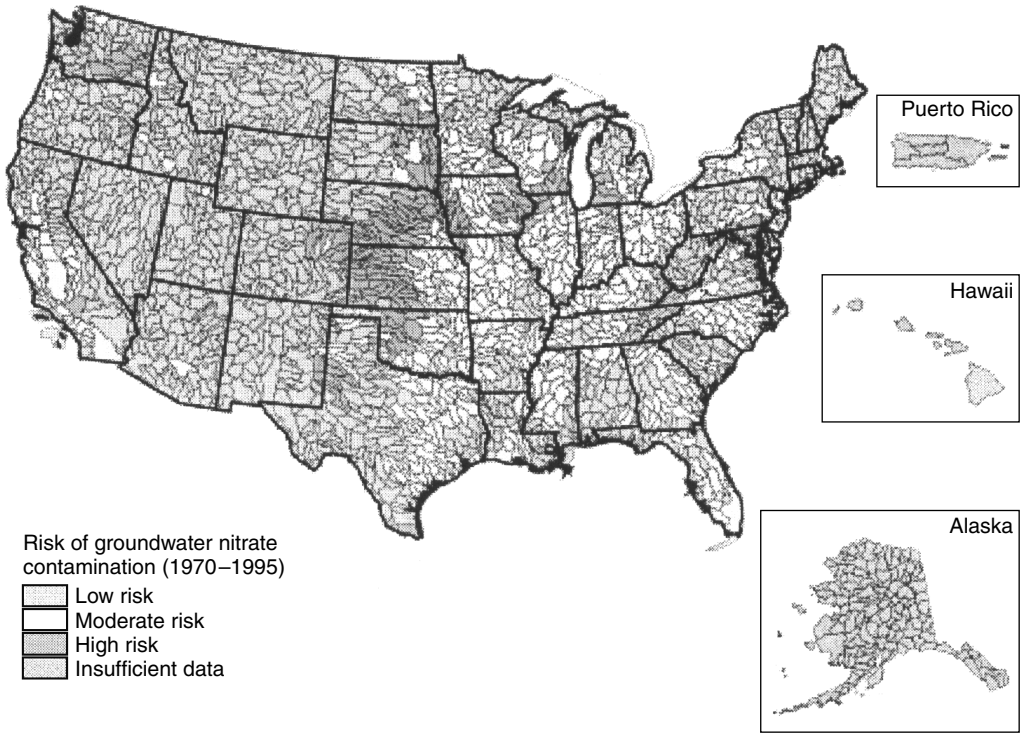


Figure 2. Risk of groundwater nitrate contamination.

bacteria, harmful chemicals, and more, some of which are attributable to leaching processes.

READING LIST

Brady, N.C. and Weil, R.R. (2002). *The Nature and Properties of Soils*, 13th Edn. Pearson Education, Upper Saddle River, NJ.

Hillel, D. (1998). *Environmental Soil Physics: Fundamentals, Applications, and Environmental Considerations*. Academic Press, New York.

Jury, W.A. and Horton, R. (2004). *Soil Physics*, 6th Edn. John Wiley & Sons, New York.

McBride, M.B. (1994). *Environmental Chemistry of Soils*. Oxford University Press, New York.

Nolan, B.T., Ruddy, B.C., Hitt, K.J., and Helsel, D.R. (1997). Risk of nitrate in groundwaters of the United States—a national perspective. *Environ. Sci. Technol.* **31**: 2229–2236.

Sawhney, B.L. and Brown, K. (Eds.). (1989). *Reactions and Movement of Organic Chemicals in Soils*. SSSA Spec. Publ. No. 22, Madison, WI.

WELL MAINTENANCE

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PREDICTIVE AND PREVENTIVE MAINTENANCE

Well maintenance consists of two overall problem-preventing scopes of work: predictive and preventive maintenance (together comprising PM). Predictive maintenance involves tasks such as monitoring water quality, power, and other indicator data to detect evidence of deterioration prior to a fault and making necessary repairs. Preventive maintenance includes tasks such as maintaining lubrication, replacing components, and preventive well treatments conducted prior to deterioration of performance. By contrast, reactive maintenance repairs deteriorated components and performance conditions.

PM GOALS

PM activities are intended to prevent or significantly slow performance deterioration and lengthen intervals between equipment replacements and service events. PM begins with design. In any engineered system, including water works and water wells, prevention of adverse water quality and performance problems begins with appropriate planning and design. These activities include

1. identifying potential problems
2. designing a system to minimize these problems
3. allowing for effective restoration.

Where industry-recommended design parameters (1,2) are followed and materials selected for resistance to deterioration due to water quality, deterioration can be slowed and prevented. These conditions are site-specific, and design is based on investigation and testing.

ANALYSES RELEVANT TO PM

PM of wells depends on analysis of water quality and well performance. The analyses performed necessarily depend

on the resources available and also on the environmental difficulties posed by the well environment and the well's purpose and use. Table 1 lists relevant parameters for commercially significant wells (e.g., public and industrial water supply, irrigation).

Data collection may be greatly simplified for wells in very low-demand environments or for low-impact use (campgrounds, low-volume domestic wells). However, some data collection should be performed systematically to avoid "run to failure" typical of such wells.

RECORDS

Records are important in establishing trends that show patterns in performance, including indication of deterioration. Records should include the following:

1. Physical locations and as-built descriptions of the wells and their equipment. The geographic location of well should include reference to fixed landmarks and coordinates.
2. As-built diagram of the well's construction, with any modifications over time.
3. Any lithologic and well construction log information.
4. Records of pumping tests and geophysical, borehole flow meter, etc. tests of the completed well over time.
5. Dates of replacement of components, manufacturer and type of component, if known, and length of service, if known. Include itemized invoices with costs. Take photos or videotapes of deteriorated components for future reference and include descriptions. Include copies of product owner operation and service literature. Document any contractor service personnel.
6. Color borehole TV survey video records: Take at any zero point, before and after well rehabilitation measures, and at service intervals. Tapes and CDs may be consolidated as summary CDs of important well features over the years. Label records by well identification and date and store properly in an accessible location. Transfer to improved media as available.

The level of complexity and schedule can vary. At a minimum, for any valuable well under stress or one that is difficult to replace, routine hydrologic performance parameters, water quality, and biofouling indicators should be checked regularly (Table 2).

ADDITIONAL PM INSPECTIONS AND PRECAUTIONS

The capture zones and immediate surroundings of wells should be free of threats to the potable or monitored water quality. The area should be inspected periodically to ensure this condition. Well tops should be securely sealed to prevent contamination and secured against unauthorized entry. However, service access should not be impaired. In some wells, pumps may be pulled, inspected, cleaned, and repaired, as necessary, on a periodic or performance basis.

Table 1. Summary of Methods Relevant to Well Maintenance

Parameter	Indicator
Fe and Mn (total, Fe^{2+}/Fe^{3+}, Fe minerals, Mn^{4+}/Mn^{2+}, Mn minerals and complexes)—sometimes other metals such as Al	Indications of clogging potential, presence of biofouling, E_h shifts. Fe transformations are the most common among redox-sensitive metals in the environment. Mn is less common but locally important.
S (total, $S^{2-}/S^0/SO_4{}^{2-}$, S minerals, and complexes)	Indications of corrosion and clogging potential, presence of biofouling, E_h shifts.
E_h (redox potential):	Direct indication of probable metallic ion states, microbial activity. Usually bulk E_h, which is a composite of microenvironments.
pH	Indication of acidity/basicity and likelihood of corrosion and/or mineral encrustation. Combined with E_h to determine likely metallic mineral states present.
Conductivity	Indication of TDS content and a component of corrosivity assessment.
Major ions, hardness and alkalinity	Carbonate minerals, F, Ca, Mg, Si, Na, Cl determine the types of encrusting minerals that may be present and are used in saturation indexes. Alkalinity used in index and cleaning solution calculations.
Turbidity and particle counts	Indication of suspended particles content, suitable for assessment of relative changes indicating changes in particle pumping or biofouling.
Sand/silt content (v/v, w/v)	Indication of success of development/redevelopment, potential for abrasion and clogging.
Biofouling parameters	Select appropriate methods to permit a complete but convenient assessment of biofouling mechanisms present.
Step-drawdown and specific capacity (Q/s) testing	Flow and drawdown testing conducted periodically. Step tests to calibrate and before and after service events. Q/s testing periodically.
Power and pump performance parameters	Volts, amps, ohms in electrical power both instantaneous and trends, megohm ground leakage, vibration analysis, pressure at various Q to indicate wear.

Table 2. Recommended Data Collection Intervals (Depends on Site Conditions).[a] The Following is for a Difficult Well Situation (Valuable Well) After Its First Year

Type of Inspection	Method	Interval
Physical inspection	Borehole color video	At pump service intervals. Concentrate on screen and other stress points.
	Surface facility inspection	Quarterly
	Examination of pulled components	As needed. Wells should be equipped for easy pulling if at all possible.
Hydraulic performance	Well discharge (flow rate and pressure)	Weekly
	Drawdown	Weekly
	Conduct graphical analysis	Quarterly.
	Specific capacity test (well hydraulic performance).	Annually or at recommended shorter intervals.
	Pump performance: Conduct 5-step "pump" test, compare to "nominal" data	At least annually or at recommended shorter intervals if pump service is severe (Q/s and pump test can be a single operation).
Electrical (power)	System and motor current and load factors	Weekly—recommend installation of current monitors with alarms.
Physicochemistry	Inorganic parameters	At least quarterly using on-site instruments (calibrated) or routine monitoring (laboratory).
	Suspended particulate matter (sand, silt, clay)	Manually at well testing then quarterly.
	Turbidity or particle counting (adds colloidal component)	In-line monitors (continuous).
Biofouling microbial component	BART (or similar) analyses: Wide suite of ecological indicators	Quarterly until patterns develops then drop all but target types.
	Biofilm flow cell for microscopy	Annually on selected wells.
Treatments and service	Well hydraulic improvement and pumping systems	As testing indicates Q/s drops below 90% or pumping system degrades.
	Instrumentation calibration	In accordance with standard protocols.

[a] After Reference 3.

PM TREATMENT

PM well treatments are those applied prophylactically to remove biofouling and clogging prior to impairment of performance, which is a relatively complex and site-specific practice. However, such treatments should be targeted to the clogging conditions, as mild as possible, and capable of being easily applied.

REVIEW AND UPDATE

Methods and experience in PM change and improve over time. Experience in specific well situations also provides the basis for refining practices. Well PM plans should include provision for periodic review and revision of the PM plan and its practices. Also important is a provision for training personnel in new methods and training new employees in PM practices and purpose.

The subject of well maintenance is too complex to consider adequately in a brief article. The following are references used in the preparation of this item and additional recommended sources of information.

BIBLIOGRAPHY

1. NGWA. (1998). *Manual of Water Well Construction Practices*. National Ground Water Association, Westerville, OH.
2. Roscoe Moss Co. (1990). *Handbook of Ground Water Development*. Wiley-Interscience, New York.
3. Alford, G., Leach, R., and Smith, S.A. (2000). *Operation and Maintenance of Extraction and Injection Wells at HTRW Sites*. EP 1110-1-27. U.S. Army Corps of Engineers, St. Louis, MO.

READING LIST

ADITC. (1997). *Drilling: The Manual of Methods, Applications and Management*. CRC Lewis, Boca Raton, FL.

Borch, M.A., Smith, S.A., and Noble, L.N. (1993). *Evaluation and Restoration of Water Supply Wells*. AWWA Research Foundation, Denver, CO.

Carruthers, R. (1994). Preventative maintenance for bores. In: *Proceedings Water Industry Workshop Operations Skills*, July 25–29, 1994, Hervey Bay, Queensland Dept. of Primary Industries, Brisbane.

Gariboglio, M.A. and Smith, S.A. (1993). *Corrosión e encrustación microbiológica en sistemas de captación y conducción de agua–Aspectos teóricos y aplicados*. Consejo Federal de Inversiones, San Martin, C.F., Argentina.

Ground Water Science. (2004). Well M&R Gateway. Available: http://www.groundwatersystems.com.

Helweg, O.J., Scott, V.H., and Scalmanini, W.C. (1983). *Improving Well and Pump Efficiency*. AWWA, Denver, CO.

Howsam, P., Misstears, B., and Jones, C. (1995). *Monitoring, Maintenance and Rehabilitation of Water Supply Boreholes*. Report 137, Construction Industry Research and Information Association, London, UK, p. 113.

Smith, S.A. (1992). *Methods for Monitoring Iron and Manganese Biofouling in Water Supply Wells*. AWWA Research Foundation, Denver, CO.

Smith, S.A. (1995). *Monitoring and Remediation Wells: Problems Prevention and Cures*. CRC Lewis, Boca Raton, FL.

Smith, S.A. (in prep). *Methods for Monitoring Common Biofouling Problems of Ground Water Systems*. Ground Water Science, Upper Sandusky, OH.

Water Systems Council. (1992). *Large Submersible Pumps Manual*. Water Systems Council, Chicago, IL.

MEGAWATERSHEDS

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The term "megawatershed" describes deep-seated subsurface aquifer systems that may consist of gravel, fracture-hosted bedrock, and/or sedimentary structures, which are integrated in terms of recharge, storage, transmissivity, and containment. They may not coincide with surface topographic divides and may receive recharge from parts of several surface watersheds including massive amounts of mountain block recharge. "Megawatershed" is a conceptual model, or paradigm, that describes this new class of groundwater domain (Fig. 1). Megawatersheds are formed over geologic time by a combination of factors, including tectonically induced brittle fracturing and displacement of rock facies and strata and solutioning of parent rock facies and regolith by chemically aggressive meteoric and hydrothermal waters. The history and nature of regional tectonic stress fields and principal bounding faults, interacting with lithology and climate, play a major role in determining the geometry and extent of megawatershed boundaries.

Megawatersheds often transcend surface topographic divides and may receive recharge from parts of several surface watersheds. Similarly, as a structurally contained water resource, wells drilled into multiple aquifers in a single megawatershed may produce water from potentially dissimilar lithologies with common hydraulics related to brittle fracturing and gravity-fed contributions from adjacent and overlying unconsolidated sediments. Megawatersheds often occupy diverse host environments exhibiting both primary (continuous) and secondary (fracture) porosities with flow systems delineated by fracture systems, faulted and/or weathered lithologic contacts, and igneous intrusions (e.g., dikes), overlying or adjoining weathered rock and overlying porous unconsolidated sediments. This model supersedes the traditional watershed and aquifer models, which describe topographically controlled, functionally two-dimensional drainages and incorrectly depict most deep groundwater resources as static, poorly recharged artifacts of surface flow, confined to local discrete bedrock or alluvial units.

The megawatershed concept operates effectively and has scientific validity and economic and management utility on a scale of 10s to 1000s of square kilometers. Studies have documented megawatershed environments in Africa, Asia, the Middle East, Europe, North America, South America, and the Caribbean.

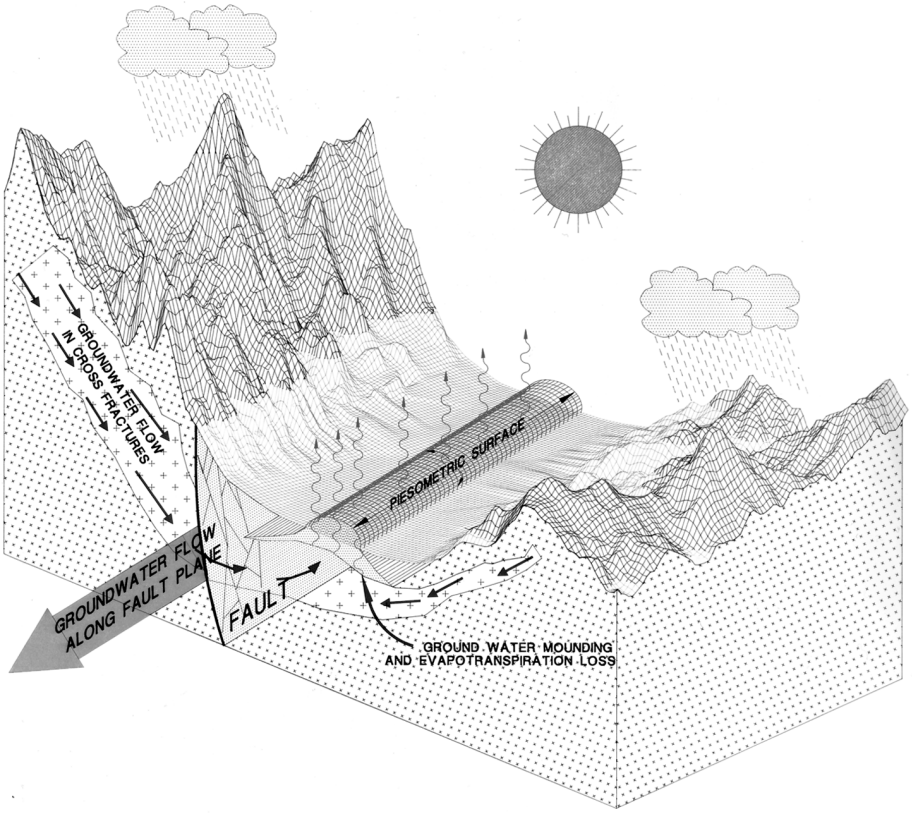


Figure 1. Megawatershed conceptual model indicating the roles of mountain block recharge and interbasin deep groundwater transfers within megawatersheds developed by Bisson Exploration Services Co. and CAD illustration by Summit Engineering, 1992.

HISTORY OF DISCOVERY

The space age has induced quantum leaps in geologic theory, and comparable advances in geophysical instrumentation and interpretive methods have permitted scientists to discover new information about the genesis, composition, and structure of the earth's crust and the internal dynamics of the many fluids, (e.g., magma, oil, water) contained within it. Equally important, the perfecting of computer-based geographic information systems (GIS) allowed skilled explorationists to combine and analyze many different types of data quickly and accurately, leading to major discoveries of oil, gas, minerals and, more recently, to breakthroughs in the understanding the nature and extent of groundwater resources, including the discovery of complex aquifer systems coined "megawatersheds" by the explorers who first documented the phenomenon, circa 1987, in the Great Rift systems of East Africa, where mountain block recharge from mountains and highlands in Ethiopia, Sudan, Kenya, and Chád remains largely untapped.

MEGAWATERSHEDS EXPLORATION PROGRAM

When the megawatershed paradigm is used as a groundwater exploration model, the result is greatly improved understanding of groundwater environments, permitting accurate, comprehensive assessments of "safe yield" from local, countrywide, or regional water resources. The megawatershed paradigm actually provides a template for measurement of all facets of the hydrologic cycle in reality-based natural hydrogeological catchments, including rainfall, evapotranspiration, surface and subsurface inflow and outflow interactions with surface water, shallow aquifers, deep fractured bedrock, and deep alluvial aquifers.

Modern explorationists employ current geologic theory, state-of-the-art exploration technologies, and interpretive methods adapted to the oil, gas, and mineral industries but rarely used in the groundwater field (Fig. 2). The "megawatersheds" paradigm of groundwater occurrence is the template the exploration program follows.

Case Studies

Two examples of megawatershed environments discovered using modern groundwater exploration methods are summarized here, one in the arid northwest region of Somaliland (1984–86) and the other in the humid small island developing state (SIDS) of Trinidad and Tobago, West Indies (1999–2002). These summaries are extracted from case studies included in Bisson and Lehr's book *Modern Groundwater Exploration: Discovering New Water Resources in Consolidated Rocks Using Innovative Hydrogeologic Concepts, Exploration, Drilling, Aquifer Testing and Management Methods*.

Somalia Case Study. In 1984, the Horn of Africa was experiencing a particularly brutal famine, brought about by the coincidence of periodic drought and regional and civil wars. America's ally, Somalia, was at war with the Soviet Union's ally, Ethiopia. At the same time, Somalia

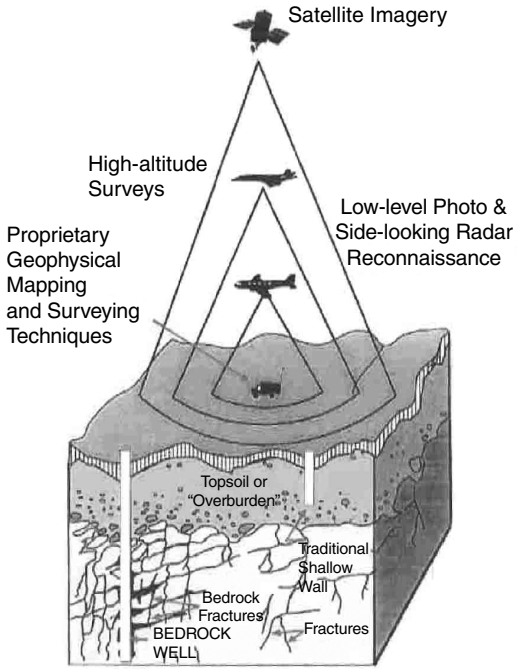


Figure 2. Illustration of megawatershed exploration program.

was mired in a bloody civil war, and the most active front for both conflicts was the remote, sparsely populated northwest part of Somalia, 1500 road-kilometers from the capital, Mogadishu, and bordered on the west and south sides by Ethiopia, to the north by the Gulf of Aden, and on the northwest, the last bastion of French colonialism in Africa, Djibouti. Several hundred thousand ethnic Somali refugees had been forced from their ancient tribal lands (annexed to Ethiopia after WWII) in the ongoing war and sought refuge in the arid Woqooyi Galbeed and Tog Dheer provinces of Somalia (Fig. 3). As a result of these circumstances, the socioeconomic fabric of the region was destabilized, cholera and other diseases were rampant in refugee camps located on the outskirts of major urban centers, and virtually no food was being produced locally.

Somalia's new patron, the United States, was working with the UNHCR and USAID to help feed and shelter those desperate people in an arid, undeveloped part of the Horn of Africa with all possible speed. Prior efforts to develop useful quantities of fresh groundwater in water-short areas had failed, and USAID's NGO contractors (New Transcentury Foundation) brought in a firm that pioneered modern groundwater exploration methods and discovered the megawatersheds phenomenon (BCI Geonetics, Inc.) to identify the groundwater resource base of the 35,000 km^2 region and develop emergency water sources for refugee camps and long-term water supplies for new refugee "cities."

Previous water development studies of northwest Somalia by other investigators focused on very limited surface and surficial water sources, but the BCI team focused on the region's bedrock groundwater potential, considering groundwater recharge and storage in unconsolidated overburden only in areas where they represented integral

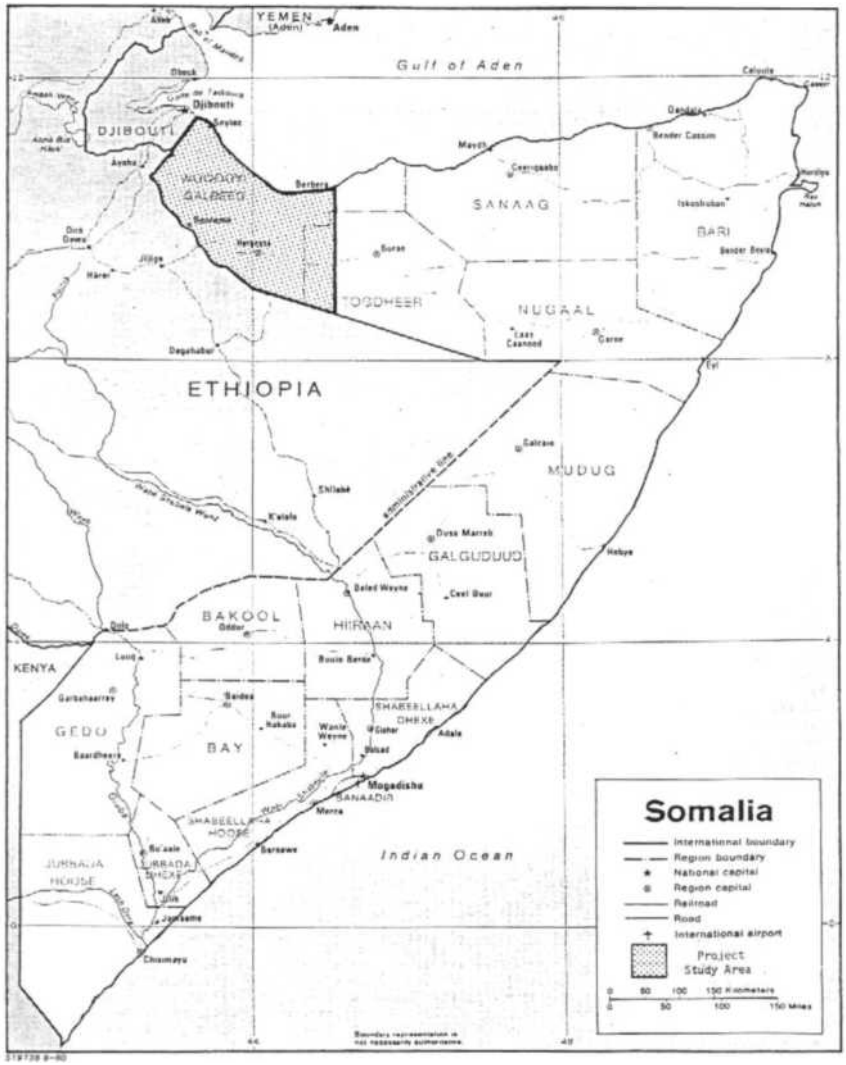


Figure 3. Somalia case study area.

hydrologic parts of deeper, underlying bedrock aquifer systems (megawatersheds).

To carry out their hydrogeologic mapping mission, the field team found only a few contemporary cultural and land-use maps and so augmented older maps with a combination of 1950s-vintage 1:125,000 scale British Ordinance Survey "spot-elevation" maps and RAF aerial photographs, plus 1980s- Tactical Pilotage Charts (TPCs), LandSat Image-maps, and high-resolution Space-Shuttle-borne Large Format Camera (LFC) photographs. The aerial and LFC photos were very useful navigational tools in certain remote areas where there were no roads leading to key bedrock outcrops and to other sites identified by BCI scientists on aerial photographs and satellite images. Thorn-bearing plants and sharp rocks punctured tires and automobile anatomies with great regularity, so undercarriage-armored Land Cruisers imported via neighboring Djibouti were outfitted with 12-ply tires for team expeditions.

The team was tasked to explore the farthest reaches of the county's lawless northwest region, and they often penetrated trackless areas where no vehicle or camel track existed and crossed unmarked borders between Ethiopia and Somalia. They were in constant danger of being captured by Ethiopian troops, strafed by MIGS during daylight, and held up at unmarked roadblocks by Somali bandits, revolutionaries, and government soldiers at night.

The region's wilderness also abounded with nonhuman predators, from hyenas to cobras, poisonous centipedes, and the nightmarish platter-sized, venomous "camel spider." The megawatersheds exploration team in Somalia encountered the most dangerous and difficult field conditions they had experienced to date, including a confrontation with Somali soldiers near the Ethiopian border that very nearly cost the lives of the team's senior scientists. BCI conducted this investigation using an advanced mineral-cum-groundwater exploration method, developed through extensive trial-and-error field-testing in the decade prior to the Somalia project. This systematic, practical approach to quantifying targeted minerals was singularly successful at identifying, drilling, and developing sustainable groundwater sources for nearby consumers in the most economical way.

The premise of the team's modern groundwater exploration program was that groundwater shares and is

controlled by the same geologic environments as minerals and is most readily identified and evaluated using modern approaches proven successful in oil, gas, and economical mineral exploration. The successful application of a sophisticated groundwater exploration program required a practiced exploration team of experts in structural geology, remote sensing, surficial geology, exploration geophysics, geochemistry, hydrology, and hydrogeology. Only with an integrated team such as this could the full groundwater potential of the study area be determined.

This was a pioneering, remote-sensing project incorporating LandSat MSS imagery and high-resolution contact prints from the ITEC-built Large Format Camera (LFC), carried aboard NASA's Space Shuttle Challenger in October 1984. NASA supplied stereo-paired photographs of the extreme westernmost part of the study area, and the BCI team used the extraordinary 60,000 square kilometer "footprint", 5-meter resolution, and high planimetric accuracy of enlarged LFC prints both as "ground truth" for BCI's geological interpretations of LandSat MSS image maps and also as road maps, navigating for 2 years through thousands of square kilometers of poorly mapped, highly dangerous terrain in Somalia. The team also integrated specially processed satellite MSS image-data and British Ordinance aerial photographs into its map database for field exploration.

The exploration team's satellite image and aerial photographic analysts first studied the geological history and structural environment of the study area and then focused on identifying true surface expressions of underlying geologic structures consistent with the known tectonic fabric of the region. This work produced accurate working maps of fracture and fault systems on a scale common with other working map products. In the final phase of this part of the analysis, correlations were made between these newly (remote-sensing) interpreted "structural lineaments" and team-constructed tectonic and hydrogeologic models, verified by published geologic maps and field mapping.

In the evaluation and selection process that led to the delineation of favorable zones for further hydrologic analysis and fieldwork, the significance attached to structural lineaments increased with the strength of expression, overall length, and spatial correlation with mapped faults and fractures shown in the fault and brittle feature map—particularly those faults belonging to one of the three major structural trends described in the full report.

An investigative hydrogeologic analytical methodology was established to quantify the amount of active recharge potentially percolating through the vadose zone and available for recharge to deeper alluvial aquifers and conductive fracture zones feeding regional groundwater flow systems in northwest Somalia. The methodology developed synoptically evaluated hydrometeorological data over the study area, including identification of the dominant variables and parameters affecting recharge. Variables evaluated included topography, elevation, slope, evapotranspiration, surface roughness and permeabilities (i.e., caliche layer occurrence), soil infiltration rates and depth, wadi bed characteristics (same as surface and soils), and wadi bed surface area. These variables were investigated using data from previous studies and in the literature, plus results from new fieldwork.

Several reporting stations had documented northwest Somalia's annual precipitation, and rainfall maps of northwest Somalia had previously been published, but meteorological stations were sparse, daily precipitation was not recorded, and the methodology and assumptions on which rainfall maps were based were uncertain. The BCI team therefore sought a means of working with existing data to make it more useful by establishing correlative relationships between documented precipitation and study area topography, thereby generating a rainfall map reflecting statistical correlations of average annual rainfall with elevation. A linear regression was done with rainfall as the dependent variable and elevation as the independent variable.

Wadi beds provide an efficient pathway to the water table and, therefore, a viable mode of recharge. No information on rates of recharge through wadi beds was found. Thus, fieldwork was carried out to estimate recharge through wadi beds. Infiltration rates of the wadi bed surfaces were tested in the field to determine just how quickly storm water would be absorbed. Surface areas of the wadi beds were measured to provide relationships between infiltration rates and volume of recharge.

The slope of the land surface affects the ratio between infiltration and surface runoff. The steeper the slope, the greater the percentage of surface runoff leading to flooding conditions in the wadi beds. Steep slopes also generally have thinner soil cover and exposed bedrock, which increases the chances of groundwater recharge from the infiltration that does take place.

In spite of the early termination of the BCI project due to civil war before large production wells were drilled, the project generated the first-ever strategic groundwater development map for the region, identifying the potential for tens of millions of gallons per day of renewable groundwater available from regional fractured bedrock aquifers (megawatersheds) and solved the water crisis for many refugees and indigenous people by supplying more than 1.5 million gallons per day of fresh, potable water from six test wells. Some of the bedrock test wells reportedly have continued to supply fresh water to Borama's citizens and others for the past 18 years.

Small Island Developing States—Trinidad and Tobago Case Studies. In 1999 and again in 2000, the Water and Sewerage Authority (WASA) of Trinidad and Tobago engaged a team of exploration scientists who utilized the megawatersheds model and modern groundwater exploration technologies in an attempt to gain independence from unreliable surface water sources and to avoid the further expense and environmental impacts of additional dams and desalination plants, especially in the highly sensitive rain forest and coral reefs of Tobago. All previous attempts to find large quantities of naturally recharged and sustainable fresh groundwater using traditional hydrogeologic models and groundwater development methods had failed.

In the quest to accomplish the most comprehensive and accurate groundwater assessment ever implemented anywhere, WASA's contractor implemented data searches on the broadest possible front and applied the most advanced digital, GIS database construction, management, and computer-visualization technologies available, collecting and digitizing diverse data never before pooled; performing analyses of regional tectonic models and satellite remote sensing; digitizing over 15,000 data points from oil and gas seismic lines; carrying out hundreds of line-kilometers of geophysical surveys; interpreting 1600 hundred logs from oil, gas, and water wells; and completing intensive on-ground geologic mapping in prospective megawatersheds.

The exploration team then employed a novel "multiple convergent datasets" method of data processing and integration to produce a working groundwater map of Tobago (Fig. 4) and a state-of-the-art digital hydrogeologic map of Trinidad (Fig. 5). The new maps identified several major new megawatersheds in Tobago and increased the known, sustainable groundwater reserves almost 40-fold, from less than 0.5 million imperial gallons per day (imgd) to 40 imgd.

Subsequent drilling and long-term pumping (>36 months in several cases) confirmed the megawatersheds models and actually developed nearly 5 imgd of new deep bedrock groundwater sources for Tobago for less than US$ 10 million in 1 year, producing an amount of new water equal to a proposed US$ 80 million dam, slated for 5 years of construction in Tobago's protected rainforest.

On the island of Trinidad, modern groundwater exploration methods were successfully employed to identify megawatersheds, bedrock and sedimentary aquifers, and aquifer systems that increased the amount of known, safely extractable groundwater more than 10-fold; the models were validated by test wells and 15.8 imgd of production well long-term pumping [>24 months in several cases to date (Sept.2004)]. Digital copies of the new island-wide maps were provided to WASA for multiagency use within all government ministries.

Trinidad and Tobago is the first country and also the first small island developing state (SIDS) to employ, the megawatersheds paradigm and modern groundwater exploration methods on a national scale, in a highly successful attempt to address short-term water shortages and long-term economic development issues. Within 3 years, Trinidad and Tobago's use of the megawatershed exploration approach resulted in groundwater discoveries in the twin-island state exceeding 300 million US gallons per day, causing a true paradigm shift in the country's vision of its fresh water resources from chronic dependence on unreliable surface water sources to drought- and contamination-resistant, deep, groundwater sources.

The benefits of the Trinidad and Tobago Water Authority's innovative water development program was evident during the 2001 and 2003 dry seasons on the island of Tobago, when surface supplies were severely curtailed and the megawatersheds wells became the primary source of reliable drinking water for the island's indigenous and tourist populations.

EXOHYDROLOGY—IMPLICATIONS OF THE MEGAWATERSHEDS PARADIGM ON MARS

In the 1980s, groundwater investigators hypothesized that the striking similarity of geomorphologies between terrestrial and Martian deserts suggests a comparable geotectonic and hydrometeorological genesis, possibly indicative of paleomegawatershed formations that might retain groundwater in deep bedrock fractures and/or provide bedrock pathways for modern, tectonically induced groundwater flows (see Bisson and El-Baz, 1988).

BIBLIOGRAPHY

AFRICA

Alam, M. (1989). Water resources of the Middle East and North Africa, with particular reference to deep artesian ground water resources of the area. *International Report–World Bank and in Water Int.* **14**: 3.

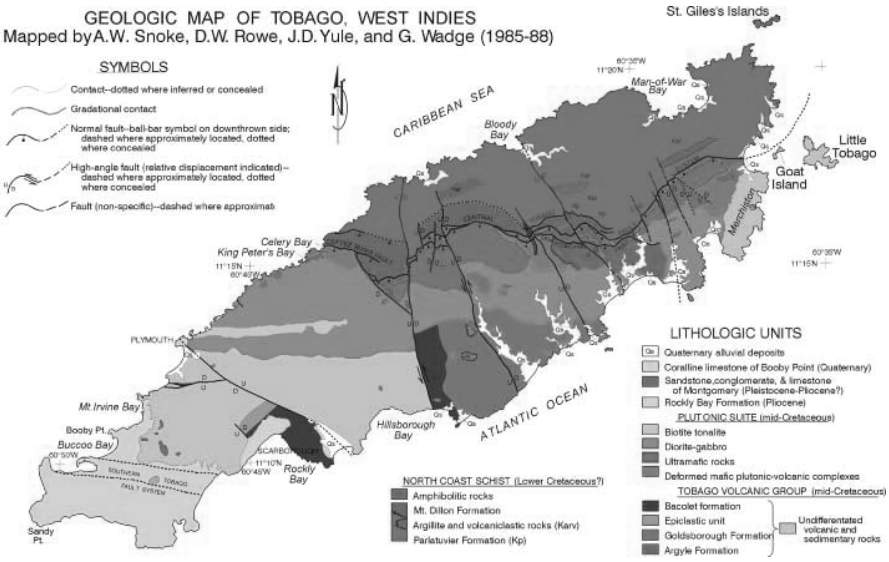


Figure 4. Tobago megawatersheds and favorable areas map.

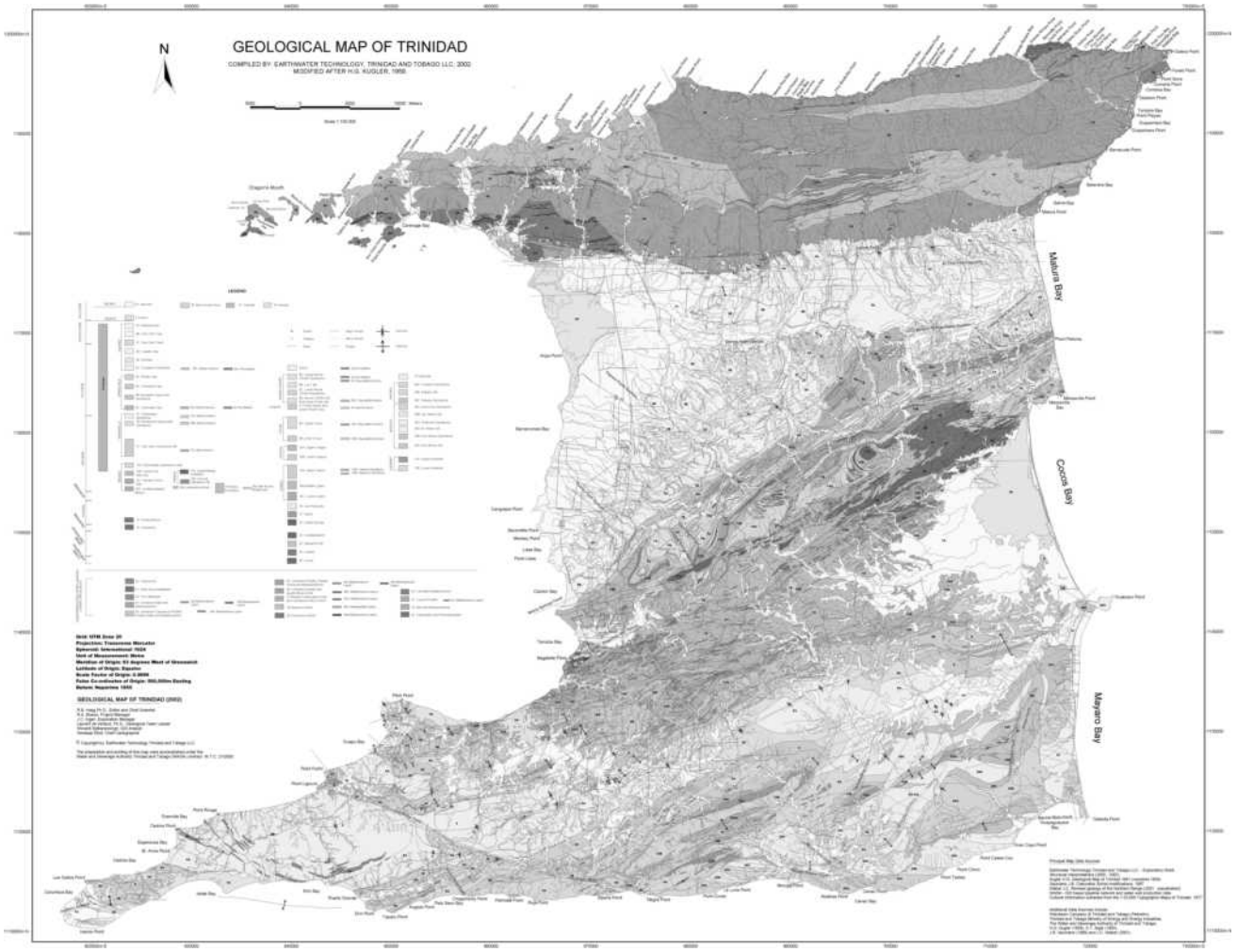


Figure 5. Hydrogeologic map of Trinidad, 2002. Copyright Earthwater Technology Trinidad & Tobago LLC and Water and Sewerage Authority of Trinidad and Tobago.

Bisson, R.A., Hoag, R.B., Jr., Ingari, J., and DeMars, R.M. (1984–1986). *BCI-Geonetics, Regional Groundwater Assessment and Development Program for Northwestern Somaliland*. Reports and Maps; for USAID.

Bisson, R.A., Bisson Exploration Services Company. (1992). *Megawatersheds Development Feasibility Study of Ethiopia*, Report and Maps, for U.S. Office of Foreign Disaster Assistance (OFDA).

Bisson, R.A. and Hoag, R.B. (1985). *BCI-Geonetics, Regional Groundwater Resources of South Africa, Namibia and Botswana*. Report and Maps, for British Petroleum Southern Africa.

Bisson, R.A. (1987). *BCI-Geonetics, Megawatersheds Development Feasibility Study of Northern Sudan*. Report and Maps; for USAID Mission Khartoum.

Bisson, R.A., Hoag, R.B., Jr., Ingari, J., Hoisington, D., and DeMars, R.M. (1990). *New Groundwater and Economic Prosperity in the Red Sea Province, Sudan*. Technical and Economic Feasibility Report, with Maps and Test and Production Well Plan, for USAID Misson Khartoum.

Bisson, R.A. (1986). *BCI-Geonetics, Inc., Megawatershed Development Feasibility Study of Eastern Zimbabwe, with Economic Analysis by Bechtel International 1983*. submitted to USAID TDA.

Ingari, J.C. (1986). *BCI-Geonetics, Inc., Sabi Basin Groundwater Geophysical Survey Report and Maps*. for USAID TDA.

ASIA

Afghanistan

Bisson, R. (2003). *Megawatersheds preferability study, Report and Maps, for Chemonics International* Earthwater Technology International.

Malaysia

Bisson, R. (1997). *Feasibility Study for Enron International*. Earthwater Technology International.

Nepal

Bisson, R. (1997). *Feasibility Study for Enron International* Earthwater Technology International.

Singapore

Bisson, R. (1997). *Feasibility Study for Enron International* Earthwater Technology International.

MIDDLE EAST

General

Bisson, R.A., Roosevelt, K., and Siski, S. (1999). New Groundwater Discoveries as a Mechanism for Regional Conflict Resolution. *Proceedings of the Conference on Water Dispute Prevention & Development*, Center for the Global South, American University, Washington, DC, October 1998.

Bisson, R.A., Sheffield, S., and Siski, S. (1995) Megawatershed Exploration: A State-of-the-Art Technique Integrating Water Resources and Environmental Management Technologies. *Proceedings of the IDA World Congress on Desalination and Water Sciences*, AbuDhabi, UAE, November 18–24, 1995.

Bisson R.A. (1994). Integrated Exploration Techniques Siscover Potential for Renewable Regional Source of Pristine Groundwater in Fractured Bedrock. *Proccedings of The Fifth International Symposium on Application of Remote Sensing and GIS Technologies to Water Resources Management*, Damascus, Syria, Oct.31–Nov.3, 1994.

Bisson R.A. (1994). Space Age Integarted Exploration and Treatment of Renewable Regional Sources of Pristine Groundwater in Fractured Rock Megawatersheds. *Desalination*, **99**: 257–273.

Bisson R.A. (1993). The Megawatersheds Discovery, The Arid World's Water Legacy of Geotectonics. *International Symposium on Water Resources in the Middle East: Policy and Institutional Aspects*, Beckman Institute, University of Illinois at Urbana, October, 1993.

Israel

Bisson, R. (1996). *Feasibility Study for Enron International* Earthwater Technology International.

Jordan

Bisson, R. (1997). *Feasibility Study for Enron International* Earthwater Technology International.

Libya

Bisson, R. and El-Baz, F. (1987). *Evaluated as part of Northern Sudan Megawatershed Study*, for USAID, BCI Geonetics, Inc.

Saudi Arabia

Western

Bisson, R.A. (1994). Integrated exploration techniques discover potential for renewable regional sources of pristine groundwater in fractured bedrock. *Proc. Fifth Int. Symp. Appl. Remote Sensing and GIS Technol. Water Resour. Manage.*, Damascus, Syria, Oct. 31–Nov. 3, 1994.

Bisson, R.A. (1994). Space Age Integrated Exploration and Treatment of Renewable Regional Sources of Pristine Groundwater in Fractured Rock Megawatersheds. *Desalination* **99**: 257–273.

Bisson, R.A. (1993). The megawatersheds discovery, the arid world's water legacy of geotectonics. *Int. Symp. Water Resour. Middle East: Policy and Institutional Aspects*, Beckman Institute, University of Illinois at Urbana, October, 1993.

Bisson, R.A. and El-Baz, F. (1990). New groundwater for Sudan - the megawatersheds exploration model. *Proc. 23rd Int. Symp.* Remote Sensing Environ., Bangkok, Thailand, April, 1990.

Bisson, R.A. and El-Baz, F. (1990). Megawatersheds exploration model for African water development. (Presented by Mr. Ghali for authors). *African Water Technol. Exhibition*, Nairobi.

Bisson, R.A. (1989). Megawatersheds exploration model. *Third World Acad. Sci. Int. Conf. Desert Environ.*, Trieste, Italy, November.

EUROPE

Ireland (Republic)

Bisson, R. and Hoag, R. (1982). *Feasibility study for private developer* BCI Geonetics, Inc.

Bisson, R.A. and El-Baz, F. (1990). Megawatershed exploration model. *Water Wastewater Int. Conf.*, Barcelona, Spain, April.

Poland–West

Bisson, R. (1991). *Feasibility study for Sargent Drilling Company* Bisson Exploration Services Company.

Sardinia

Bisson, R. (1997). *Feasibility Study for Enron International* Earthwater Technology International.

Spain, Andalucia

Bisson, R. (1997). *Feasibility Study for Enron International* Earthwater Technology International.

NORTH AMERICA

Angillilo, O.R. (1959). *Replenishing Source of Waters Flowing Through Rock Fissure Aquifers*. Unpublished manuscript, presented to State of California.

Bisson, R.A. (1989). Groundwater—The Ultimate Economic Mineral. *Proceedings, the 2nd Annual Conference on Profiting from Water*. Santa Monica, CA, May 1989.

Bisson, R.A. (1999). *Privatization Water Delivery Economics and Updating the Global Water Balance: A Win-Win Scenario* U.S. Water Report, Saringa Group, Inc., November.

Bisson, R.A. and Hofmann, P.D.(1982). No Risk/Turnkey Water Supply Contracts. *Journal of the New Hampshire Water Works Association*, Feb. 1982.

Bisson, R.A. and Hofmann, P.D.(1989). Groundwater—The Paradoxical Economic Mineral, *Water and Wastewater Magazine*. April 1989.

Bisson, R.A. and Widger, W.K.(1977). Innovative Techniques for Water Resources Studies. *Journal of the New England Water Works Assn*, June 1977.

Burbey, T.J. and Prudic, D.E. (1991). *Conceptual Evaluation of Regional Ground-Water Flow in the Carbonate-Rock Province of the Great Basin, Nevada, Utah, and Adjacent States*. Regional Aquifer System Analysis. U.S.G.S Professional Paper 1409-D.

Church, T.M. (1996). An underground route for the water cycle. *Nature* 380.

Clark, R.D. (1983). Geophysical Exploration—No Water Shortage? *Geophysics: The Leading Edge of Exploration*. **2**(7) July.

Eastoe, C.J., Gu, A., and Long, A. (2004). The origins, ages, and flow paths of groundwater in the Tucson Basin: results of a study of multiple isotope systems. In: *Groundwater Recharge in a Desert Environment: The Southwestern United States.* Hogan, J.F., Phillips, F.M., and Scanlon, B.R., (Eds.). American Geophysical Union, Washington, DC.

Hoag, R.B., Jr. and Vernon, J.H. (1993). Wellhead Protection Area Delineation in a Fractured Bedrock Aquifer in Fayetteville, Georgia. *Proceedings of the 1993 Georgia Water Resources Conference*, Athens, GA.

Long, A. and Eastoe, C. (2003) Mountain-block recharge. In: *Sustainability of Semi-Arid Hydrology And Riparian Areas (SAHARA)*, September.

Manheim, F.T. (1967). Evidence for submarine discharge of water on the Atlantic Continental Slope of the Southern United

States, and suggestions for further search. *Trans. N. Y. Acad. Sci., Sect. Geol. Sci. Ser. II* **28**: 839–853.

Manning, A.H., Canie, J.S., and Landis, G.P. (2003). Mountain-Block Recharge To The Western Denver Basin, Colorado, Paper 11-4, *Rocky Mountain—55th Annual Meeting of the Geological Society of America*, Durango, CO, May.

Person, M. and Baumgartner, L. (1995). New Evidence for long-distance fluid migration within the earth's crust. US. National Report to International Union of Geodesy and Geophysics 1991–1994, Rev. *Geophys.*, Suppl. 1083–1091, July.

Person, M., Raffensperger, J.P., Ge, S., and Garven, G. (1996). Basin-scale hydrogeologic modeling. *Rev. Geophys.* **34** (1/Feb.): 61–87.

Widger, W.K. and Bisson, R.A. (1974). News From and About the Earth Resources Technology Satellite (ERTS). *NH Society of Professional Engineers' Journal*. OBSERVER Sept. 1974.

Williams, M., Liu, F., and Gertson, J. (2004). Mountain block recharge from snowmelt runoff in the Colorado Rocky. *Conference Proceedings AGU 24th Annual Hydrology Days 2004*. Colorado State University, American Geophysical Union, March.

SOUTH AMERICA

Magaritz Aravena, M., Pena, R.H., Suzuki, O., and Grilli, A. (1990). Source of ground water in the deserts of Northern Chile: Evidence of deep circulation of ground water from the Andes. *Ground Water* **28**: 4.

CARIBBEAN

Bisson, R.A., Hoag, R.B., Ingari, J.C., Maharaj, U.S., and Jadoo, L. (2001). Megawatersheds groundwater assessment and recharge calibration on the Island of Tobago, W.I.; A comparison of results using megawatersheds versus traditional methods of groundwater assessment. *CWWA 10th Annu. Conf. & Exhibition*, Grand Cayman, October.

Bisson, R.A., and Maharaj, U., (2003). Megawatersheds of the Caribbean: New Water from Old Rocks. Presented at the *Caribbean Water and Wastewater Association (CWWA) 12th Annual Conference*, Paradise Island, Bahamas, September 29–October 3, 2003.

de Verteuil, L., Stawicki, A.W., Hoag, R.B., Bisson, R.A., Ingari, J.C., Maharaj, U.S., and Mulchansingh, K. (2001). Sedimentary megawatersheds delineation: The role of genetic sequence stratigraphy and Complex fault systems analysis in groundwater resource assessment in Trinidad. *CWWA 10th Annu. Conf. & Exhibition*, Grand Cayman, October.

Durham, B., Yoxtheimer, D., Alloway, C. and Diaz, C. (2003). Innovative water Resources for Islands. *Desalination* **156**: 155-161.

Hoag, R.B., Bisson, R.A., Ingari, J.C., Maharaj, U.S., and Sankar, R. (2000). The megawatershed concept and recharge analyses—sustainable groundwater extraction from bedrock aquifers in Tobago. *9th Annu. Conf.* Exhibition, October 2–6, Trinidad and Tobago.

Hoag, R.B., Bowman, C. and Bisson, R.A. (2001). Estimation of Groundwater Recharge in Trinidad Using Meteorological, Geographic Information Systems(GIS), and Watershed Modeling. *CWWA 10th Annual Conference & Exhibition*, Grand Cayman Island, October 2001.

Hoag, R.B., Cormier, C., Bisson, R.A., Sankar, R., Jadoo, L., and Ingari, J. (2001). Exploration and pumping test results for a high-yield crystalline bedrock well in Tobago. *CWWA 10th Annu. Conf. & Exhibition*, Grand Cayman, October.

Maharaj, U.S., Bisson, R.A., and Hoag, R.B. (2001). Novel groundwater development technology and contract structure solves long-standing water shortage problems on the Island of Tobago, West Indies. *Fourth Inter-Am.* Dialogue Water Manage., Parana, Brazil, September.

Maharaj U.S. and Tota-Maharaj, T. (2001). High-Risk Groundwater Development Option for Small Island Developing States(SIDS). *CWWA 10th Annual Conference & Exhibition*, Grand Cayman Island, October 2001.

EXOHYROLOGY-MARS

Bisson, R.A. and El-Baz, F. (1988). *Paleowatersheds on Mars: The bedrock legacy, a feasibility proposal submitted to the Lunar and Planetary Institute*, Houston Texas, by Bisson, R.A. principal investigator and El-Baz, F. co-investigator.

MASS TRANSPORT IN SATURATED MEDIA

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ADVECTION AND HYDRODYNAMIC DISPERSION

Most of the matter transported by groundwater is in dissolved form, which is referred to as solute. Principally, advection and hydrodynamic dispersion affect the movement of solutes in groundwater. Advection occurs when flowing groundwater carries along dissolved solutes. Hydrodynamic dispersion is the spreading of groundwater and its dissolved constituents by mechanical mixing and diffusion. Mechanical mixing is spreading caused by the aquifer matrix. Diffusion, which can take place in groundwater that is not flowing, is the movement of solutes from areas of high to low concentration. This latter process can be illustrated by placing a drop of dye in a beaker of stagnant water. The dye will spread even though the water is not flowing.

Longitudinal dispersion expresses mixing along flow paths. At the pore scale, mechanical causes of longitudinal dispersion include (1) fluid moving faster in the center of pores than along the edges, (2) some fluid traveling along longer pathways than other fluid, and (3) fluid in larger pores traveling faster than fluid in smaller pores (1).

Transverse dispersion occurs in all directions in a plane perpendicular to groundwater flow. However, studies of mass transport often report only the vertical and horizontal components of transverse dispersion. Bifurcating flow paths cause transverse dispersion (Fig. 1).

Beyond the pore scale, bodies of rock or sediment with different hydraulic conductivity may induce mechanical dispersion within an aquifer. For example, groundwater and dissolved solutes may diverge around a clay lense within a predominantly sandy aquifer. This process is called macrodispersion.

The magnitude of longitudinal dispersion exceeds that of transverse dispersion, as solutes spread more in the direction of groundwater flow than in any direction within a perpendicular plane. Coefficients of longitudinal (subscript L), transverse horizontal (subscript

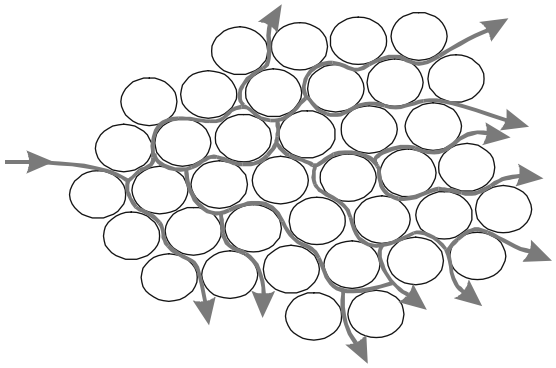


Figure 1. Pore-scale transverse dispersion in groundwater flowing between sand particles.

TH), and transverse vertical (subscript *TV*) hydrodynamic dispersion can be defined as follows:

$$D_L = \alpha_L v + D^* \quad (1)$$

$$D_{TH} = \alpha_{TH} v + D^* \quad (2)$$

$$D_{TV} = \alpha_{TV} v + D^* \quad (3)$$

where α is the dispersivity of the medium and D^* is the effective molecular diffusion coefficient. Dispersivity and the diffusion coefficient have units of length and length-squared/time, respectively. D^* ranges from 10^{-11} to 10^{-8} m^2/s for most ions in groundwater. Table 1 lists diffusion coefficients of several solutes in open water, which should be multiplied by a coefficient (less than one) to account for slower diffusion rates in tortuous, porous media. For unconsolidated media, this coefficient ranges from approximately 0.01 to 0.5 (3).

Dispersivity quantifies the ability of a medium to induce spreading by mechanical means. The magnitude of the mechanical mixing component of hydrodynamic dispersion (first term in Eqs. 1 to 3) usually exceeds molecular diffusion in flowing groundwater. Diffusion is a significant component of Eqs. 1 to 3 only for very slow-moving groundwater.

Dispersivity is a scale-dependent parameter, which attains higher values as the length of the transport domain increases. Laboratory estimates of dispersivity are routinely smaller than are field estimates. In a critical review of dispersivity observations from 59 different field sites, Gelhar et al. (4) found that, for data of high reliability, longitudinal dispersivity ranged from approximately 0.4 to 4 m. Transverse horizontal dispersivity was typically an order of magnitude less than longitudinal dispersivity, and transverse vertical dispersivity was an order of magnitude smaller than transverse horizontal dispersivity.

Table 1. Diffusion Coefficients in Water at 25 °C (2)

Solute	Coefficient (m^2/s)
Na^{+1}	1.33×10^{-9}
K^{+1}	1.96×10^{-9}
Mg^{+2}	7.05×10^{-10}
Ca^{+2}	7.93×10^{-10}
Fe^{+2}	7.19×10^{-10}
F^{-1}	1.46×10^{-9}
Cl^{-1}	2.03×10^{-9}
Br^{-1}	2.01×10^{-9}
HCO_3^{-2}	1.18×10^{-9}
SO_4^{-2}	1.07×10^{-9}
CO_3^{-2}	9.55×10^{-10}

Laboratory sand column experiments demonstrate the process of hydrodynamic dispersion. Distilled water runs through a column at a constant rate. The chloride concentration of the influent is suddenly changed from 0 to C_0 (any arbitrary concentration significantly higher than 0, for example, 1000 mg/L). Chloride concentrations, C, are monitored at the outlet, and the ratio C/C_0 is plotted against time (Fig. 2).

Early on, there are no chloride ions at the outlet; thus C and C/C_0 equal 0. Among the first group of chloride ions entering the tube, some arrive at the outlet ahead of others (because of hydrodynamic dispersion). As more chloride ions reach the outlet, C gradually increases to C_0. Had the solute been transported only by advection, the plotted curve would rise suddenly rather than gradually to C_0. The solute front "breaks through" the outlet when C/C_0 equals 0.5.

REACTIVE SOLUTES

Groundwater transports both chemically conservative and reactive solutes. Conservative solutes do not react with the aquifer medium or groundwater. Examples of conservative solutes are nitrate, chloride, and bromide. Reactive solutes have a tendency to sorb to aquifer media, moving from the liquid to solid phase, and they may go back into solution later on. Many synthetic organic chemicals are reactive, as are many cations. Negatively charged surfaces of clay particles are good sorbing media. If a solute is reactive, it will travel at a slower rate than the groundwater.

The velocity at which a reactive solute travels relative to flowing groundwater depends on both the solute and

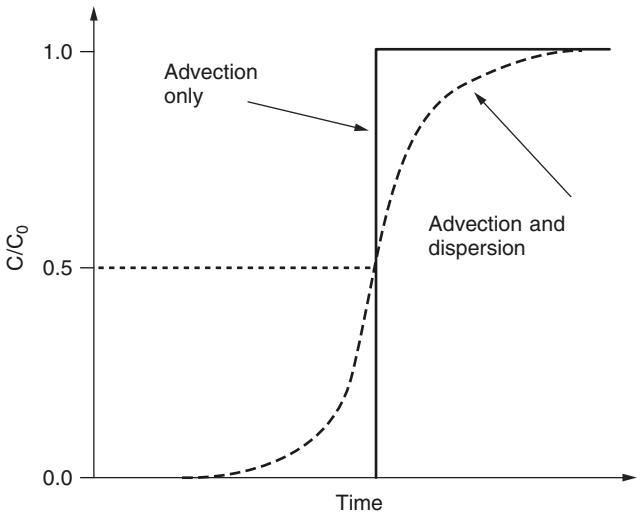


Figure 2. Solute breakthrough curve.

the aquifer material. A retardation factor, R_f, of 2 implies that the reactive solute travels at one half the velocity of groundwater, a factor of 5 implies one-fifth the velocity of groundwater, and so forth. Higher R_f values indicate slower solute transport.

Retardation factors should be carefully considered when delineating contaminant plumes. Multiple contaminants originating from the same source may occupy vastly different volumes in groundwater. Contaminants with higher retardation factors will occupy smaller volumes of aquifer. Conservative contaminants will have migrated further, and they best describe the maximum spatial impact of a leaking source. Chemical transformations and biodegradation, not quantified in R_f, also affect the spatial extent of a contaminant plume.

R_f can be computed as

$$R_f = 1 + \frac{\rho_b}{n} K_d \tag{4}$$

where K_d (commonly mL/g or L/kg) is the distribution coefficient for the solute with the aquifer. K_d can exceed 100 mL/g for reactive solutes and equals 0 for conservative solutes (5).

The distribution coefficient for a compound with a particular soil sample can be determined in a laboratory. An analyst fills jars containing soil with solutions of various contaminant concentrations. Several batches are created in this manner. The concentration of the contaminant in solution and the concentration in sediment are measured for each batch. These data are plotted on a curve (called an isotherm) fitted through the points (Fig. 3). The isotherm can take on different shapes. In the simplest case, it is linear, and K_d is the slope of the line (3). Thus, K_d has units of volume (of solution) per mass (of sediment). Langmuir (5) discusses methods for computing K_d for nonlinear isotherms.

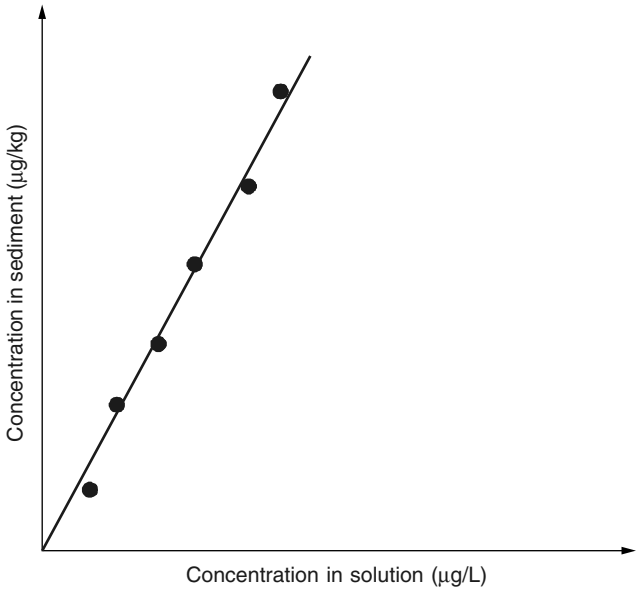


Figure 3. Data from laboratory batch experiment.

BIBLIOGRAPHY

1. Fetter, C.W. (2001). *Applied Hydrogeology*. 3rd Edn. Macmillan, New York.
2. Li, Y.H. and Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*: 38.
3. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
4. Gelhar, L.W., Welty, C., and Rehfeldt, K.R. (1992). A critical review of data on field-scale dispersion in aquifers. *Water Resour. Res.* **28**(7): 1955–1974.
5. Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice-Hall, Upper Saddle River, NJ.

SOIL AND WATER CONTAMINATION BY HEAVY METALS

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Soil and water contamination by heavy metals has a major adverse environmental impact. Concern has long existed over the threat of contamination of soil and water resources by heavy metals but has heightened in recent years as more knowledge has been gained about the negative and potentially serious affects that chronic exposure to heavy metals may have on the health of humans and other living organisms. Long-term exposure to lead affects human cognition; cadmium affects kidney, liver, and gastrointestinal tract functioning; and arsenic affects the skin, kidneys, and central nervous system (1). This article will address terminology, sources, mobility, risk assessment, and management and remediation alternatives for heavy metals in the environment that may contaminate soil and water resources.

TERMINOLOGY

Heavy metal is a term used to describe a subset of a large number of metals and metalloids, listed in the periodic table of the elements, which have properties of both metals and nonmetals. In general, heavy metals are elements in which the differentiating electrons are bonding electrons and typically include the top row of transition elements in the periodic table [i.e., scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), and mercury (Hg)]. Arsenic (As), selenium (Se), and lead (Pb) may have electrons in outer shells (i.e., d electrons), as the differentiating electrons depending on the charge on the ion and thus are usually considered heavy metals. Heavy metals, except Fe, are also often referred to as trace metals due to their relatively small abundance in the environment.

SOURCES OF HEAVY METALS IN THE ENVIRONMENT

There are a wide variety of natural and anthropogenic sources of heavy metals in the environment that may impact or contaminate soil, surface water, and groundwater resources. Some heavy metals occur naturally in relatively small quantities as constituents of igneous and sedimentary rocks. For example, Fe composes 8.6% of basalt and only 0.38% of limestone. Titanium and Mn are also present in rocks in relatively high concentrations (0.1—1.0% range). The remainder of the heavy metals is present in rocks as trace elements ranging in concentration from 0.05–130 $mg\,kg^{-1}$ (0.05 to 130 ppm) and typically are present in the 10–100 $mg\,kg^{-1}$ range. Generally, heavy metals are present in higher concentrations in mafic rocks, such as basalt, and in shale. Mafic refers to igneous rocks that are largely composed of silicate minerals rich in Fe and Mg (ferromagnesium minerals), such as olivine, pyroxene, amphibole, and biotite. Physical and chemical weathering of heavy-metal-containing rocks release heavy metals into the environment. Some heavy metals contained in secondary minerals become part of the silt or clay fractions of soil; other forms of heavy metals may be retained in soil by complexing with soil clays and organic matter.

The former Kesterson Wildlife Refuge is a prime example of how naturally occurring heavy metals can adversely impact the surrounding environment. Selenium occurs naturally in the bedrock and soils of the San Joaquin Valley of central California where the former Kesterson Wildlife Refuge was located. Centuries of bedrock and soil weathering caused increased concentrations of Se in the local groundwater, which was used to irrigate crops in the region. Until 1978, much of the water flowing into the marsh was fresh water. However, the regional hydrology had changed such that by 1981 much of the influent water was from subsurface agricultural drainage water that had elevated concentrations of Se (2). The Se-contaminated marsh water was consumed and Se bioaccumulated in birds and other wildlife causing embryonic mortalities and severe deformities in aquatic birds (3) and the disappearance of most fish species (4). The marsh was ultimately drained in the mid-1980s and capped with noncontaminated soil to mitigate further loss of wildlife. Numerous additional examples exist within the United States and throughout the world of contamination and adverse environmental impacts from naturally occurring heavy metals. Some additional examples are Lake Ontario from Pb and Zn, Lake Cayuga in central New York from Cd, Co, Cu, Pb, and Zn; and Fränkische Saale in Germany from various heavy metals (5). Other natural mechanisms of heavy metal introduction into and transport within the environment include volcanic eruptions and windblown dust. The rate of human-induced heavy metal introduction into the environment has increased exponentially since the Industrial Revolution of the late 1800s.

Anthropogenic sources of heavy metals in the environment generally include atmospheric emissions, land-surface application of various heavy-metal-containing materials, and seepage from damaged or compromised containment structures. Particulate-bound heavy metals are emitted to the atmosphere during various high-temperature processes, such as fossil fuel burning for electric power, smelting of nonferrous ores, melting of ferrous ores, refuse incineration, and kiln operations (6). Due to its volatility, Hg can also be emitted in to the air as a gas and distributed over large areas. This type of transport mechanism is often cited as the source of Hg for methyl mercury contamination of aquatic ecosystems. Atmospheric emissions can be transported long distances and ultimately are deposited and accumulate on the land surface or in surface waters as dry dust particles or as part of precipitation. Heavy-metal-containing residual materials left over from high-temperature industrial processes, such as ashes, and other activities, such as municipal wastewater treatment, are also anthropogenic sources due to their disposal in and discharge to the environment.

A common practice of disposing of some types of industrial by-products is spreading them on the land surface or discharging them to surface waters. These are accepted practices as long as the heavy-metal content does not exceed regulated standards. According to the United States Environmental Protection Agency's Risk Reduction Engineering Laboratory Treatability Database (7,8), industrial sources, such as fabricated metal products except machinery and transportation equipment, chemical and allied products, and electronic and electric equipment, commonly discharge wastewaters containing Cd, Cr, Cu, Ni, and Zn in the range of 10–100 $mg\,L^{-1}$. Lead and Hg are also commonly detectable in industrial discharges. Similarly, municipal sewage sludge is often land applied as an organic amendment and fertilizer for agricultural purposes. In 1997, sewage sludge from publicly owned wastewater treatment facilities in Pennsylvania that was disposed of by land spreading contained between 5 and 800 $mg\,kg^{-1}$ of As, Cd, Cr, Cu Pb, Hg, Ni, Se, and Zn (9). However, the same study also demonstrated that the concentrations of Cd, Cr, Cu, Pb, Ni, and Zn in Pennsylvania sewage sludge decreased significantly between 1978 and 1997 (9).

Aside from industrial sources and sewage sludge, another significant mode for introducing heavy metals into the environment is agriculturally related sources, including fertilizers, liming materials, animal wastes, and pesticides. Heavy metals and other trace metals are important to agriculture because of their essential roles in plant and animal nutrition. Inorganic fertilizers and liming materials are rarely pure substances and often contain other additives, fillers, or impurities that may consist of heavy-metal constituents. For example, some phosphate fertilizers contain Cd and Zn (10). Similarly, heavy metals are often contained in animal wastes (manures and litters) from confined animal feeding operations, such as for dairy, swine, and poultry, due to the use of heavy-metal-containing compounds in feed additives for growth enhancement or disease suppression. Even more so than in industrial by-products or sewage sludge, animal wastes are typically land applied as an organic amendment for agronomic benefit, thus introducing any heavy metals contained in the animal wastes into the environment. For example, poultry litter typically

contains notable amounts of heavy metals. On average and depending on production and management practices, poultry litter can contain between 20 and 40 mg kg^{-1} of As, Cd, and Pb and between 370 and 660 mg kg^{-1} of Cu, Fe, Mn, Se, and Zn (11). Poultry litter in Alabama has also been found to contain relatively high levels of Co, Ti, and V (12). Numerous pesticides used in agronomic crops also contain heavy metals, such as As, Cu, Pb, Hg, and Zn (10).

Landfill leachate is an additional significant source of concentrated heavy metals in the environment. The wide variety of domestic refuse, especially household and unregulated small generator inputs, disposed of in landfills contain and, within the appropriate chemical conditions, may release soluble metal ions (13,14). For example, Cd, Ni, Pb, and Zn can be released from batteries; Cd and Cr can be released from paint residues; and As and Hg can be released from pesticide residues (15). These potentially toxic metals comprise the solutes of leachates produced as water percolates through landfills and discharges eventually into the surrounding soil or groundwater. Landfill leachate also contains a variety of organic compounds that may interact with toxic metal ions and, hence, influence their mobility (13).

HEAVY METAL MOBILITY

The mobility of heavy metals in the environment largely depends on the degree to which the metal is soluble. In turn, heavy metal solubility is governed by the chemical characteristics of the media in which the metal exists and the chemical nature of the metal itself.

Some heavy metals can exist in multiple valence states and in multiple forms or species in soil, such as free ions or complexes. For example, As can exist as the trivalent (As^{3+}) or pentavalent (As^{5+}) ion, Cr can exist as the trivalent (Cr^{3+}) or the hexavalent (Cr^{6+}) ion, and Fe can exist as the divalent (Fe^{2+}) or trivalent (Fe^{3+}) ion. For these metals, speciation is affected by the oxidation–reduction (redox) potential of the surrounding media. The redox potential determines the direction of a redox reaction; this is a reaction in which the complete transfer of electrons from one species to another occurs (16). Depending on the redox potential, certain metal species may be soluble or insoluble, thus affecting their mobility. For example, Fe in the oxidized state (Fe^{3+}) is relatively insoluble and typically exists as an oxide precipitant on surfaces of aggregates in soil, but Fe in the reduced state (Fe^{2+}) is highly soluble and is easily removed as water percolates through the soil. Table 1 lists the dominant chemical species in soil and water and the most toxic species of selected heavy metals.

The mobility of heavy metals in soil is affected by retention and release reactions, which include precipitation–dissolution, ion exchange, and adsorption–desorption reactions (17). Retention and release reactions in turn are affected by numerous soil properties, including pH, organic matter, bulk density, and texture (18).

Precipitation–dissolution reactions are governed by the concentrations of the reactants or solutes and the chemical characteristics of the solvent. Under the proper chemical conditions, some heavy metals may react with other solutes to form precipitates. The reverse reaction is dissolution of a fraction or all of the solid into its ionic components.

Table 1. Dominant Chemical Species in Soil and Water and Most toxic Species for Selected Heavy Metals. Adapted from Table 3 (23)

	Dominant Chemical Species		
Metal	Soil	Water	Most Toxic Species
As	AsO_4^{3-}	AsO_4^{3-}, AsO_3^{3-}	AsO_4^{3-}
Cd	Cd^{2+}	Cd^{2+}	Cd^{2+}
Co	Co^{2+}	Co^{2+}	Co^{2+}
Cr	Cr^{3+}	Cr^{3+}, Cr^{6+}	Cr^{6+}
Cu	Cu^{2+}	Cu^{2+}-fulvate	Cu^{2+}
Hg	Hg^{2+}, CH_3Hg	$Hg(OH)_2^0$, $HgCl_2^0$	CH_3Hg
Mn	Mn^{2+}, Mn^{4+}	Mn^{2+}	Mn^{2+}
Ni	Ni^{2+}	Ni^{2+}	Ni^{2+}
Pb	Pb^{2+}	$Pb(OH)^+$	Pb^{2+}
Se	$HSeO_4^{3-}$, SeO_4^{2-}	SeO_4^{2-}	SeO_4^{2-}
Zn	Zn^{2+}	Zn^{2+}	Zn^{2+}

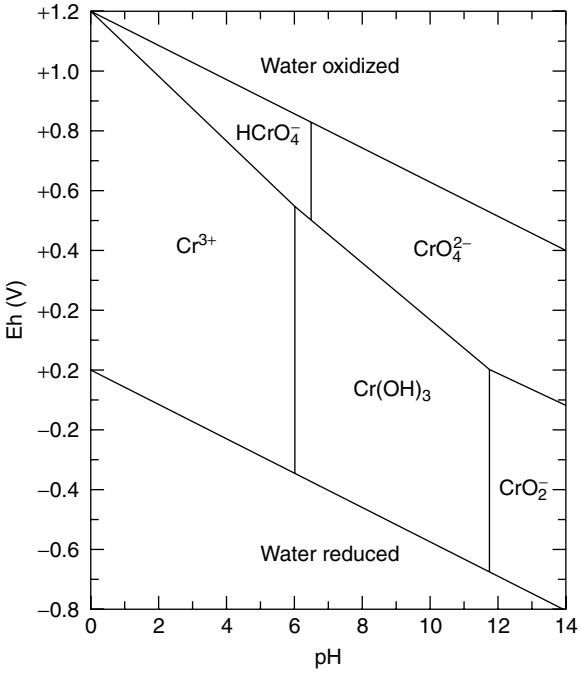


Figure 1. Eh-pH diagram for chromium (Cr) at an activity level of 10^{-6}.

Two of the most important chemical characteristics that influence precipitation–dissolution reactions and general metal speciation are pH and redox potential. The effects of pH and redox potential can best be illustrated using an Eh–pH diagram, where Eh is the reduction/oxidation potential in volts for a redox-influenced heavy metal, for example, Cr (Fig. 1). Depending on the redox conditions and pH, Cr can exist in one of five different forms, ranging from the reduced free ion (Cr^{3+}) at a pH<6 and Eh potential between ~ -0.3 and $+1.2$ volts to the chromate ion at a pH>$\sim$ 6.5 and Eh potential between ~ -0.12 and

+0.84 volts, where Cr exists as the oxidized (Cr^{6+}) species bound with four oxygen atoms. As the Eh–pH diagram depicts for Cr activity of 10^{-6}, the pH and Eh must be high for Cr to be mobile in natural waters, where the typical pH range is 5.5 to 8.5 and the typical Eh range is 0.1 to 0.45 V (19). pH and Eh affect metal speciation and solubility, so pH and Eh also influence the ability of ionic metals to interact with the surfaces of soil particles.

Due to the presence of many clay particles that have negatively charged surfaces, most soils have some cation exchange capacity (CEC) in which cationic heavy metal species can interact by electrostatic attraction with the surface of these negatively charged clay particles. However, the type of clay minerals present is also important. For example, kaolinite, a 1:1 clay mineral, has a relatively low CEC, typically in the range of 2–5 cmol charge kg^{-1} (20). However, 2:1 clay minerals, such as those in the smectite group (e.g., montmorillonite and vermiculite), have a relatively large CEC typically in the range of 80–180 cmol charge kg^{-1} (20). Humus (organic matter) also has a relatively large CEC, typically in the range of 100–550 cmol charge kg^{-1} (20). The process of ion exchange retains metals in their ionic form in soil and reduces their mobility until the soil–solution concentration of a different cation that has a stronger affinity for the binding site increases enough to replace the cationic metal on the clay surface.

In contrast to ion exchange, adsorption is the process whereby an ionic metal species binds to the surface of a soil particle to form a complex. The degree of adsorption of a metal species depends greatly on the chemical nature of the metal species itself, but also can typically be enhanced by clay and organic matter. Organic matter sometimes acts as a chelating agent. Chelation is the binding of organic chemicals that have multiple functional groups with metals to form ring structures; the end products are organometallic complexes (20).

Many metals form inorganic and organic complexes in soil. Depending on how the metal speciates, some metal complexes, such as complexes containing As^{3+} and As^{5+}, are highly soluble in water (21). Consequently, certain metal species like inorganic As (10), organic complexes of Pb, Zn, and Cr, and oxygen complexes of Cr and Se (22) are considered relatively mobile in soil and pose a health threat when introduced into the environment.

Once in solution, either as free ions or soluble complexes, heavy metals move by mechanisms similar to those of other solutes in the soil or groundwater systems. Diffusion and advection (also called convection) are the two most common mechanisms of solute transport in soil and groundwater. Diffusion is the process by which metals move in response to a concentration gradient; therefore, diffusion occurs relatively slowly. In contrast, advection or mass flow is the process by which metal movement occurs as a result of bulk fluid (i.e., water) movement and typically occurs at a rate much faster than that of diffusion. Some heavy metals may move in the environment via air transport of metal-bound dust particles. Heavy metals may also be transported in the environment in plant tissue after root absorption and translocation to aboveground biomass.

RISK ASSESSMENT

All heavy metals are toxic to some degree when absorbed in excess of an organism's assimilative capacity (23). Once absorbed by plants, animals, or other living organisms, heavy metals can "bioaccumulate" and persist in the organism's system without dissipation. One of the most common pathways of human exposure to heavy metals is by ingestion of either contaminated drinking water or plant or animal tissue. Human exposure to heavy metals can cause a variety of adverse health effects, so acceptable limits have been set for assessing potential human health risks from exposure to heavy metals.

Maximum contaminant limits (MCLs) are standards used to define excessive exposure to metals in drinking water. An MCL is calculated to allow consuming 2 L of water per day that has a concentration up to the MCL for a period of 70 years without increasing the human risk of acquiring cancer to more than 1 in 100,000 people. In addition, the United States Environmental Protection Agency uses oral reference doses for noncarcinogenic and risk-specific doses for carcinogenic metals (24). Table 2 lists the MCLs, potential health risks to humans, common sources of drinking water contamination, and general mammalian toxicity for selected heavy metals.

MANAGEMENT AND REMEDIATION ALTERNATIVES

Prevention of environmental heavy-metal contamination is crucial because the cleanup of contaminated natural resources is difficult, time-consuming, and extremely expensive. Remediation strategies for heavy-metal contaminated soil may be employed *in situ*, where the contaminated material remains in place on-site, or *ex situ*, where the contaminated material is removed and treated off-site. Typically, the first step in the cleanup of contaminated soil is containment, which is only a temporary measure. Traditional *in situ* treatments include high temperature to produce a nonleachable material or the addition of solidifying agents to produce a cement-like material (1). More recent "advancements" in *in situ* remediation of heavy-metal-contaminated soil have included bioremediation and phytoremediation. *Ex situ* treatments most often include excavation followed by landfilling, incineration, repeated washing, incorporation into asphalt mixes, or land farming, a process by which contaminated soil is spread out and actively managed with fertilizers or plants so that degradation processes occur naturally (25).

Remediation of contaminated waters is more difficult than that for contaminated soil partly because the number of potential remediation strategies for contaminated waters is more limited. Removal of contaminated sediments from aquatic ecosystems is difficult. Dredging of contaminated sediments often exacerbates the problem by mixing the sediment with the water. A common remedial activity for groundwater is to pump contaminated water out of the saturated zone followed by treatment and disposal or reinjection into the aquifer (25). Although groundwater can be pumped out and treated, once an aquifer is contaminated, any subsequent flush of water into or through the aquifer will cause the release of more

Table 2. Limits and Potential Health Risks Associated with Selected Heavy Metals (26)

Metal	MCL[a] (mg L^{-1})	MCLG[b] (mg L^{-1})	Potential Health Effects from Exposure Above the MCL	Common Sources of Metal in Drinking Water	Mammalian Toxicity[c]
As	0.01[d]	none	Skin damage, problems with circulatory system, increased risk of contracting cancer	Erosion of natural deposits, runoff from orchards and glass and electronics-production wastes	H
Cd	0.005	0.005	Kidney damage	Corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries and paints	H
Cr	0.1[e]	0.1[e]	Allergic dermatitis	Discharge from steel and pulp mills, erosion of natural deposits	H (Cr^{6+}) M (Cr^{3+})
Cu	1.3[f]	1.3	Gastrointestinal distress, liver or kidney damage	Corrosion of household plumbing systems, erosion of natural deposits	M
Hg	0.002	0.002	Kidney damage	Erosion of natural deposits, discharge from refineries and factories, runoff from landfills and croplands	H
Pb	0.015[f]	0	Delays in physical or mental development, deficits in attention span and learning abaility, kidney problems, high blood pressure	Corrosion of household plumbing systems, erosion of natural deposits	H
Se	0.05	0.05	Hair or fingernail loss, numbness in fingers or toes, circulatory problems,	Discharge from petroleum refineries, erosion of natural deposits, discharge from mines	H

[a] Maximum contaminant level (MCL) is the highest level of a contaminant that is allowed in drinking water and is an enforceable standard.
[b] Maximum contaminant level goal (MCLG) is the level of a contaminant in drinking water below which there are no known or expected health risks. MCLGs are non-enforceable public health goals.
[c] Letters represent the toxicity risk as moderate (M) or high (H); taken from table 9.1 (27).
[d] Effective as of January 23, 2006.
[e] MCL and MCLG are for total Cr.
[f] MCLs for Cu and Pb represent action levels and are based on a treatment technique to control the corrosiveness of the water.

contaminant into solution. Therefore, complete cleanup of groundwater aquifers requires a very long time.

Once the contaminated soil is remediated, several management practices may be used to help immobilize heavy metals in the soil and minimize the potential for transport and adverse environmental effects (1). The soil pH can be adjusted to 6.5 or higher, which will decrease the availability and potential mobility of cationic heavy metals. However, raising the soil pH will generally increase the availability and mobility of anionic heavy-metal complexes (1). Improving soil aeration by draining the soil will sometimes allow heavy metals to oxidize, making most heavy metals less available, except for those that form oxygen complexes (e.g., Cr) and sulfides (e.g., Hg). However, for Cr to exist as CrO_4^{2-}, requires a dissolved oxygen concentration above that which occurs naturally. Dredging often moves metal sulfides into oxidizing environments where the sulfide can potentially oxidize to sulfate, resulting in release of the metal. The addition of phosphate to a contaminated soil will help reduce the availability of cationic heavy metals due to the high binding affinity of the anionic phosphate ion for cations, but the addition of phosphate would increase the availability of anionic contaminants like As.

The use of plants to extract heavy metals from contaminated soil and water (phytoremediation) is also a very useful and cost-effective remediation strategy. There are three general mechanisms by which plants are used to stabilize or remove metals and other contaminants from soil and water. Phytoextraction is the process of cultivating plants called hyperaccumulators in metal-contaminated soil that have root systems that can absorb and translocate relatively large quantities of metals to their aboveground biomasses. After the plants have been allowed to grow for some time, the plants are harvested and incinerated or composted. There are approximately 400 hyperaccumulating plant species, but determining the appropriate species or group of plants to use depends on the heavy metal contaminant at a site (1). Rhizofiltration is used to remediate contaminated surface waters, whereby plants are initially grown hydroponically in a greenhouse using water from the contaminated site, and are then transplanted at the site. After enough time has elapsed to allow the roots to become saturated with the contaminant by a combination of adsorption and absorption, the plants, including the roots, are harvested and typically incinerated (1). Phytostabilization is a remediation process in which perennial, nonharvested, metal-tolerant plants are used to immobilize soil and water contaminants into roots and aboveground biomass by adsorption, absorption, or precipitation in the rhizosphere and reduce the mobility and bioavailability of some metals (1).

SUMMARY

Soil and water contamination by heavy metals impacts the environment negatively. Scandium, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, as well as As, Se, and Pb, are generally considered heavy metals. There are numerous natural and anthropogenic sources of heavy metals in

the environment. Soil and groundwater properties, such as pH and redox potential, and the characteristics of a particular metal itself affect heavy-metal mobility in the environment. Once in the environment, excessive exposure to heavy metals poses a health risk to any living organism. A wider variety of strategies that can be used to remediate heavy-metal-contaminated soil exists than for remediating contaminated groundwater.

BIBLIOGRAPHY

1. Soil Quality Institute (SQI). (2000). *Heavy Metal Soil Contamination*. United States Department of Agriculture, Natural Resource Conservation Service, Urban Technical Note No. 3, Auburn, AL.
2. National Research Council (NRC). (1989). *Irrigation-Induced Water Quality Problems: What Can be Learned from the San Joaquin Valley Experience*. National Acad. Press, Washington, DC.
3. Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., and Aldrich, T.W. (1986). Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium or irrigation drainwater. *Sci. Total Environ.* **52**: 49–63.
4. Ohlendorf, H.M. (1984). The biologic system. In: *US Bureau of Reclamation and Ecological Analysis. Proceedings of a research meeting on toxicity problems at Kesterson Reservoir, California*. US Bureau of Reclamation, Mid-Pacific Region, Sacramento, CA, pp. 8–15.
5. Leland, H.V., Copenhaver, E.D., and Wilkes, D.J. (1975). Heavy metals and other trace elements. *J. Water Poll. Contr. Fed.* **47**: 1635–1656.
6. Pacyna, J.M., Münch, J., and Axenfeld, F. (1991). European inventory of trace metal emissions to the atmosphere. In: *Heavy Metals in the Environment*. J.P. Vernet (Ed.). Elsevier, New York.
7. Patterson, J.W., Minear, R.A, Gasca, E., and Petropoulou, C. (1998). Industrial discharges of metals to water. In: *Metals in Surface Waters*. H.E. Allen, A.W. Garrison, and G.W. Luther. (Eds.). Ann Arbor Press, Ann Arbor, MI.
8. United States Environmental Protection Agency (USEPA). (1993). *Risk Reduction Engineering Laboratory (RREL)*. Treatability Database, Ver. 5.0., Cincinnati, OH.
9. Stehouwer, R.C., Wolf, A.M., and Doty, W.T. (2000). Chemical monitoring of sewage sludge in Pennsylvania: Variability and application uncertainty. *J. Environ. Qual.* **29**: 1686–1695.
10. Adriano, D.C. (1986). *Trace Metals in the Terrestrial Environment*. Springer-Verlag, New York.
11. Gupta, G. and Charles, S. (1999). Trace elements in soils fertilized with poultry litter. *Poultry Sci.* **78**: 1695–1698.
12. Kpomblekou, A.K., Ankumah, R.O., and Ajwa, H.A. (2002). Trace and nontrace element contents of broiler litter. *Comm. Soil Sci. Plant Anal.* **33**: 1799–1811.
13. Gintautas, P.A., Huyck, K.A., Daniel, S.R., and Macalady, D.L. (1993). Metal-organic interactions in Subtitle D landfill leachates and associated groundwaters. In: *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown. (Eds.). Lewis Publishers, Chelsea, MI, pp. 275–308.
14. Pohland, F.G., Cross, W.H., and Gould, J.P. (1993). Metal speciation and mobility as influenced by landfill disposal practices. In: *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown (Eds.). Lewis Publishers, Chelsea, MI, pp. 411–429.
15. Jones, J.B. (2003). *Agronomic Handbook: Management of Crops, Soils, and their Fertility*. CRC Press, New York.
16. Sposito, G. (1989). *The Chemistry of Soils*. Oxford University Press, New York.
17. Amacher, M.C., Kotuby-Amacher, J., Selim, H.M., and Iskandar, I.K. (1986). Retention and release of metals by soils—evaluation of several models. *Geoderma*. **38**: 131–154.
18. Selim, H.M. and Amacher, M.C. (1997). *Reactivity and Transport of Heavy Metals in Soils*. CRC Press, New York.
19. Baas Becking, L.G.M., Kaplan, I.R., and Moore, D. (1960). Limits of the natural environment in terms of pH and oxidation-reduction potentials. *J. Geol.* **68**: 243–284.
20. Brady, N.C. and Weil, R.R. (1996). *The Nature and Properties of Soils*, 11th Edn. Prentice-Hall, Upper Saddle River, NJ.
21. Vaughn, G.T. (1993). *Investigation Report CET/LHIR148: The environmental chemistry and fate of arsenical pesticides in cattle tick dip sites and banana plantations*. CSIRO, Division of Coal and Energy Technology, Centre for Adv. Analyt. Chem., Sydney, Australia.
22. Davis, D.A., Kent, D.B., Rea, B.A., Maest, A.S., and Garabedian, S.P. (1993). Influence of redox environment and aqueous speciation on metal transport in groundwater: Preliminary results of trace injection studies. In: *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown. (Eds.). Lewis Publishers, Chelsea, MI, pp. 223–273.
23. Logan, T.J. and Traina, S.J. (1993). Trace metals in agricultural soils. In: *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown (Eds.). Lewis Publishers, Chelsea, MI, pp. 309–347.
24. Rubenstein, R. and Segal, S.A. (1993). Risk assessment of metals in groundwater. In: *Metals in Groundwater*. H.E. Allen, E.M. Perdue, and D.S. Brown. (Eds.). Lewis Publishers, Chelsea, MI, pp. 209–221.
25. National Research Council (NRC). (1997). *Innovations in Ground Water and Soil Cleanup*. National Acad. Press, Washington, DC.
26. United States Environmental Protection Agency (USEPA). (2002). *National Primary Drinking Water Sandards*. Office of Water, EPA 816-F-02-013. Washington, DC.
27. McBride, M.B. (1994). *Environmental Chemistry of Soils*. Oxford University Press, New York.

SOURCE, MOBILITY, AND REMEDIATION OF METALS

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It is estimated that over 60% of CERCLA sites in the United States have contamination because of metals. Similarly, RCRA, general industrial, DOD, and DOE facilities also have problems with metals, which, in conjunction with a paucity of innovative approaches to deal with metal problems, means that metal contamination represents a serious environmental concern and a significant market opportunity for environmental service companies.

Metals (or other inorganics) typically become groundwater problems under the following situations:

- Activities associated with plating shops, where a wide variety of metals are present at high concentrations in forms that are soluble.
- Sites with releases of radionucleides that, because of unique health risks, can have significant impact at very low concentrations. In addition, the use of chelating and complexing agents that make these contaminants mobile in the environment is common during processing of these materials.

Metals and high levels of inorganic Total Dissolved Solids (TDS) are associated with leaks from sanitary, solid waste, and hazardous waste landfills.

High TDS impacts are also associated with salt storage areas and petroleum production activities.

Innovation in the area of hydrocarbon remediation has been significant in the last decade. However, metals may only be mobilized or immobilized, unlike hydrocarbons they cannot be degraded to less innocuous components, such as CO_2 and H_2O, for example. This limited reactivity is one of the reasons that innovative remediation technology has been slow to develop for soils or groundwater contaminated with metals, which will likely change with time, however.

Often particulate metal contamination is confined to the upper few feet of soil beneath a contaminated area. However, instances exist where metal contamination has impacted groundwater. The purpose of this article is to discuss the physical/chemical behavior of metals with a particular focus on conditions that make metals mobile and thus able to impact groundwater. Also evaluated will be remediation alternatives to metal contaminated groundwater.

The important issue with regard to metals is mobility. Specifically, under what conditions are metals mobile and under what conditions are metals immobile? Metals in the environment can take four fundamental forms: (a) raw metallic elements, (b) hydrated ionic salts, (c) covalently bonded molecules termed inorganic complexes, (d) associated with a chelating agent. Elemental metals are generally not highly soluble under normal groundwater conditions. However, naturally occurring elemental metals may cause soil samples to be deemed hazardous using a Toxic Characteristic Leaching Procedure (TCLP) test and guidelines set forth in 40 CFR 261.4. The TCLP test uses strong acids during the laboratory leaching procedure. The TCLP is an EPA SW-846 analytical method (Method 1311) that simulates sanitary landfill contaminant leaching of waste materials, which could include mobilizing naturally occurring metals in the soil sample.

The mobility of metals as hydrated ionic salts is dependent on which metallic element is participating as the positively charged ion (termed the cation) and which anion makes up the negatively charged component of the salt.

Following is a brief summary of cationic/anionic solubility relationships:

- Sodium (Na^+), Potassium (K^+), and Ammonium (NH_4^+) are cations that form salts that are all soluble.
- All metal salts of the Nitrate (NO_3^-), Nitrite (NO_2^-), Acetate ($C_2H_3O_2^-$), Permanganate (MnO_4^-), Perchlorate (ClO_4^-), and Chlorate (ClO_3^-) anions are soluble.
- All Chloride (Cl^-), Bromide (Br^-), and Iodide (I^-) salts are soluble except those of Lead (Pb^{2+}), Silver (Ag^+), and Mercury (Hg^{2+}).
- All Sulfate (SO_4^{2-}) salts are soluble except those of Barium (Ba2+), Strontium (Sr^{2+}), and Lead (Pb^{2+}).
- All Oxides (O_2^-), Sulfides (S_2^-), and Hydroxides (OH^-) are insoluble except those of Calcium (Ca^{2+}), Barium (Ba^{2+}), and Strontium (Sr^{2+}).
- With the exception of Sodium (Na^+), Potassium (K^+), and Ammonium (NH_4^+), all metallic salts are insoluble for anions of Carbonate (CO_3^{2-}), Phosphate (PO_4^{3-}), Sulfite (SO_3^{2-}), Borate (BO_3^{3-}), Fluoride (F^-), and Silicate (SiO_3^{2-}).

A covalently bonded inorganic molecule that contains several atoms (one of more of which are metal atoms) is termed an inorganic complex. Of particular interest and environmental concern are a class of inorganic complexes termed oxyanions, which are compounds composed of metal and oxygen atoms forming an entire molecule (rather than just an isolated metal ion) that is capable of forming a hydrated complex charged ion. These oxyanionic complexes are often soluble and, more importantly, have physical/chemical qualities that make them valuable in various industrial processes. In a modern industrial environment, metallic and metalloid oxyanions are not rare substances. The most troublesome and the most common industrial oxyanion is chromate, which contains hexavalent chromium (Cr^{+6}). The chromate molecule, in turn, forms an extremely soluble, anionically charged ion. Contributing to its high mobility in the environment is a property of the chromate ion that allows it to be soluble over the entire range of pH. From acidic to basic conditions, the chromate ion simply changes the overall negative charge it carries, all while staying soluble and not precipitating. This high degree of mobility, in conjunction with its common use, and the fact that it is a known carcinogen, makes it one of the most common problem metals found to contaminate groundwater.

The ability of chromium to form soluble oxyanionic complexes is not unique to it only. Other metals and metalloids exist that form inorganic complexes having more or less the same solubility profiles. This list includes molybdenum, vanadium, tungsten, arsenic, selenium, and tellurium. These compounds are not commonly used by our industrial society. However, arsenic and selenium can have significant groundwater impact around mining areas, irrigation complexes in the west, and, in some moderately common instances, soluble arsenic is a common component in groundwater that flows through arsenic-rich geology (such as volcanics).

Industrial chemistry often makes use of complexing agents with more than one point of attachment to a central metal atom in a complex. This type of complexing

agent is termed a polydentate ligand or a chelating agent. Chelating agents form strong bonds with metals and are, in turn, extremely soluble. EDTA (ethylenediaminetetra-acetic acid) is a commonly used chelating agent. Chelating agents are used in industrial chemical systems with transition metals, heavy metals, and radionucleides. If released into the groundwater, these metal-bearing chelates are extremely mobile.

It should also be remembered that, under some conditions, metals in groundwater can be mobile as colloidal-sized particles, even though the metal is in an insoluble form. Although not soluble, colloidal particles are so small they may approach within an order of magnitude the size of ionized species. As such, they are transportable in the pore spaces of some aquifer formations.

Last, it is important to understand that metals in groundwater will interact with and adsorb to components of the soil matrix. Clays, other mineral components, and carbonaceous material (especially humic and fulvic substances) can all act in this manner. However, in the case of metals, the dominant adsorptive component of the soil matrix is iron. Iron oxides (particularly of Ferric (Fe^{+3}) iron) have a very high adsorptive affinity and total capacity for metal ions and oxyanionic metal complexes. This capacity is so great that ferric hydroxide is often used in waste water treatment systems to aid in the removal of soluble metallic species such as chromate or arsenic. Knowing the total iron content of the soil matrix is paramount in understanding the fate and transport of metals in groundwater.

METALS AND GROUNDWATER PART II: *IN SITU* BIOREMEDIATION OF METALS CONTAMINATED GROUNDWATER

Significant technical developments have improved our ability to remediate groundwater contaminated with hydrocarbons. There has not been similar growth in treatment alternatives for sites contaminated with metals.

When groundwater is contaminated with metals, remediation alternatives are limited to mobilization or immobilization. Unlike hydrocarbons, biodegradation into innocuous carbon dioxide and water is not possible. Irrespective of the available of *in situ* reactions, the same metal will still ultimately be present.

The choice of mobilization or immobilization is dependent on the hydrogeologic setting of the site, the chemical properties of the metal contaminant, the geochemistry of the site soils and groundwater, and the current and future use of the contaminated groundwater. Generally, it is easier to immobilize a metal than it is to mobilize and recover it. However, an immobilized metal may still be a source of future problems if subsurface ambient conditions change.

MOBILIZATION

Metal mobilization and recovery is vulnerable to the same limitations encountered with pump and treat systems for hydrocarbons. Adsorption to components of the soil matrix can significantly increase the required duration for operation of the recovery system.

Aggressive metal mobilization (beyond that achievable with passive pump and treat) is an approach to be applied only under extreme conditions. However, given proper geochemical conditions, what may be possible is the use of complexing ligands to enhance the mobility of particularly troublesome metal contaminants (such as radionucleides). In such an application, it would be essential to maintain hydraulic control of the site. Injection wells would introduce organic complexing agents (such as gluconate) to mobilize the targeted metals. Groundwater, with the solubilized metals, could then be recovered. Once the metal removal process has been completed, conventional *in situ* bioremediation could be used to degrade the residual concentrations of the organic complexing agent. Another aggressive approach to metal mobilization is methylation. Mercury can be methylated by a number of microorganisms (methanobacterium, for example), resulting in the conversion of Hg^{+2} salts to extremely volatile methylmercury compounds. Arsenic, selenium, and tellurium can undergo similar reactions. Such volatilized methylated metals are very mobile in the subsurface. In addition, the methylated forms of these metals are extremely toxic. The unusual use of this approach would be predicated on a substantial need for total removal of the metal and the ability to exercise complete hydraulic control of groundwater and soil gas at the site.

IMMOBILIZATION

A critical component of applying metal immobilization will be the use of risk assessments to establish the safety of allowing the presence of contaminating metals in an insoluble form within the aquifer matrix.

Mechanisms for microbial mediated metal immobilization can be divided into two categories, active and passive.

Active mechanisms operate directly on the metal and include:

- precipitation;
- intracellular accumulation; and
- oxidation/reduction.

Passive mechanisms act indirectly by modifying the surrounding environment. They include:

- complexing with extracellular biological chelates;
- biosorption to cell surfaces; and
- destruction of complexing ligands.

ACTIVE IMMOBILIZATION

Precipitation

In anaerobic environments, sulfate reducing bacteria, such as Desulfovibrio and Desulfotomaculum, produce hydrogen sulfide by the reaction $SO_4{}^{2-} + 10H = H_2S + 4H_2O$. The hydrogen sulfide reacts with soluble metals forming insoluble metal sulfides. The following solubility products (in parts per billion) illustrate that point:

- Cadmium Sulfide 8.7×10^{-7};
- Copper Sulfide 8.8×10^{-14};
- Lead Sulfide 4.3×10^{-6};
- Mercury Sulfide 1.1×10^{-16}.

Intracellular Accumulation

Intracellular accumulation is a two-stage process. First, metal ions are bound passively to the surface of the bacterial cell wall by physical/chemical processes. Then, the metal ions are transferred to the interior of the cell by microbial energy systems normally associated with magnesium and potassium transport. Pseudomonas and Thiobacillus are examples of common bacterial species that are capable of this process.

Oxidation and Reduction

Many known metal redox reactions mediated by microbes exist. For example, Chromate ions (Cr^{+6}) can be reduced to insoluble trivalent chromium (Cr^{+3}) with soluble reductase enzymes generated by Escherichia coli (E. coli). Soluble uranium ions (U^{+6}) precipitate as the mineral uraninite when reduced to the U^{+4} species. This reduction reaction can be driven by reductase enzymes produced by the bacteria Desulfovibrio vulgaris.

PASSIVE IMMOBILIZATION

Extracellular Complexation

Extracellular complexation occurs from interactions of metals with extracellular polymers excreted by bacteria or from organic matter accumulated from the dead microbes.

Extracellular polymers include:

- polysaccharides,
- proteins, and
- nucleic acids.

Indigenous bacteria can be stimulated to specifically produce extracellular polysaccharides.

Another class of microbial chelating agents are siderophores, which are low-molecular-weight ligands synthesized and excreted by bacteria for capturing and supplying iron to support metabolic activity. Other metals may also complex with these ligands.

Siderophore producers include Psuedomonus, Actinomyces, and Azotobacter.

Cell Wall Binding

Three mechanisms exist for the binding of metals to bacterial cell walls:

1. Ion exchange reactions with peptidoglycan and teichoic acid (important biochemical components of the bacterial cell wall);
2. precipitation through nucleation reactions; and
3. complexation with nitrogen and oxygen ligands.

Gram positive bacteria have high adsorptive capacity, particularly Bacillus, because of the high peptidoglycan and teichoic acid content in their cell walls. In general, gram negative bacterial cell walls are low in these components and exhibit poor metal adsorption.

Destruction of Complexing Ligands

Metals associated with the plating, mining, and nuclear industries are sometimes released into the environment complexed with organic ligands such as EDTA or cyanide. These organic ligands can be biodegraded by conventional *in situ* bioremediation methods to destroy the ligand and immobilize the metal.

CONCLUSION

The use of microbiological methods for environmental remediation is not an entirely new concept. Microbial interactions with metals have long been recognized, and since the 1960s work in the field by biohydrometallurgists and biogeochemists has exploded. Given adequate hydraulic controls, this is a technology that may be easier to physically implement than *in situ* bioremediation of hydrocarbons. The success of the latter has been contingent on the ability to induce adequate mass transfer of oxygen into the impacted zone, which is often difficult. Stimulation of microbes for the manipulation of metals *in situ* is usually dependent on the mass transport of soluble salts, which is a much easier task.

METALS AND GROUNDWATER PART III: REMEDIATION OF METALS CONTAMINATED GROUNDWATER WITH ELECTROCHEMICAL PROCESSES

The remediation of groundwater contaminated with metals is constrained by the fact that metals can only be mobilized or immobilized not destroyed, as with the biodegradation of hydrocarbons. However, the use of electrochemical technology is an approach that is uniquely applicable to metals. What follows is a brief review the application of electrochemical techniques to the remediation of groundwater contaminated with metals.

Introduction to Metal Chemistry

Terminology for the technology includes electrokinetic remediation, electroreclamation, electrokinetic soil processing, and electrochemical decontamination. For purposes of this review, electrochemical remediation processes are broken into two primary areas: electromigration and electroosmosis. Electromigration is used in relatively porous formations that are capable of supporting advective groundwater flow. Electroosmosis is applied to saturated fine-grained formations such as silts or clays.

Electrochemical reactions can be used with any groundwater contaminant that has a charge such as soluble metal ions, other inorganic ions, and organic acids or phenols. Electrochemical reactions are stimulated by placing two or more electrodes in the subsurface that are connected to a direct current power source. The electrode with a positive charge is termed the cathode, and the electrode with a negative charge is formed the anode. Cations migrate toward the negative electrode and anions toward the positive electrode. Power supplies should be capable of delivering currents around one amp per square

foot of cross-sectional area between the electrodes and voltage potentials of 10 to 30 volts per foot between electrodes. Estimates for the total power consumption required to treat a cubic yard of saturated soil are in the range of 50 to 250 Kilowatt Hours.

Electromigration is the process of mobilizing metal (or other) ions through an aquifer matrix without advective fluid flow. Mass transport is strictly by ion migration driven by an induced electrical field. The rate of migration for any given ion is dependent on factors that include the concentration of total ions (TDS) in the groundwater and the concentration of individual ions of concern, the charge of those ions, the electrical potential between the electrodes, the mobility of the individual ionic species, and the porosity and tortuosity of the pore spaces in the aquifer. Any groundwater will have multiple soluble ions that make up the TDS. The fraction of the total current carried by a particular ionic species in the TDS is represented by the transference number for that ion. The numerical value of the transference number is dependent on the electromagnetic gradient (the greater the gradient, the higher the mass transport rate) and concentration of the individual ionic species. The dynamics of this system are such that the application of electromigration to metal contaminated groundwater is best suited to conditions in which the metal ion makes up a major component of the TDS. Recovery efficiencies are very low if the metal ion is present at trace levels. One peripheral, but inevitable, process that occurs, and has direct impact on the physical/chemical reactions induced by electromigration, is the electrolytic decomposition of water. Water at the cathode undergoes the following reaction:

$$2H_2O + 2e^- H_2(gas) + 2OH^-$$

Water is oxidized at the anode by the following reaction:

$$2H_2O - 4e^- O_2(gas) + 4H^+$$

Hydrogen ions have an effective ionic mobility 1.8 times greater than that of the hydroxyl ion. Hydrogen ions lower the pH, and their preferential migration through a formation will contribute toward the desorption of metal species from soil particles.

The term electroosmosis refers to a technology that has been used for decades by geotechnical engineers to remove water from clays, silts, and fine sands. The effect was first described in 1809. It has been used by the construction industry to stabilize embankments, dewater foundation soils, and increase the loading capacity of pilings. Electroosmosis is primarily an electrically induced hydraulic flow rather than an ionic flow. Water flows in the same direction as electrons in the electrical field loop, from anode to cathode.

The mechanism inducing the advective flow can be described as follows:

In fine-grained soils, pore space can be visualized as a capillary tube in which the tube walls (clay soil particles) are negatively charged. Water in such a tube exists as a double layer, with an adsorbed layer tightly held directly adjacent to the pore space wall. The water in the center of the pore space and the core of the tube is less strongly held by these attractive forces. The application of an electrical gradient across the tube will cause cations in the tightly adsorbed layer adjacent to the walls of the pore space to migrate toward the cathode, taking the free water in the core of the tube (and between the adsorbed layers) along with it. In contrast, under hydraulic pumping conditions, only the free water in the core of the pore space will flow. Contaminant mass transport is induced through hydraulic flushing, in addition to some electromigration of soluble metal ions.

The finer the grain of the pore space, the greater the significance of the electroosmotic effect. In fine-grained soils, electroosmotic-induced mass transport can be two to three orders of magnitude higher than that capable of being induced hydraulically.

Potential problems in the field application of electrochemical technology include:

- High current densities and subsequent reactions at the anode can cause low pH conditions resulting in corrosion and dissolution of the electrode element.
- Precipitation of metal hydroxides or other TDS components near the cathode can cause pore space blockage.
- If contaminant and general TDS ion concentrations are not favorable, electrical costs can be unreasonably high because all ions (even undesirable ones) participate in the reactions.
- The number and spacing of electrodes can be prohibitive. Subsidence or settlement is a potential under some conditions.

Some of these issues can be addressed through process enhancements, such as using additives to depolarize the cathode and anode. Reactions induced in groundwater under an electric field are complex and will change with time. Low pH, high pH, ion mobilization, precipitation, dissolution, and desorption are all reactions that can take place within different locations in the subsurface electrical cell at different times during the operation of the system. The electrochemistry in such a system evolves with time. The successful use of this technology requires operation of the system to exploit those geochemical changes.

GENETICS OF METAL TOLERANCE AND ACCUMULATION IN HIGHER PLANTS

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Phytoremediation of metals is rapidly developing as a cost-effective and environmentally friendly solution for cleaning up heavy-metal-contaminated sites. The most important requirements for effective phytoremediation are fast-growing, high biomass plants that uptake

and accumulate large amounts of toxic metals in their aboveground harvestable parts. A relatively small group of hyperaccumulator plants sequesters metals in their shoot tissues at high concentrations. In recent years, major scientific progress has been made in understanding the physiological mechanisms of metal uptake and transport in these plants. The majority of metal hyperaccumulators are slow growing and typically have low biomass, so bioengineering of nonaccumulators that have high biomass is essential for more effective phytoremediation. Biotechnology offers the opportunity to transfer hyperaccumulator phenotypes into fast-growing, high biomass plants that could be highly effective in phytoremediation. However, comprehensive knowledge of the genetics of metal tolerance and accumulation is essential to design transgenic plants capable of phytoremediation. After an initial focus on plants with an immediate promise of application, research is now being directed at understanding the underlying mechanisms involved in heavy metal hyperaccumulation in plants. Once the rate-limiting steps for uptake, translocation, and detoxification of metals in hyperaccumulator plants are identified, more informed construction of transgenic plants could become rather routine, which will help tremendously in more effective use of phytoremediation technology for cleaning up heavy-metal-contaminated sites.

INTRODUCTION

Mining, manufacturing, and other anthropogenic activities have contributed to extensive soil contamination during the past century, and metals are the main group of inorganic contaminants (1). Several technologies exist for remediating metal-contaminated soils (2) that can be broadly classified into five general categories: isolation, immobilization, toxicity reduction, physical separation, and extraction. Immobilization and extraction by physicochemical techniques can be expensive and are appropriate only where rapid and complete decontamination is required (3). In addition, some of these techniques such as soil washing have an adverse effect on biological activity, soil structure, and fertility. Plants that take up metals from soil offer an alternative and less expensive method of stripping metals directly from soil. The majority of plants have constitutive and adaptive mechanisms for accumulating or tolerating high contaminant concentrations in their rhizospheres. Phytoremediation, the use of such plants to clean up soils and water contaminated with pollutants, is emerging as a new tool for *in situ* metal remediation. Phytoremediation takes advantage of the fact that a living plant is a solar-driven pump that can extract and concentrate certain metals from the environment (4). This remediation method maintains the biological properties and physical structure of soil. The technique is environmentally friendly, cost-effective, visually unobtrusive, and offers the possibility of biorecovery of precious metals.

The majority of phytoremediation-related research to date has focused on hyperacccumulator plants that accumulate metals to concentrations more than 100 times higher than those in nonaccumulators (5). However, metal hyperaccumulation is a relatively rare phenomenon that occurs in only a few terrestrial plants. Only about 400 species have been identified so far as natural metal hyperaccumulators; they represent $<0.2\%$ of all angiosperms (6). Threshold values of metal concentrations are used to define metal hyperaccumulation, which varies from element to element, for example, 10,000 mg/kg dry shoot weight for Zn and Mn; 100 mg/kg for Cu, Co, Ni, As, and Se; and 100 mg/kg for Cd (7). The common traits shared by all hyperaccumulators include (1) a bioconcentration factor greater than 1, in some cases as high as 50–100; (2) a shoot-to-root ratio of metal concentration greater than 1, indicating efficient root-to-shoot transport; and (3) enhanced tolerance to metals in the medium and inside plant cells, indicating strong internal detoxification (7). A great deal of research has been conducted to elucidate the physiology and biochemistry of metal hyperaccumulation in plants, but still certain limitations must be overcome for this technology to become efficient and cost-effective on a commercial scale (8). Plants ideal for phytoremediation should be fast growing, have high biomass and extensive root systems, be easy to harvest, and tolerate and accumulate a range of metals in their harvestable parts. No single plant with all these traits has been found so far, but it is possible that high biomass nonaccumulators that are fast growing could be modified using the transgenic approach to achieve some of the properties of hyperaccumulators (9). However, this approach can be used only when the molecular mechanisms of metal uptake, tolerance, accumulation, and translocation are better understood. The primary objective of this article is to evaluate the progress made so far in understanding the physiological and molecular-genetic mechanisms that control uptake and detoxification of metals in plants.

METAL HYPERACCUMULATION IN PLANTS

Hyperaccumulation of metals by higher plants is a complex phenomenon that involves the following steps: (1) transport of metals across the plasma membrane of root cells, (2) xylem loading and translocation, and (3) detoxification and sequestration of metals at the whole plant and cellular levels (10). The term "phytoextraction" describes the use of plants to remove metals from soil by concentrating them in their harvestable parts (11). This process depends on hyperaccumulating plants that can grow naturally on soils rich in metals. The first hyperaccumulators characterized were members of the Brassicaceae and Fabaceae families. About 400 plant species have been reported so far that hyperaccumulate metals (6). Many of the Zn hyperaccumulators identified so far belong to the family Brassicaceae and are in the genus *Thlaspi.* In addition, *Cardaminopsis halleri* and *Viola calaminaria* also hyperaccumulate Zn. Several species of plants that hyperaccumulate Zn have been investigated, but only one Cd hyperaccumulator, *Thlaspi caerulescens,* has been extensively studied. The first indication of the possibility of phytoextraction of Zn was obtained from pot experiments in background and sludge-treated soils using *Thlaspi caerulescens* (12). It was estimated that a crop of *T. caerulescens* could take

up 34 kg/ha of Zn and 0.16 kg/ha Cd. Recently, the Chinese brake fern *Pteris vittata* has been found able to hyperaccumulate As from soil (13). It can accumulate up to 22,630 mg As/kg in the shoot (frond) dry weight. Furthermore, the bioconcentration factor, defined as the ratio of shoot As concentration to soil As concentration, was greater than 10 for brake fern. The fern possesses three key features that are typical of metal/metalloid hyperaccumulator plants: an efficient root uptake, efficient root-to-shoot translocation, and much enhanced tolerance to As inside the plant cells (13). After the discovery of this first As hyperaccumulator, several other fern species, including *Pityrogramma calomelanos* (14), *Pteris cretica, Pteris longifolia*, and *Pteris umbrosa* (15) have recently been added to the list of As hyperaccumulators. The hyperaccumulation trait of these ferns may be exploitable in phytoremediation of As contaminated soils.

Several plant species reportedly accumulate Ni, and some of them also accumulate Co and Cu. A few species accumulate Mn and Cd (11). The major disadvantage of the continuous phytoextraction method is that majority of the plants, except for As hyperaccumulating ferns, have low biomass and slow growth rates (11).

MECHANISM OF METAL UPTAKE BY PLANTS

Transport proteins and intracellular high-affinity binding sites mediate the uptake of metals across the plasma membrane in root cells of plants. Several studies have shown that metal hyperaccumulation of Zn and Cd by *T. caerulescens* involves enhanced metal uptake by roots (15,16). Several Zn transporter genes have been cloned recently from *T. caerulescens,* which belong to the ZIP (Zn-regulated transporter/Fe-regulated transporter-like proteins) family (17). These genes, named *ZNT1* and *ZNT2*, are highly expressed in the roots of *T. caerulescens,* but their expression is not responsive to the Zn status of the plant. Through functional complementation in yeast, it was shown that *ZNT1* mediates high-affinity uptake of Zn^{2+} and low-affinity uptake of Cd^{2+} (18). Specific alterations in Zn-responsive elements, such as transcriptional activators, may play an important role in Zn hyperaccumulation in *T. caerulescens* (18). However, increased uptake of Cd by *T. caerulescens* cannot be explained by the Zn transport pathway but may be related to enhanced expression of the *IRT1* gene, which is essential for Fe uptake (10). The *IRT1* gene mediates high-affinity uptake of Cd^{2+} in *A. thaliana* (19,20).

Several classes of proteins are implicated in metal transport in plants, which include the metal (or CPx-type) ATPases that are involved in overall metal ion homeostasis and tolerance in plants, the natural resistance-associated macrophage protein (Nramp) family of proteins, and the cation diffusion facilitator (CDF) family proteins (21). CPx-type metal ATPases have been identified in a wide range of organisms and have been implicated in the transport of essential as well as potentially toxic metals, such as Cu, Zn, Cd, and Pb, across cell membranes (21). These transporters use ATP to pump a variety of charged substrates across cell membranes and are distinguished by the formation of a charged intermediate during the reaction cycle. Metal transporters have been classified as type IB and are called the CPx-ATPases because they share a common feature of a conserved intramembranous cystein-proline-cystein, cystein-proline-histidine, or cystein-proline-serine (CPx) motif, which, it is thought, functions in metal transduction. *Arabidopsis* P-type ATPase (PAA1) was the first CPx-ATPase reported in higher plants (22). Most CPx-type ATPases identified so far have been implicated in Cu or Cd transport. The physiological role of the metal ATPases in higher plants is not known. *Arabidopsis* CPx-ATPases show fairly low similarities to each other, so it is possible that they transport different substrates. They may be present in the plasma membrane and function as efflux pumps removing potentially toxic metals from the cytoplasm or may also be present at various intracellular membranes and be responsible for compartmentalization of metals, for example, sequestration in the vacuoles, Golgi, or endoplasmic reticulum. Intracellular levels of metals must be carefully controlled, so transporters represent good candidates for regulation. How they may be regulated in higher plants is not yet known, which could occur at the transcriptional level (control on initiation rates, mRNA stability, differential mRNA splicing) or at the posttranslational level (targeting, stability), which has been observed in bacteria and yeast (21).

As mentioned earlier, *Nramp* is a novel family of related proteins that has been implicated in the transport of divalent metal ions. The corresponding genes that code for these proteins are called *Nramp* genes. In higher plants, three *Nramp* homologues have been identified in rice (23). Subsequently, two *Arabidopsis* genes showing similarity to *Nramp*s were also been identified (24). Initial results suggest that *Arabidopsis Nramp* homologues encode functional metal transporters (25). Northern blot analysis indicates that the rice *Nramp* gene *OsNramp1* is expressed primarily in the roots, *OsNramp2* in the leaves, and *OsNramp3* in both tissues of rice (23). This distinct pattern of expression could mean that they are regulated differently and have distinct functions in different tissues or that they transport distinct but related ions in different parts of the plant (23).

CDF proteins have been implicated primarily in the transport of Zn, Co, and Cd in bacteria and some eukaryotes. Certain members of CDF have been implicated in Cu or Cd transport. A related Zn transporter (*ZAT1*) from *Arabidopsis* was reported by Van der Zaal et al. (26). This *ZAT1* transporter may have a role in Zn sequestration in plants. Enhanced Zn resistance was observed in transgenic plants that overexpress *ZAT1*, expressed constitutively throughout the plant. High Zn exposure of these plants led to increased Zn content in the roots. Zinc transporter (ZIP) proteins are involved in Zn and Fe uptake (27).

To enhance metal uptake, (1) the number of uptake sites could be increased, (2) the specificity of the uptake proteins could be altered, and (3) the sequestration capacity could be enhanced by increasing the number of intracellular high-affinity binding sites or the rates of transport across organelles. A comprehensive understanding of metal transport processes in plants is essential

for formulating effective strategies to develop genetically engineered plants that can accumulate specific metals.

DETOXIFICATION OF METALS IN PLANTS

A general mechanism for detoxification of metals in plants is chelation of the metals by a ligand, followed by sequestration of the metal–ligand complex into the vacuole. Complexation with ligands can be extracellular, for example, the mechanism of Al tolerance by efflux of organic acids such as malate and citrate from roots. Intracellular complexation involves peptide ligands such as metallothioneins (MTs) and phytochelatins (PCs). Metallothioneins are cystein-rich polypeptides, first identified in mammalian tissues as Cd-binding peptides (11). Several MT genes and proteins have been identified in plants. MTs are gene encoded, but PCs are enzymatically synthesized. PCs have been identified in a wide variety of plant species, including angiosperms (both monocots and dicots), gymnosperms, algae (28), fungi (29,30), and marine diatoms (31), but not in animals.

PCs are a family of sulfur-rich peptides that were first identified in yeast. Most of the current knowledge of these peptides has resulted from molecular-genetic studies on yeast and *Arabidopsis* during the last few years. PCs are rapidly induced in cells and tissues exposed to a range of metal ions, such as Cd, Ni, Cu, Zn, Ag, Hg, and Pb, and anions, such as arsenate and selenite (32). PCs consist of only three amino acids, glutamine (Glu), cysteine (Cys) and glycine (Gly). They are structurally related to the tripeptide glutathione (GSH) and are enzymatically synthesized from GSH. PCs form a family of structures with increasing repetitions of the γ-Glu-Cys dipeptide followed by a terminal Gly, (γ-Glu-Cys)n-Gly, where n is generally in the range of 2–5, but could be as high as 11 (33). It was shown that GSH-deficient mutants of *Arabidopsis* are also PC-deficient and Cd-sensitive (34). GSH-dependent PC-synthase activity was identified in cultured cells of *Silene cucubalis* (35). The enzyme is active only in the presence of metal ions such as Cd, Cu, Zn, Ag, Hg, and Pb. Similar activities have been identified in *Arabidopsis* (36), tomato (37), and pea (38). Several studies have suggested that PC-synthase activity is regulated by metal ions at the level of enzyme activation. The fact that PC-synthase activity has an important role in Cd tolerance was shown in *Vigna angularis* (adzuki beans) that are hypersensitive to Cd. Cell-suspension cultures of adzuki bean did not synthesize PCs when challenged with Cd. These cells also lacked PC-synthase activity. Externally applied GSH failed to stimulate PC synthesis or confer Cd tolerance on the cells, which demonstrated the importance of PC synthesis in Cd tolerance in plants (39).

Despite the identification of PC-synthase activity more than a decade ago, the identification of a corresponding gene remained elusive until recently. PC-synthase genes were first isolated almost simultaneously by two research groups. Vatamaniuk et al. (40) identified an *Arabidopsis* cDNA, named *AtPCS1*. The expression of *AtPCS1* protein mediated an increase in Cd accumulation, pointing to a possible role in Cd chelation or sequestration. Clemens et al. (41) identified a wheat cDNA, *TaPCS1*, that increased Cd-resistance in wild-type yeast. Just like *AtPCS1*, the Cd-resistance mediated by *TaPCS1* was associated with an increase in Cd accumulation and was GSH-dependent. Both *AtPCS1* and *TaPCS1* mediated Cd tolerance are GSH-dependent and function in vacuole-deficient mutants, suggesting a cytosolic localization, and mediate *in vivo* PC biosynthesis in yeast. Further evidence of the role of PCs in metal hyperaccumulation comes from the overexpression of a bacterial glutathione synthetase, an enzyme that synthesizes GSH, by Indian mustard plants (42). These transgenic plants have increased GSH and PC concentrations and increased Cd tolerance and accumulation relative to controls. Overexpression of plant PC synthetase in transgenic yeast also increased the tolerance to and the accumulation of Cd (40). These studies show that the manipulation of GSH and PC concentrations has significant potential for increasing the accumulation of metals by plants (43).

Regulation of PC-synthase activity is likely to be the most important regulatory mechanism of the PC biosynthetic pathway. Evidence pointing to the role of posttranslational activation was obtained using plant cell cultures. PC biosynthesis reportedly occurs within minutes of exposure to Cd and is independent of de novo protein synthesis. In *Silene cucubalis* cell cultures (35), tomato (36), and *Arabidopsis* (37), PC-synthase expression is independent of metal exposure. These studies suggest that PC synthase is regulated by enzyme activation by metals. However, there are conflicting reports regarding the induction of transcript levels in response to metal exposure. PC biosynthesis probably varies among different plant species and is regulated at transcriptional and posttranscriptional levels or both, which suggests that PC-synthase activity is regulated differently in different plant species.

PC biosynthesis may also be regulated by the biosynthesis of GSH. In transgenic Indian mustard plants, increases in the expression of enzymes in GSH biosynthetic pathways led to an increase in PC biosynthesis and Cd tolerance (42,44). Wild-type Indian mustard plants respond to increased Cd exposure with increased levels of γ-glutamylcysteine synthatase (γ-*ECS*) transcript, which codes for the first enzyme in the PC biosynthetic pathway (45). Similarly, evidence also exists supporting posttranscriptional regulation of γ-ECS expression (46).

SEQUESTRATION OF METALS IN VACUOLES

Within plant cells, PC–metal complexes accumulate in the vacuole, which appears to be driven by various membrane transporters. Several classes of proteins have been implicated in metal transport, including CPx type ATPases, the Nramp family of proteins, and CDF family proteins. In yeast, PC–Cd complexes are reportedly sequestered in the vacuole. The mutant *hmt1* cannot form the HMW complex on Cd exposure. The *hmt1* gene encodes a member of the ATP-binding cassette (ABC) membrane transport protein that is located in the vacuolar membrane (47). The transport of PCs and PC–Cd complexes across the vacuolar membrane was not dependent on the proton gradient established across the

membrane by vacuolar H^+-ATPase (48). When mesophyll protoplasts from tobacco plants were exposed to Cd, all Cd and PCs accumulated in the vacuole (49). Salt and Rauser (50) also identified an ATP-dependent, but proton gradient-independent activity, capable of transporting both PCs and PC–Cd complexes into tonoplast vesicles from oat roots.

GENETIC ENGINEERING OF PLANTS FOR PHYTOREMEDIATION

Effective phytoextraction of metals depends on the ability of plants to tolerate high levels of toxic metals and also on their ability to take up increased amounts of metals and translocate them to the shoots. Plants that have the ability to translocate metals from roots to shoots at high rates are more effective hyperaccumulators. In nonaccumulators, root concentrations of Zn, Cd, or Ni are ten or more times higher than shoot concentrations, but in hyperaccumulators, shoot metal concentrations can far exceed root levels (51,52). Biotechnology offers the opportunity to transfer hyperaccumulator phenotypes into fast growing, high biomass plants that could be highly effective in phytoextraction. Several recent studies have succeeded in bioengineering plants to hyperaccumulate a variety of toxic metals. Modification or overexpression of the enzymes that are involved in synthesizing glutathione and PCs might be a good approach to enhance metal tolerance and accumulation in plants. Zhu et al. (42) overexpressed the *Escherichia coli* counterparts of γ-ECS and glutathione synthetase in Indian mustard plants that accumulate more Cd than wild-type plants. Rugh et al. (53) modified yellow poplar trees with two bacterial genes, *merA* and *merB*, to detoxify methylmercury from contaminated soil. In transformed plants, *merB* catalyzes the release of Hg^{2+} from methylmercury, which is then converted to Hg^o by *merA*. Elemental mercury is less toxic and more volatile than the mercuric ion and is released into the atmosphere. Pilon-Smits et al. (54) overexpressed the ATP-sulfurylase (*APS*) gene in Indian mustard. The transgenic plants had fourfold higher APS activity and accumulated three times more Se than wild-type plants. Recently, Dhankar et al. (55) reported a genetics-based strategy to remediate As from contaminated soils. They overexpressed two bacterial genes in *Arabidopsis*. One was the *E. coli arsC* gene encoding arsenate reductase that reduces arsenate to arsenite coupled to a light-induced soybean *rubisco* promoter. The second gene was the *E. coli* γ*-ECS* coupled to a strong constitutive actin promoter. The AsrC protein, expressed strongly in stem and leaves, catalyzes the reduction of arsenate to arsenite, whereas γ-ECS, which is the first enzyme in the PC-biosynthetic pathway, increases the pool of PCs in the plant. The transgenic plants that expressed both AsrC and γ-ECS proteins showed substantially greater As tolerance when grown on As, these plants accumulated 4- to 17-fold greater fresh shoot weight and accumulated two- to threefold more As than wild-type plants.

Most metal hyperaccumulators are slow growing and have low biomass, so bioengineering of nonaccumulators is essential for more effective phytoremediation. Conventional breeding approaches have also been proposed to improve plants for metal extraction. However, the success of this approach is doubtful due to sexual incompatibility between parent lines (56). Biotechnology has the potential of overcoming this limitation. However, a comprehensive knowledge of the genetic basis for hyperaccumulation is essential for effective use of biotechnology to design transgenic plants capable of efficient phytoremediation.

SUMMARY AND FUTURE DIRECTIONS

Phytoremediation as a cleanup process for metal contaminants is very attractive because it is effective, relatively inexpensive, and environmentally friendly. The majority of phytoremediation-related research to date has focused on hyperacccumulator plants that accumulate metals to concentrations more than 100 times higher than those in nonaccumulators. However, most of the known hyperaccumulators are slow growing and have low biomass, which are not ideal traits for optimal metal uptake. Plants ideal for phytoremediation should be fast growing, have high biomass, an extensive root system, be easy to harvest, and tolerate and accumulate a range of metals in their harvestable parts. No single plant that has all these traits have been found so far, but it is possible that nonaccumulators that are fast growing are have high biomass could be modified using the transgenic approach to achieve some of the properties of the hyperaccumulators. However, this approach can be used only when the molecular mechanisms of metal uptake, tolerance, accumulation, and translocation are better understood. Advances have been made in understanding root uptake mechanisms and the identification of transporters that sequester metals in the vacuoles and lead to hyperaccumulation of metals. Once taken up, the general mechanism for detoxification of metals in plants is chelation by a ligand, followed by sequestration of the metal–ligand complex into the vacuole. A lot of work has been done to understand metal tolerance and detoxification, but many questions regarding the genes involved in the processes controlling transport, sequestration, and detoxification of metals still remain. Once the rate-limiting steps for uptake, translocation, and detoxification of metals in hyperaccumulator plants are identified, more informed construction of transgenic plants will help tremendously in improving phytoremediation technology, paving the way for wider application.

BIBLIOGRAPHY

1. Adriano, D.C. (1992). Bioengineering of trace metals. In: *Advances in Trace Substances Research*. Lewis, Boca Raton, FL.
2. Evanko, C.R. and Dzombak, D.A. (1997). *Remediation of metals-contaminated soil and groundwater*. Technology Evaluation Report Oct. 1997, Groundwater Remediation Technology Analysis Center.
3. BIO-WISE. (2000). *Contaminated Land Remediation: A Review of Biological Technology*. D.T.I., London.
4. Raskin, I., Smith, R.D., and Salt, D.E. (1997). Phytoremediation of metals: using plants to remove pollutants from the environment. *Curr. Opin. Biotechnol.* **8**: 221–226.
5. Raskin, I. and Ensley, B.D. (2000). *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment*. John Wiley & Sons, New York.

6. Baker, A.J.M., McGrath. S.P., Reeves, R.D., and Smith, J.A.C. (2000). Metal hyperaccumulator plants: A review of the ecology and physiology of a biochemical resource for phytoremediation of metal polluted soils. In: *Phytoremediation of Contaminated Soil and Water*. N. Terry and G. Banuelos (Eds.). Lewis, Boca Raton, FL, pp. 85–107.
7. McGrath, S.P. and Zhao, F.J. (2003). Phytoextraction of metals and metalloids from contaminated soils. *Curr. Opin. Biotechnol.* **14**: 1–6.
8. Khan, A.G., Kuek, C., Chaudhry, T.M., Khoo, C.S., and Hayes, W.J. (2000). Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere* **41**: 197–207.
9. Clemens, S., Palmgren, M.G., and Kramer, U. (2002). A long way ahead: Understanding and engineering plant metal accumulation. *Trends Plant Sci.* **7**: 309–315.
10. Lombi, E. et al. (2002). Influence of iron status on calcium and zinc uptake by different ecotypes of the hyperaccumulator *Thlaspi caerulescens*. *Plant Physiol.* **128**: 1359–1367.
11. Salt, D.E., Smith, R.D., and Raskin, I. (1998). Phytoremediation. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **49**: 643–668.
12. Baker, A.J.M., Reeves, R.D., and McGrath, S.P. (1991). *In situ* decontamination of metal polluted soils using crops of metal-accumulating plants—a feasibility study. In: *In Situ Bioreclamation*. R.E. Hinchee and R.F. Olfenbuttel (Eds.). Butterworth-Heinemann, Stoneham, MA, pp. 539–544.
13. Ma, L.Q. et al. (2001). A fern that hyperaccumulates arsenic: A hardy, versatile, fast-growing plant helps to remove arsenic from contaminated soils. *Nature* **409**: 579.
14. Francesconi, K., Visoottiviseth, P., Sridokchan, W., and Goessler, W. (2002). Arsenic species in an arsenic hyperaccumulating fern, *Pityrogramma calomelanos*: A potential phytoremediator of arsenic-contaminated soils. *Sci. Total Environ.* **284**: 27–35.
15. Zhao, F.J., Hamon, R.E., Lombi, E., McLaughlin, M.J., and McGrath, S.P. (2002). Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator, *Thlaspi caerulescence*. *J. Exp. Bot.* **53**: 535–543.
16. Lasat, M.M., Baker, A.J.M., and Kochian, L.V. (1996). Physiological characterization of root Zn^{2+} absorption and translocation to shoots in Zn hyperaccumulator and nonaccumulator species of *Thlaspi*. *Plant Physiol.* **112**: 1715–1722.
17. Maser, P. et al. (2001). Phylogenetic relationships within cation transporter families of *Arabidopsis*. *Plant Physiol.* **126**: 1646–1667.
18. Pence, N.S. et al. (2000). The molecular physiology of heavy metal transport in the Zn/Cd hyperaccumulator, *Thlaspi caerulescence*. *Proc. Natl. Acad. Sci. USA.* **97**: 4956–4960.
19. Vert, G. et al. (2002). *IRT1*, an *Arabidopsis* transporter essential for iron uptake from the soil and for plant growth. *Plant Cell* **14**: 1223–1233.
20. Connolly, E.L., Fett, J.P., and Guerinot, M.L. (2002). Expression of the IRT1 metal transporter is controlled by metals at the levels of transcript and protein accumulation. *Plant Cell* **14**: 1347–1357.
21. Williams, L.E., Pittman, J.K., and Hall, J.L. (2000). Emerging mechanisms for heavy metal transport in plants. *Biochim. Biophys. Acta* **1465**: 104–126.
22. Tabata, K., Kashiwagi, S., Mori, H., Ueguchi, C., and Mizuno, T. (1997). Cloning of a cDNA encoding a putative metal-transporting P-type ATPase from *Arabidopsis thaliana*. *Biochim. Biophys. Acta* **1326**: 1–6.
23. Belouchi, A., Kwan, T., and Gros, P. (1997). Cloning and characterization of the OsNramp family from *Oryza sativa*, a new family of membrane proteins possibly implicated in the transport of metal ions. *Plant Mol. Biol.* **33**: 1085–1092.
24. Alonso, J.M., Hirayama, T., Roman, G., Nourizadeh, S., and Ecker, J.R. (1999). *EIN2*, a bifunctional transducer of ethylene and stress responses in *Arabidopsis*. *Science* **284**: 2148–2152.
25. Thomine, S., Clemens, S., Kim, E.J., Neumann, D., Wang, R., Crawford, N.M., and Schroeder, J.I. (1999). *Molecular Analysis of Metal Transport and Metal Tolerance in Plants*. *Plant Biol. 1999*, Meeting abstract No. 13004. Available: http://abstracts.aspb.org/aspp1999/public/cgi-bin/showabs.cgi?0958+M03.
26. Van der Zaal, B.J. et al. (1999). Over-expression of a novel *Arabidopsis* gene related to putative zinc-transporter genes from animals can lead to enhanced zinc-resistance and accumulation. *Plant Physiol.* **119**: 1047–1055.
27. Guerinot, M.L. and Eide, D. (1999). Zeroing in on zinc uptake in yeast and plants. *Curr. Opin. Plant Biol.* **2**: 244–249.
28. Gekeler, W., Grill, E., Winacker, E.-L., and Zenk, M.H. (1989). Survey of the plant kingdom for the ability to bind heavy metals through phytochelatins. *Z. Naturforsch. C.* **44**: 170–178.
29. Mehera, R.K., Tarbet, E.B., Gray, W.R., and Winge, D.R. (1988). Metal-specific synthesis of two metallothioneins and -glutamyl peptides in *Candida glabrata*. *Proc. Natl. Acad. Sci. USA* **85**: 8815–8819.
30. Kneer, R., Kutchan, T.M., Hochberger, A., and Zenk, M.H. (1992). *Saccharomyces cerevisiae* and *Neurospora crassa* contain heavy metal sequestering phytochelatin. *Arch. Microbiol.* **157**: 305–310.
31. Morelli, E. and Pratesi, E. (1997). Production of phytochelatins in the marine diatom *Phaeodactylum tricornutum* in response to copper and cadmium exposure. *Bull. Environ. Contam. Toxicol.* **59**: 657–664.
32. Rauser, W.E. (1995). Phytochelatins and related peptides. Structure, biosynthesis and function. *Plant Physiol.* **109**: 1141–1149.
33. Cobbett, C.S. (2000). Phytochelatin biosynthesis and function in metal detoxification. *Curr. Opin. Plant Biol.* **3**: 211–216.
34. Cobbett, C.S., May, M.J., Howden, R., and Rolls, B. (1998). The glutathione deficient cadmium-sensitive mutant *cad2-1* of *Arabidopsis thaliana* is deficient in γ-glutamylcysteine synthatase. *Plant J.* **16**: 73–78.
35. Grill, E., Loffler, S., Winnacker, E.L., and Zenk, M.H. (1989). Phytochelatins, the heavy-metal-binding peptides of plants, are synthesized from glutathione by a specific γ-glutamylcysteine dipeptidyl transpeptidase (phytochelatin synthase). *Proc. Natl. Acad. Sci. USA* **86**: 6838–6842.
36. Chen, J., Huang, J.W., Caster, T., and Cunningham, S.D. (1997). *Arabidopsis* as a model system for studying lead accumulation and tolerance in plants. In: *Phytoremediation of Soil and Water Contaminants*. K.L. Kruger et al. (Eds.). American Chemical Society, Washington, DC, pp. 264–273.
37. Howden, R., Goldsbrough, P.B., Anderson, C.R., and Cobbet, C.S. (1995). Cadmium-sensitive *Cad1* mutants of *Arabidopsis* are phytochelatin deficient. *Plant Physiol.* **107**: 1059–1066.
38. Klapheck, S., Schlunz, S., and Bergman, L. (1995). Synthesis of phytochelatins and homophytochelatins in *Pisum sativum* L. *Plant Physiol.* **107**: 515–521.
39. Inouhe, M. et al. (2000). Adzuki bean cells are hypersensitive to cadmium and do not synthesize phytochelatins. *Plant Physiol.* **23**: 1029–1036.

40. Vatamaniuk, O.K., Mari, S., Lu, Y.-P., and Rea, P.A. (1999). AtPCS1, a phytochelatin synthase from *Arabidopsis*: Isolation and *in vitro* reconstitution. *Proc. Natl. Acad. Sci. USA* **96**: 7110–7115.
41. Clemens, S., Kim, E.J., Neuman, D., and Schroeder, J.I. (1999). Tolerance to toxic metals by a gene family of phytochelatin synthases from plants and yeast. *EMBO J.* **18**: 3325–3333.
42. Zhu, Y.L., Pilon-Smits, E.A.H., Jouanin, L., and Terry, N. (1999). Over-expression of glutathione synthase in Indian mustard enhances cadmium accumulation and tolerance. *Plant Physiol.* **119**: 73–79.
43. Meagher, R.B. (2000). Phytoremediation of toxic elemental and organic pollutants. *Curr. Opin. Plant Biol.* **3**: 153–162.
44. Yong, L.Z. et al. (1999). Cadmium tolerance and accumulation in Indian mustard is enhanced by over-expressing γ-glutamylcysteine synthetase. *Plant Physiol.* **121**: 1169–1179.
45. Schafer, H.J., Haag-Kerwer, A., and Rausch, T. (1998). cDNA cloning and expression analysis of genes encoding GSH synthesis in roots of the heavy metal accumulator *Brassica juncea* L.: Evidence of Cd-induction of a putative mitochondrial gamma-glutamylcysteine synthetase isoform. *Plant Mol. Biol.* **37**: 87–97.
46. May, M.J., Vernoux, T., Sanchez-Fernandez, R., van-Montagu, M., and Inze, D. (1998). Evidence for post-transcriptional activation of γ-glutamyl-cysteine synthetase during plant stress responses. *Proc. Natl. Acad. Sci. USA* **95**: 12049–12054.
47. Ortiz, D.F. et al. (1992). Heavy metal tolerance in fission yeast requires an ATP-binding cassette type vacuolar membrane transporter. *EMBO J.* **11**: 3491–3499.
48. Ortiz, D.F., Ruscitti, T., McCue, K.F., and Ow, D.V. (1995). Transport of metal-binding peptides by HMT1, a fission yeast ABC-type B vacuolar membrane protein. *J. Biol. Chem.* **270**: 4721–4728.
49. Vogeli-Lange, R. and Wagner, G.J. (1990). Subcellular localization of cadmium and cadmium-binding peptides in tobacco leaves: Implications of a transport function for cadmium-binding peptides. *Plant Physiol.* **92**: 1086–1093.
50. Salt, D.E. and Rauser, W.E. (1995). MgATP-dependent transport of phytochelatins across the tonoplast of oat roots. *Plant Physiol.* **107**: 1293–1301.
51. Brown, S.L., Angle, J.S., Chaney, R.L., and Baker, A.J.M. (1995). Zinc and cadmium uptake by *Thlaspi caerulescens* and *Silene vulgaris* grown on sludge-amended soils in relation to total soil metals and soil pH. *Environ. Sci. Technol.* **29**: 1581–1585.
52. Kramer, U., Cotter-Howells, J.D., Charnock, J.M., Baker, A.J.M., and Smith, J.A.C. (1996). Free histidine as a metal chelator in plants that accumulate nickel. *Nature* **379**: 635–638.
53. Rugh, C.L., Senecoft, J.F., Meagher, R.B., and Merkle, S.A. (1998). Development of transgenic yellow poplar for mercury phytoremediation. *Nat. Biotechnol.* **33**: 616–621.
54. Pilon-Smits, E.A.H. et al. (1999). Over-expression of ATP sulfurylase in Indian mustard leads to increased selenate uptake, reduction and tolerance. *Plant Physiol.* **119**: 123–132.
55. Dhankar, O.P. and Meagher, R.B. et al. (2002). Engineering tolerance and hyperaccumulation of arsenic in plants by combining arsenate reductase and γ-glutamylcysteine synthetase expression. *Nat. Biotechnol.* **20**: 1140–1145.
56. Lasat, M.M. (2002). Phytoextraction of toxic metals: A review of biological mechanisms. *J. Environ. Qual.* **31**: 109–120.

IN SITU GROUNDWATER REMEDIATION FOR HEAVY METAL CONTAMINATION

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THE METALS PROBLEM

Highly toxic and highly soluble heavy metals are contained in numerous waste streams, including those from power, chemical, electronics, and general manufacturing plants, and mining facilities. Heavy metals can create significant health risks to humans.

HISTORY

Arsenic, lead, copper, zinc, cadmium, molybdenum, uranium, and cyanide have been used in a variety of industrial activities such as plating and circuit board manufacturing, and occur in mining and power plant waste streams and from other processes.

Chromium is an example of one metal used by various industries for different purposes. Chromium is used in wood preservation. In that process, copper-chrome-arsenic wood preservatives are used extensively by the timber industry for pressure-treated or green wood. Chromium is also used as a nontarnishing surface coating in the metal plating industry. For making kiln bricks, chromium, due to its large capacity to withstand high temperatures, is used in the refractory industry. Finally, trivalent chromium salts are used widely as a tanning agent transforming animal hides and skins into leather. Chromium is just one heavy metal but illustrates the complexity and variability of industrial uses. With each use comes a series of associated industrial processes, waste streams, recycling programs, fate and transport of the metal in the environment, toxicity to humans, and the various oxidation states of the metal and other factors. All these factors greatly affect the cleanup process.

OVERVIEW OF METAL TREATMENT

Metal remediation has been documented. *In situ* methods using natural systems and enhanced bioremediation have shown promise (1). Various *in situ* treatment technologies, including metal remediation, are described in Nyer et al. (2). Environmental restoration of metal-contaminated soils is described in Ikandar (3). Mining and processing facilities are a source of metal contamination. Remediation of mining wastes is described in Davis et al. (4). Figure 1 shows a conceptual model of metal contaminants moving through the soil and into groundwater.

The success of *in situ* metal remediation requires adequate site characterization of both soil and groundwater zones, good understanding of the valence states of the associated metals and their likely source location, and complete chemical characterization. Chemical analyses include dissolved oxygen (DO), E_h, soil and groundwater

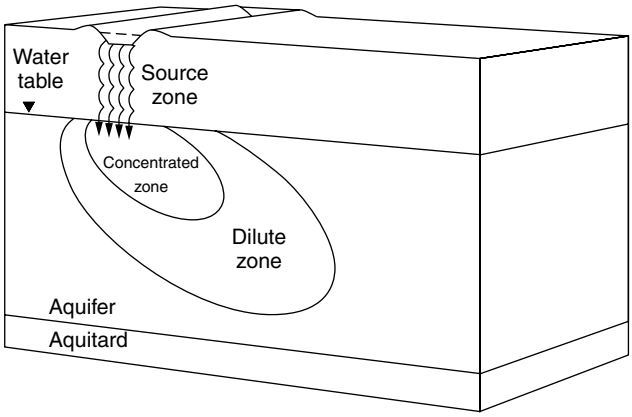


Figure 1. Conceptual model of geochemical zones in a metal contaminant plume (5,6).

pH, total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), cation exchange capacity (CEC), alkalinity, temperature, specific metals, and other analytes. Bench testing in the laboratory using soil and groundwater from the site allows for optimizing the chemistry in the laboratory prior to a field pilot test and an ultimate full-scale remediation program. Chemical bench tests can range from simple beaker tests where only groundwater is mixed with the reactants to soil column tests. For microbiological testing, heterotrophic count and anaerobic microbes can be evaluated. In addition, microbial bench tests can be performed with soil or groundwater, and microbial colonies can be cultured and evaluated for growth potential in various pH conditions with various bioenhancement chemicals, typically carbon sources such as molasses, cheese whey, sucrose, corn syrup, lactic acid, milk, or propane.

IN SITU TREATMENT TECHNOLOGY

Remediation of heavy metals such as lead, chromium, arsenic, and others in soil and groundwater frequently uses reduction reactions to lower the solubility of an oxidized metal in the higher of two or three valence states to a lower energy and less toxic state. Ultimately, the metal is precipitated as a sulfide or in another immobile and low toxicity form.

The solubilities of arsenic, lead, copper, zinc, cadmium, molybdenum, uranium, and cyanide are pH dependent. Recently, sulfur-based metals treatment technologies have been the focus of an increasing number of research studies and commercial applications for treating metal contamination in soil and groundwater.

Reduction Chemistry

In situ metal remediation by reduction can be either chemical or biological. For chemical reactions, sulfur compounds have been used successfully in a variety of settings. Precipitation of metals in reducing environments as sulfides, hydroxides, and carbonates has been documented as a remediation method. Even zero-valent iron has been used to reduce hexavalent chromium in groundwater through reactive permeable barrier walls, as part of a funnel and gate system. Reactive barriers for *in situ* metal treatment are documented.

Various sulfur-based reductants are available, and the more common ones include metabisulfite, ferrous sulfate, calcium polysulfide, and sodium sulfide. Selected reactions are described below:

Reductant. Metabisulfite ($S_2O_6^{2-}$).
In the presence of excess sulfite, Cr(VI) is reduced (7):

$$6H^+ + 2HCrO_4^- + 3HSO_3^-(\text{excess}) \Longrightarrow 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} = 6H_2O$$

In the presence of excess Cr(VI), reduction to Cr(III) by sulfite is performed by this reaction (7):

$$5H^+ + 2HCrO_4^-(\text{excess}) + 3HSO_3^- \Longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O$$

Reductant. Ferrous sulfate ($FeSO_4$)
Dissolved Cr(VI) can be precipitated as $Cr(OH)_3$ by injecting ferrous sulfate (1).

$$\text{Acidic conditions: } Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \Longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Neutral or alkaline conditions:

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O \Longrightarrow Cr^{3+} + 3Fe^{3+} + 8OH^-$$

Both Cr(III) and Fe(III) ions are highly insoluble in natural groundwater, and these ions precipitate out as hydroxides as follows (1):

$$Fe^{3+} + 3OH^- \Longrightarrow Fe(OH)_3\ (\text{precip})$$
$$Cr^{3+} + 3OH^- \Longrightarrow Cr(OH)_3\ (\text{precip})$$

Reductant. Calcium polysulfide (CaS_5)

$$2CrO_4^{2-} + 3CaS_5 + 10H^+ \Longrightarrow 2Cr(OH)_3 + 15S^\circ + 3Ca^{2+} + 2H_2O$$

A reductant, such as calcium polysulfide (CaS_4), precipitates the highly soluble metal as a less soluble and nontoxic sulfide (Fig. 2). Metal hydroxides change solubility with changes in pH. Metal sulfides remain insoluble within a pH range of about 5 to 9. Calcium polysufide has a pH of 11.3 to 11.5, a specific gravity of 1.273, and is deep orange-red in solution. The excess calcium precipitates as calcium carbonate, gypsum, or calcium sulfate. Calcium polysulfide is soluble in water and comes as 29% concentration of calcium polysulfide. The extent of metals precipitation is a function of pH.

Delivery System

To deliver sulfur-based chemical reductants into the subsurface, an *in situ* delivery method uses close spacing of high-pressure injection ports, allowing the treatment

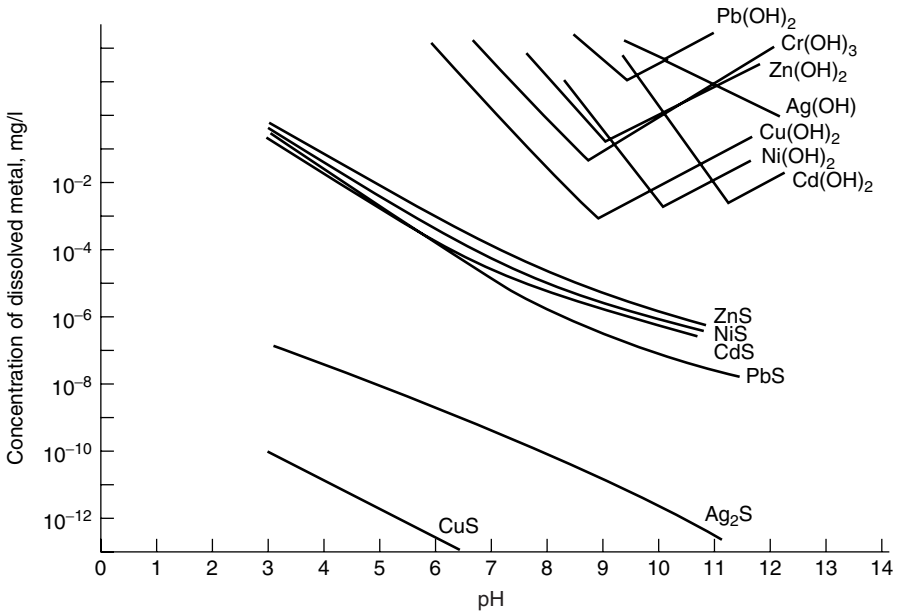
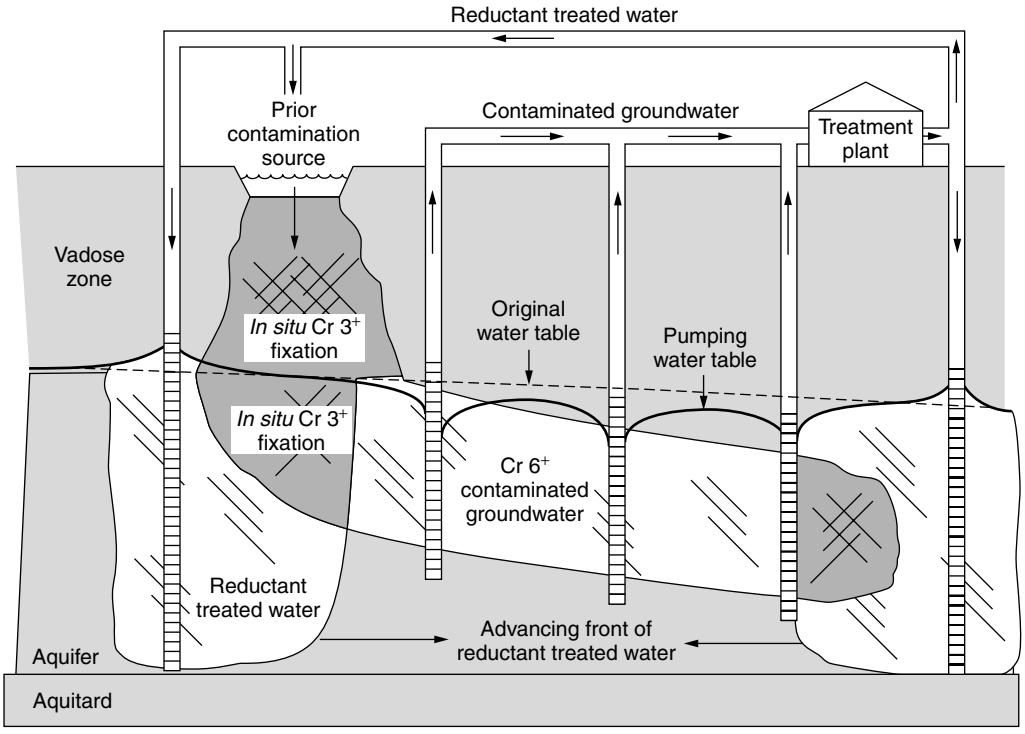


Figure 2. Solubility of metal hydroxides and sulfides as a function of pH (8).



Source: Rouse, 1997

Figure 3. Schematic of an *in situ* chromium remediation process (5,9).

chemicals to contact the contaminant fully. The delivery of the reductant chemicals can be through trenches or wells. A schematic of an *in situ* remediation process for chromium is shown in Fig. 3 (5,6).

In addition, the direct push method allows placing injection ports as well as a specialized lance system to deliver treatment chemicals (10).

Besides sulfur-based reductants, lime [$Ca(OH)_2$] and other alkaline solutions such as potash (KOH) are used for chemical reduction and hydroxide precipitation (Table 1).

BIOLOGICAL METHODS OF *IN SITU* METAL REMEDIATION

Plant-based *in situ* remediation of metals, generically called phytoremediation, can be accomplished using a variety of plants that uptake the metals. An overview

Table 1. *In situ* Metal Remediation

Metal	Arsenic	Lead	Copper	Zinc
Treatment notes:	Acid medium only	Wide range (pH: 4–9)	Close to neutral (optimal pH: 5–7)	Wide range (pH: 4–9)
Metal	Cadmium	Molybdenum	Uranium	Cyanide
Treatment notes:	Wide range (pH: 4–9)	Wide range (pH: 4–9)	Wide range (pH: 4–9)	Chemical conversion produces thiocyanate[a]

[a]Thiocyanate is treated with lime, producing calcium carbonate, gypsum and ammonia.
Chromium (Cr VI) can be treated with calcium polysulfide, and Cr (VI) is reduced to Cr (III), which is then precipitated as chromium hydroxide.

of phytoremediation and other subcategories is included in Lehr (11).

Microbe-induced reduction of metals has been documented (1). Using chromium as an example, microorganisms may reduce chromium [Cr(VI)] under anaerobic conditions to trivalent chromium [Cr(III)] by exuding reducing agents or by lowering the pH. Other methods can be used to create anaerobic conditions for enhanced bioremediation and consequently reduction of metals. These enhancements use the injection of a carbon source.

PAST REMEDIATION OPTIONS

In the past, conventional remediation of soil and groundwater impacted by heavy metals has relied on soil excavation, which was expensive and disruptive. In addition, moving the soil only moved the problem, without treating the soil or reducing the long-term liability. For groundwater, pump and treat remediation relied on pumps to remove groundwater from the aquifer through a series of extraction wells or trenches. The extracted water was then treated above ground or disposed of off site. Pump and treat methods fail to address the source of the contamination in the vadose zone. Although the construction of passive permeable treatment walls containing zero-valent iron filings can reduce some metals to less toxic varieties, the passive barriers are expensive and do not treat source areas.

The chemical and biological reducing methods of remediating metals *in situ* are technically effective in significantly lowering metals concentrations in 1 to 5 years at reasonable cost. Delivery systems for the chemical reductants and bioenhancements have been developed and used at a variety of sites. The keys to success in most of these projects involve accurate subsurface assessments prior to field remediation, properly designed bench tests to optimize chemistry in the laboratory, realistic regulatory targets for site closure, and a well-designed remediation delivery system.

BIBLIOGRAPHY

1. Suthersan, S.S. (2002). *Natural and Enhanced Remediation Systems*. Lewis, Boca Raton, FL.
2. Nyer, E.K., Palmer, P.L., Carman, E.P., Boettcher, G., Bedessem, J.M., Lenzo, F., Crossman, T.L., Rorech, G.J., and Kidd, D.F. (2001). *In Situ Treatment Technology*. 2nd Edn. CRC Press, Lewis, Boca Raton, FL, p. 536.
3. Ikandar, I.K. (2001). *Environmental Restoration of Metals-Contaminated Soils*. I.K. Ikandar (Ed.). CRC Press, Lewis, Boca Raton, FL, p. 304.
4. Davis, A., Moomaw, C., Fennemore, G., and Buffington, R. (2002). Innovative strategies in remediating mining wastes. In: *Handbook of Complex Environmental Remediation Problems*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 7.1–7.62.
5. Rouse, J.V., Leahy, M.C., and Brown, R.A. (1996). A geochemical way to keep metals at bay. *Environ. Eng. World* **May–June**.
6. Sabatini, D.A., Knox, R.C., Tucker, E.E., and Puls, R.W. (1997). *Innovative Measures for Subsurface Chromium Remediation: Source Zone, Concentrated Plume, and Dilute Plume*. U.S. Environmental Protection Agency, Environmental Research Brief, Washington, DC.
7. Palmer, C.D. and Wittbrodt, P.R. (1991). Processes affecting the remediation of chromium-contaminated sites. *Environ. Health Perspect.* **92**: 25–40.
8. United States Environmental Protection Agency. (1981). *US EPA Chart Comparing Sulfide and Hydroxide Solubilities*. EPA publication, Washington, DC.
9. Rouse, J.V. (1997). Natural and Enhanced Attenuation of CCA Components in Soil and Groundwater. Paper presentation for the *93rd Annu. Meet. Am. Wood-Preservers Assoc.* April pp. 27–29, Washington, DC.
10. Jacobs, J. (2001). In-Situ Liquid Delivery Systems for Chemical Oxidation, Bioremediation and Metals Stabilization, Association for Environmental Health and Sciences, *11th Annu. West Coast Conf. Contaminated Soils, Sediments Water*, March 21, 2001, San Diego, CA.
11. Lehr, J. (2000). Phytoremediation: A promising path to the elimination of heavy metals and radionuclides in groundwater and soil. In: *Standard Handbook of Environmental Science, Health and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.26–14.29.

METHANE IN GROUNDWATER

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Methane is a colorless, odorless, and tasteless gas, which is produced by biological decay of organic materials or by high temperatures acting on organic materials in

unconsolidated and geologically young deposits. These materials include coals, organic rich shales, landfill materials, compost piles, and other accumulations of organic materials both above and underground. For example, a buried oak log, only 1 ft in diameter and 5 ft long, can generate enough methane when it decomposes underground to form an explosive mixture in 400 to 1200 m^3 of air (1).

Methane is produced by biological processes where oxygen is excluded (anaerobic conditions). Methane can be oxidized in water that contains dissolved oxygen, so the amount that reaches the surface depends on the depth of water. Its rate of production generally increases with temperature (2). It is produced only in a strongly reducing medium ($E_h < 100$ mV). Anaerobes that produce methane are called methanogens. Molecular oxygen is very toxic to them. Methane can be produced by fermenting a few simple organic compounds such as acetate, formate, methanol, or methylamines. Molecular hydrogen can also be used to reduce inorganic carbonate to methane (3). During methanogenesis, carbon dioxide is used as an electron acceptor, and methane is produced. The presence of methane in groundwater is indicative of strongly reducing conditions and occurs after oxygen, nitrate, iron, and sulfate have been depleted in the treatment zone.

Methane in water wells becomes a problem when it is allowed to build up in confined spaces. High concentrations of methane can displace oxygen or in the presence of a spark, can explode. Extensive testing for methane in water wells in southwest Colorado has been conducted during the past 10 years. As a result of this testing, many believe that methane concentrations below 1 mg/L are harmless. Methane levels up to 7 mg/L usually are not a concern but should be monitored for changes. Between 7 mg/L and 13 mg/L, additional monitoring and treatment should be considered. Also, care should be taken to ventilate confined spaces where well water is used. When methane levels are 13 mg/L or above, treatment is a must.

Theoretically, water containing as little as 1 to 2 mg/L of methane can produce an explosion in a poorly ventilated air space. Fires and explosions in well pits, basements, and water tanks have occurred from methane emitted by groundwater; safety measures include analysis to detect the presence of the gas, aeration of water before use, and adequate ventilation where the water is being used. There is a danger of people suffocating in dug wells and pump pits where high methane concentrations form (4).

BIBLIOGRAPHY

1. Anon. (1969). Gas in the ground water. *J. Am. Water Works Assoc.* **61**: 42.
2. Wild, A. (1996). *Soils and the Environment*. Cambridge University Press, New York, pp. 223–224.
3. U.S. Environmental Protection Agency. (1987). *Groundwater Hand Book*. Academic, Jaipur, India, p. 44.
4. Todd, D.K. (1995). *Groundwater Hydrology*. Wiley, Toronto, Canada, p. 307.

FOSSIL AQUIFERS

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Fossil aquifers are bodies of very deep aquifers that are disconnected from our contemporary hydrologic cycle. Water in these aquifers can be hundreds to thousands of years old and thousands of feet deep. As they are not recharged by today's precipitation, using them as a water supply is not sustainable. Other deep aquifers may still be connected to surface precipitation, but recharge so slowly relative to human time scales that they can practically be considered nonreplenishable fossil aquifers as well. Not only are these supplies finite, but their depth also makes them more expensive, not only for the initial drilling but also for the increased energy required to pump water from these depths.

WHY DEVELOP AN UNSUSTAINABLE AND EXPENSIVE WATER SUPPLY?

The use of fossil aquifers is a symptom of the larger world water deficit that has developed in recent history. As populations grow, and as cheap fossil fuel encourages overpumping (or mining), accessing fossil water is an easier choice than restricting current water use. Moreover, the increased import/export grain trade has globalized regional water deficits (1). For example, demand to import wheat goes up in water-stressed countries, because it takes roughly 1000 tons of water to produce one ton of wheat. Essentially, importing wheat is a surrogate for importing water, and farmers in other countries that are motivated by the increased world demand for wheat will grow wheat even if they have to pump fossil water to do it.

Fossil aquifers are often accidentally found when drilling for gas and oil, or when communities run out of surface and shallow groundwater supplies and begin exploring for deeper water. Water discovered when drilling for gas and oil has no exploration costs or risks to future water users, because the costs are already borne by the oil exploration. However, when new wells are sunk only to search for fossil water, costs are relatively high because there is no fossil fuel subsidy and some test wells come up dry.

Regions around the world have various reasons to turn to fossil aquifers for more water. Growing populations increase demand for potable water to provide at least the subsistence amounts of water that individuals need. If these populations migrate to cities in search of work, they create an increased localized water demand that may not be satisfied by current water supplies. These growing populations must also be fed, raising demand for agricultural production that requires irrigation water. As 85% of the world's fresh water is used for irrigation, inefficient irrigation methods used in developing countries waste a good deal of their available water. Countries that are recently industrializing also need more water for each new industry that comes online.

New water supplies are also needed when traditional water supplies have become polluted from sewage or industrial effluent. This polluted water essentially removes some accessible water from consideration as a potable water source. For example, in China, there are several rivers whose water is so polluted from industrial waste that the water is dangerous to touch. The famous Ganges River in India is so filled with untreated sewage that its bacterial counts are dangerously high. Some aquifers in India have become so polluted from pesticides that they can no longer be used for drinking water.

INTERNATIONAL EXAMPLES

Developing countries with dry regions, such as China, India, and Mexico, have overpumped their shallow aquifers and have sunk deeper wells to access fossil water. In China's Northern Plain, water tables have dropped 2–3 m per year in some areas (2). Water tables in the agricultural state of Guanajuato, Mexico, have dropped up to 3.3 m/yr. In various regions of India, water tables have fallen from 1 to 3 m/yr.

Countries in the arid climates of northern Africa and the Middle East have been pumping from fossil aquifers for years. Iran, Pakistan, Saudi Arabia, Yemen, Algeria, and Libya, among others, have been relying on these aquifers to provide more potable water that does not cost quite as much as desalinized water. To develop some food independence, Saudi Arabia has used fossil aquifers to support experimental wheat growing in the desert but is now dropping this program after finding it is more practical to import their wheat. Soon, the desert alfalfa fields will also be gone, which will decrease the experimental projects for raising their own milk cows. Sana'a, the capital of Yemen, relies on a fossil aquifer that will run out by 2010, forcing either a mass migration (unlikely) or constructing desalting plants to supply their two million residents. Libya has its famous $27 billion "Great Manmade River," a massive pumping and distribution project to transport fossil water from the Nubian aquifer, underlying Libya, Chad, Egypt, and Sudan, to Libyan cities on the Mediterranean coast (3). This aquifer is large enough to provide Libyans with water for over 100 years, but most of these other countries are using aquifers with a life of perhaps 10–30 years more.

Just as shared shallow aquifers have been sources of conflict between users, pumping from fossil aquifers can generate competition and conflict as well. As more countries move to access fossil aquifers, agreements between countries will have to be crafted to avoid such conflict. Aside from the Nubian aquifer (4) mentioned above, South Africa, Namibia, and Botswana share the Kalahari/Karoo aquifer, and Argentina, Brazil, Paraguay, and Uruguay share the Guarani aquifer. All are looking at how to exploit this resource.

AMERICAN EXAMPLES

In America, two good examples of fossil aquifers are the Ogallala, underlying several states, and numerous smaller aquifers in the dry Southwest. The Ogallala, which consists primarily of fossil water, is shared by eight states where water tables have dropped 100 ft in some areas. This overpumping was primarily driven by irrigation demands. Some areas have been overpumped to the point that deeper drilling has stopped once it becomes economically infeasible, which has caused a depopulation of some High Plains counties as farms go out of business and then towns lose the service jobs that supported the farmers.

The increasing use and/or hunt for fossil aquifers in pockets of the American Southwest has been driven by recent population migration to these warmer cities. Growing cities in arid regions create inevitable water crises. As demand increases and water supply decreases, these cities must either use their current sources more efficiently or continue to hunt for "new" water in competition with other cities doing the same. Reluctant to impose onerous restrictions on residents or scare off industries, these cities then turn to fossil water once surface sources and shallow groundwater sources are fully tapped, often at the expense of other communities. Las Vegas is the most infamous example, as it is now planning to pump fossil water from 28 sparsely populated basins to its west and north and transport this water through pipelines to the city (5).

Globally, more fossil water is being pumped every day. This water is important not so much as an interesting link to the past or a particular challenge to hydrogeologists, but because increasing reliance on these ancient waters in rich and poor countries alike portends an abrupt halt to regional and national economies when the pumps finally run dry.

BIBLIOGRAPHY

1. Brown, L. (2004). *Plan B: Rescuing a Planet Under Stress and a Civilization in Trouble*. W.W. Norton, New York.
2. Brown, L., Larsen, J., and Fischlowitz-Roberts, B. (2002). *The Earth Policy Reader*. W.W. Norton, New York.
3. Tyler, P. (2004). Libya's Vast Pipe Dream Taps into Desert's Ice Age Water. *New York Times*, Mar. 2.
4. http://www.heritage.umd.edu/CHRSWeb/World%20Heritage/Heritage%20Spots/Heritage%20Spots%20PH.htm. Accessed Sept. 1, 2004.
5. Ward, D.R. (2002). *Water Wars: Drought, Flood, Folly, and the Politics of Thirst*. Riverhead Books, New York.

WHAT IS A HYDROCHEMICAL MODEL?

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INTRODUCTION

A hydrochemical model is a set of mathematical algorithms that calculate water discharge ("hydro") and concentrations of sediment and chemical constituents ("chemical")

in a stream or river. The computations are based on adjustable, empirical, or theoretical variables (parameters) and meteorological data for the drainage basin of the river or stream (input data). A variety of hydrochemical models have been employed by researchers, engineers, and environmental planners to predict hydrochemical responses in areas where there are no measurements or in areas where measurements are available but under different management scenarios. In general, a hydrochemical model is calibrated (adjusted to fit) with a set of observations, validated (tested for errors) with a set of reserved observations, and then applied to future or past conditions (forecasting or hindcasting, respectively) to predict watershed responses. From an environmental perspective, a hydrochemical model is a tool to investigate the effects of watershed management (e.g., changes of land use or land cover, human population, etc.) on the hydrology and chemistry of a stream or river.

Generally speaking, a hydrochemical model comprises three simulation submodels (compartments or blocks). Here we use "submodel" to represent a smaller unit or component of a hydrochemical model, and the three major submodels are generally responsible for computing (1) hydrology, (2) soil erosion, and (3) nutrient or metal geochemistry within the drainage basin.

The first submodel estimates the hydrology. This submodel partitions rainfall into physical evaporation, transpiration by plants, surface storage (puddles), overland flow during storms (runoff), and groundwater recharge because of infiltration during storms. Water storage in groundwater slowly flows to streams, creating stream flow (baseflow) between rain events, and overland flow during storms creates stormflow (see Fig. 1). Streamflow is the sum of storm and base flows and is usually integrated over a storm event or a fixed time period such as a day, month, or year.

The hydrology submodel is usually accompanied by an erosion submodel. This model component simulates the export of soil eroded by overland flow generated in the hydrology submodel. The rate of soil erosion is often based on the U.S. Department of Agriculture's universal soil loss equation (USLE), which uses basin characteristics such as vegetation cover, slope angle and length, cultivation practices, and soil properties such as particle size and density.

Additional geochemical submodels are responsible for the simulation of chemical constituents, which are nutrients such as N, P, or Si, or metals such as Fe, Al, Pb, and so on, from both natural and anthropogenic (manmade) sources. Within the geochemical submodel, these chemical constituents are transported with sediment or in the water flows that are simulated in the first submodel. Despite important differences between hydrochemical models, it is important to realize that the modeling principles developed in a variety of hydrochemical models are similar (2); i.e., the hydrology submodel is developed first and then followed by erosional and geochemical submodels.

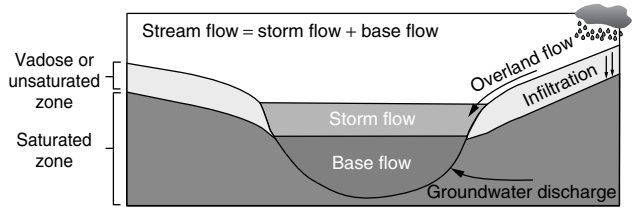


Figure 1. Simplified concept of the hydrological cycle used in hydrochemical models. Stream flow is the sum of storm flow and base flow, as used in GWLF (1) as well as in other models. However, some models may adopt different modeling approaches that differ from this illustration.

Numerous hydrochemical models are freely available. Many can be downloaded from websites or can be requested from the model developers. In Table 1, we list some commonly used hydrochemical models. Each hydrochemical model has its specific designs and limitations, such as model time step (minimum temporal resolution), number of parameters required (internal complexity), or input requirements. For detailed comparisons between these models, see Donigian and Huber (12). Because all models require at least some data input, many hydrochemical models have been ported from their original code (e.g., Fortran or Visual Basic) to more user-friendly windows applications for better visualization or to integrate with a geographic information system (GIS), which provides advanced computing power to manipulate data as subsequent input for the models (see 13–17).

PROPERTIES OF HYDROCHEMICAL MODELS

Hydrochemical models generally can be categorized as lumped-parameter and distributed models. A lumped-parameter model simplifies the watershed properties and ignores the spatial heterogeneity and distributions of these properties, using only the average watershed properties (see 18,19). Although a lumped-parameter model can efficiently generate simulation results, model users cannot spatially identify the locations where problems (e.g., nutrient or metal sources) occur. However, lumped-parameter models linked with a GIS may be applied in spatially contiguous polygons to provide some spatial resolution within a larger watershed (e.g., 15). Conversely, a distributed model can explicitly represent the spatial effects of topography or the spatial variations of properties within a watershed to locate sources; however, a distributed model requires more computer resources because of more intensive computation and more extensive data requirements.

As discussed earlier, a hydrochemical model can be designed either for long-term predictions or as an event simulation tool (or both). Time series of weather data (hourly or daily) are usually required for continuous simulation at hourly, daily, or monthly time steps. Models that predict at longer time steps ($\geq$ monthly; e.g., GWLF) do not resolve individual hydrographs (stream responses to individual storm events; see Fig. 2), whereas models used with shorter time steps (e.g., HSPF) attempt to predict both the timing and magnitude of a watershed's response to a rain event. The storm usually occurs over hours to days, whereas the watershed response is usually days to weeks, depending on the size of the watershed. Other models (e.g., ANSWERS and AGNPS—earlier versions) have

Table 1. Hydrochemical Models Commonly Used in Watershed Ecology. Models Typically Use a Lumped Parameter Approach, Where Average Watershed Properties Such as Soil Drainage or Land Cover are Used, Without Regard to Spatial Distribution, Whereas Distributed Models Require Information on the Spatial Distributions of Watershed Properties

Acronym	Full Name	Property	Type	Model Complexity	Reference
AGNPS*	Agricultural Nonpoint Source Pollution Model	Distributed	C, S	Moderate	Young et al. (3)
ANSWERS*	Areal Nonpoint Source Watershed Environment Response Simulation	Distributed	C (2000 version), S (older version)	Moderate	Beasley and Huggins (4)
CREAMS*	Chemical, Runoff, and Erosion from Agriculture Management Systems	Distributed	C, S	High	Knisel (5)
GWLF*	Generalized Watershed Loading Functions	Lumped	C	Simple	Haith & Shoemaker (1)
HSPF	Hydrological Simulation Program—Fortran	Lumped	C, S	High	Bicknell et al. (6)
SWAT*	Soil and Water Assessment Tool	Distributed	C	Moderate	Arnold et al. (7)
SWIM*	Soil and Water Integrated Model	Distributed	C	High	Krysanova et al. (8,9)
SWMM	Storm Water Management Model	Lumped	C, S	High	Huber & Dickinson (10)
SWRRB*	Simulator for Water Resources in Rural Basins	Distributed	C	High	Williams et al. (11)

* The SCS Curve Number method calculates surface runoff.
C: Continuous; S: Single Event.

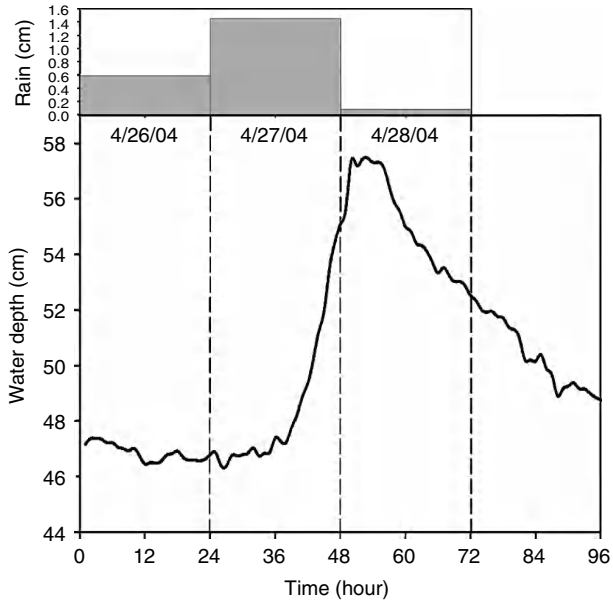


Figure 2. A hydrograph in response to a storm event that started to occur on 4/26/2004 at the Norwick Creek subwatershed of the Choptank River basin, Maryland. Note that precipitation (cm) was recorded on the daily basis (upper panel), whereas water depth (cm) at the watershed outlet was measured at a 30-min interval (lower panel). Data were compiled from Sutton (20).

been developed for the explicit purpose of predicting short-term hydrograph events such as the observations in Fig. 2.

PARAMETERIZATION OF THE HYDROCHEMICAL MODEL

A hydrochemical model generates a time series of predicted data for a time span defined by the user. To assess the accuracy and precision of the model's behavior, model output is compared on a daily, monthly, or annual basis with observed measurements. Comparisons between model output and model simulations are usually expressed in charts, bar graphs, or as tabular values to assess the model's accuracy (average ability to predict the observations without positive or negative bias, i.e., without underprediction or overprediction over a time interval) and precision (ability to reproduce the observations without scatter). These are often quantified as the cumulative model error over a given time period (model accuracy, e.g., ability to predict the observed annual stream flow for a given year) and root-mean-square (RMS) error at a given time scale (model precision, e.g., the deviations of modeled and observed stream flow at the defined time step). During calibration, model parameters are adjusted to minimize RMS or cumulative errors between the predicted and observed values, and the success of a calibration is then quantified by validation with an independent dataset not used during calibration.

The first comparison of a model's performance is called "Model Calibration." During this process, parameters are adjusted within reasonable ranges to minimize model errors. Model calibration often is a cyclical (21) and time-consuming process to adjust parameter values, although some optimization computer programs are available to automatically calibrate for the most suitable parameters. For example, HSPFEXP is an expert system that can be linked to HSPF to optimize the hydrology parameters (22). Monte Carlo methods (23) can perform statistical probability analyses to obtain the optimal values of variables. The parameter estimation software PEST (24) can also be linked to any existing model for parameter calibration. Despite different approaches to optimize the parameters, it is important to constrain the

ranges of model parameters within reported values (14) during model calibration.

The second comparison of model performance is called "Model Verification" or "Model Validation." This process uses the calibrated model parameters with a different set of meteorological data not used in model calibration. In this phase, a similar set of statistical analyses is generated that set the limits of interpretation of model predictions and to investigate the model's ability to simulate natural conditions (25). For example, if validation RMS errors at the daily time scale are ±100%, then only model predictions exceeding this threshold can be considered significantly different. Model verification ensures the validity of calibrated model parameters under the current conditions, and to confirm that the model can predict the stream hydrology and chemistry under different scenarios. Model validation errors are typically large at short time scales (hours-days) and become both more accurate and more precise at longer times scales (years-decades); i.e., it is easier to predict the cumulative discharge or material flux for a given year than it is to predict the daily flow or flux.

MODELING AND REALITY

In most cases, a well-calibrated hydrochemical model can predict water flows and chemistry in situations where no data exist. It is important, however, to remember that models sometimes do not predict well in some areas or under some conditions because model parameters may be difficult to measure (26) or because the model was developed under experimental conditions or with dominant processes that may not fully represent all other cases (27). In this case, a model's predicting performances are substantially affected by these factors when applied elsewhere. For example, AGNPS and ANSWERS are limited to watershed size <200 km^2, whereas SWRRB can be applied to much larger areas (9). In other words, model parameters are often designed for particular geographical areas or watershed sizes. The alpine hydrochemical model (AHM) was, for example, originally developed for the hydrologic and biogeochemical responses of seasonally snow-covered alpine areas (28), and SWMM was mainly designed to perform predictions in urbanized areas, although both can be used elsewhere.

To simplify the natural processes, hydrochemical models often possess unique assumptions. Assumptions may be based on field observations (29) and/or empirically derived functions to simplify the response processes. For example, the Soil Conversation Service (SCS) Curve Number (30) computes direct surface runoff merely based on land use and soil information, which has empirically simplified the estimation of other processes such as interception, depression storage, and infiltration (31). Because of its simplicity, the SCS CN method has been adopted to most hydrochemical models (marked * in Table 1). However, these processes may need to be parameterized for some models, such as HSPF and SWMM.

When rain infiltrates the soil, models often incorporate other empirical assumptions and simplifications borrowed from observations. For example, the soil column above the water table can be separated into two layers—unsaturated and saturated layers (e.g., GWLF). The disadvantage of this simplified approach is reduced model flexibility when applied to other areas. Conversely, SWIM (14) divides the root zone vertically into as many as 10 layers, which increases the model flexibility when applied elsewhere. However, these models require more model variables and intensive input data.

Furthermore, it is often seen that a fixed value is used for a variable throughout all modeling tasks. For example, both GWLF and SWMM use constant values for concentrations of groundwater chemical constituents (e.g., N and P) associated with each land use because both models assume that there are no geochemical interactions for the chemical constituents in the subsurface flow. Also models often assume that the observed chemical measurements in a stream or river have promptly responded to the geochemical reactions that occur in the soil or in the groundwater during a storm event, which is usually not true because groundwater may take years to decades to become the baseflow of streams, and important geochemical reactions may occur at this time scale (29).

Hence, hydrochemical models because of model assumptions and simplifications inevitably produce prediction errors. Those errors are intensified and transferred from the hydrology submodel to the subsequent submodels, which results in decreasing reliability in predictions (32). Therefore, it is important to understand the model assumptions and limitations, and to evaluate the strength and weakness of each hydrochemical model before use in each situation (33).

BIBLIOGRAPHY

1. Haith, D.A. and Shoemaker, L.L. (1987). Generalized watershed loading functions for stream flow nutrient. AWRA. *Water Resour. Bull.* **23**(3): 471–478.
2. Krysanova, V., Meiner, A., Roosaare, J., and Vasilyew, A. (1989). Simulation modeling of the coastal waters pollution from agricultural watershed. *Ecol. Modeling* **49**: 7–29.
3. Young, R.A., Onstad, C.A., Bosch, D.D., and Anderson, W.P. (1986). AGNPS: A nonpoint source pollution model for evaluating agricultural watersheds. *J. Soil Water Conservation.* **44**(2): 168–173.
4. Beasley, D.B. and Huggins, L.F. (1981). *ANSWERS Users Manual*. EPA-905/9-82-001, U.S. EPA, Region V, Chicago, IL.
5. Knisel, W. (1980). *CREAMS: A Field-Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems*. U.S. Department of Agriculture. Conservation Research Report No. 26.
6. Bicknell, B.R., Imhoff, J.C., Kittle, J.L., Jr., Donigian, A.S., Jr., and Johanson, R.C. (1993). *Hydrological Simulation Program—FORTRAN, User's Manual for Release 10*. EPA/600/R-93/174, U.S. Environmental Protection Agency, Office of Research and Development, Athens, GA.
7. Arnold, J.G., Williams, J.R., Srinivasan, R., King, K.W., and Griggs, R.H. (1994). *SWAT—Soil and Water Assessment Tool*. USDA, Agricultural Research Service, Grassland, Soil and Water Research Laboratory, Temple, TX.
8. Krysanova, V., Müller-Wohlfeil, D.I., and Becker, A. (1996). *Integrated Modeling of Hydrology and Water Quality in*

Mesoscale Watersheds. PIK Report, No. 18, July 1996, Potsdam Institute for Climate Impact Research (PIK), Posdam, Germany.

9. Krysanova, V., Müller-Wohlfeil, D.I., and Becker, A. (1998). Development and test of a spatially distributed hydrological/water quality model for mesoscale watersheds. *Ecol. Modeling* **106**: 261–289.
10. Huber, W.C. and Dickinson, R.E. (1988). *Storm Water Management Model*. Version 4, User's Manual, EPA/600/3-88/001a (NTIS PB88-236641/AS), U.S. EPA, Athens, GA.
11. Williams, R.R., Nicks, A.D., and Arnold, J.G. (1985). Simulator for water resources in rural basins. *ASCE Hydraulics J.*: 67–103.
12. Donigian, A.S. and Huber, W.C. (1993). *Modeling of Nonpoint Source Water Quality in Urban and Non-Urban Areas*. Environmental Research Laboratory, Office of Research and Development, U.S. EPA. EPA/600/3-91-039.
13. Needham, S.E. and Young, R.A. (1994). ANN-AGNPS: A Continuous Simulation Watershed Model. *Proceedings of the Federal Interagency Workshop on Hydrological Modeling Demands for the 90's*. U.S. Geological Survey Water-Resources Investigations Report 93–4018.
14. Krysanova, V. and Becker, A. (2000). Integrated modeling of hydrological processes and nutrient dynamics at the river basin scale. *Hydrobiologia* **410**: 131–138.
15. Lee K.-Y., Fisher, T.R., and Rochelle-Newall, E. (2001). Modeling the hydrochemistry of the Choptank River basin using GWLF and ArcInfo: 2. Model Validation and Application. *Biogeochemistry* **56**: 311–348.
16. USEPA. (2001). *Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) v. 3.0 User's Manual*. EPA-823/B01-001, Office of Water, USEPA, Washington, DC.
17. Evans, B.M. et al. (2002). A comprehensive GIS-based modeling approach for predicting nutrient loads in watersheds. *J. Spatial Hydrol.* **2**(2).
18. Lee, K.-Y., Fisher, T.R., Jordan, T.E., Correll, D.L., and Weller, D. (2000). Modeling the hydrochemistry of the Choptank River basin using GWLF and ArcInfo:1. Model calibration and validation. *Biogeochemistry* **49**: 143–172.
19. Helliwell, R.C. and Kernan, M. (2004). Modeling hydrochemical and ecological trends in acid sensitive surface waters in the Scottish Highlands. *J. Limnol.* **63**(1): 111–122.
20. Sutton, A.J. (2005). *Effectiveness of CREP: Reducing Nutrient Loads to Chesapeake Bay*. Ph.D. dissertation. University of Maryland, College Park, MD.
21. Love, J.T. and Donigian, A.S., Jr. (2002). *The Connecticut Watershed Model—Model Development, Calibration, and Validation*. WEF-Watershed 2002, February 23–27, 2002. Ft. Lauderdale, FL, WEF-2002 Specialty Conference Proceedings on CD-ROM.
22. Lumb, A.M., McCammon, R.B., and Kittle, J.L., Jr. (1994). *Users Manual for An Expert System (HSPEXP) for Calibration of the Hydrologic Simulation Program—Fortran*: U.S. Geological Survey Water-Resources Investigations Report 94–4168.
23. Niederreiter, H. and Spanier, J. (2000). Monte Carlo and Quasi-Monte Carlo Methods 1998. *Proceedings of a Conference held at the Claremont Graduate University, Claremont, California, June 22–26, 1998*, Springer-Verlag, Berlin.
24. Dorthy, J. (2004). *PEST, Model-Independent Parameter Estimation, User Manual*. 5th Edn. Watermark Numerical Computing, Brisbane, Australia.
25. Stone, A. and Seip, H.M. (1990). Are mathematical models useful for understanding water acidification? *Sci. Total Environ.* **96**: 159–174.
26. Hooper, R.P. (2001). Applying the scientific method to small catchment studies: A review of the Panola Mountain experience. *Hydrol. Processes* **15**: 2039–2050.
27. Beven, K. (1993). Prophecy reality and uncertainty in distributed hydrological modeling. *Adv. Water Resour.* **16**: 41–51.
28. Wolford, R.A. (1992). *Integrated Hydrochemical Modeling of an Alpine Watershed: Sierra Nevada, California*. Report 92-040, Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ.
29. Kirchner, W.J., Hooper, R.P., Kendall, C., Neal, C., and Leavesley, G. (1996). Testing and validating environmental models. *Sci. Total Environ.* **183**: 33–47.
30. Soil Conservation Service (SCS). (1975). *Urban Hydrology for Small Watersheds*. Tech. Rel. no. 55, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, DC.
31. Chow, V.T., Maidment, D.R., and Mays, L.W. (1988). *Applied Hydrology*. McGraw-Hill, New York.
32. Novotny, V. and Olem, H. (1994). *Water Quality: Prevention, Identification, and Management of Diffuse Pollution*. Van Norstrand Reinhold, New York.
33. Dunne,T. and Leopold, L.B. (1978). *Water in Environmental Planning*. W. H. Freeman and Company, San Francisco, CA.

MODELING NON-POINT SOURCE POLLUTANTS IN THE VADOSE ZONE USING GIS

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NON-POINT SOURCE POLLUTION: DEFINITION, SOURCES, SIGNIFICANCE, GLOBAL IMPACT, AND JUSTIFICATION FOR MODELING

Non-point source (NPS) pollutants are defined as "contaminants of [air, and] surface and subsurface soil and water resources that are diffuse in nature and cannot be traced to a point location" (1). Characteristically, NPS pollutants (1) are difficult or impossible to trace to a source; (2) enter the environment over an extensive area; (3) are related, at least in part, to certain uncontrollable meteorological events, and existing geographic and geomorphologic conditions; (4) have the potential for maintaining a relatively long active presence in the global ecosystem; and (5) may result in long-term, chronic effects on human health, and soil-aquatic degradation (2). The most common global NPS pollutants of soil and groundwater resources include biosolids and manure, persistent organic pollutants (POPs), nutrients (e.g., nitrates and phosphates), salinity, toxic heavy metals (e.g., Bi, Co, Sn, Te, Ag, Pt, Tl,

Sb, Hg, As, Cd, Pb, Cr, Ni), trace elements (e.g., Se, B, Mo, Cu, Zn), and pathogens.

Often, NPS pollutants occur naturally, such as salts and trace elements in soils, or are the consequence of direct application by humans (e.g., pesticides and fertilizers), but regardless of their source, they are generally the direct consequence of human activities including agriculture, urban runoff, feedlots, hydromodification, and resource extraction (2). Specific sources of NPS pollutants include (1) excess fertilizers, herbicides, and insecticides from agricultural lands and residential areas; (2) oil, grease, and toxic chemicals from urban runoff and energy production; (3) sediment from improperly managed construction sites, crop and forest lands, and eroding stream banks; (4) naturally occurring salts and trace elements from irrigation practices; (5) acid drainage from abandoned mines; (6) pathogens (i.e., viruses and bacteria) and nutrients from livestock, and pet wastes; and (7) atmospheric deposition (2).

The significance of NPS pollutants as an environmental issue stems from their potential global impact and resultant chronic effects on human health. Because of their widespread use and often persistent and mobile nature, NPS pollutants have the capacity not only to injure the surrounding environment and ourselves, but also remote environments and their inhabitants (like the Arctic) and future generations of humans through the buildup of persistent toxic substances that mimic and disrupt human hormone systems (3). The impact of NPS pollutants on soil and water resources extends over millions of hectares of land and billions of liters of water. Throughout the world, 30% to 50% of Earth's land is believed to be affected by NPS pollutant degradation from erosion, fertilizers, pesticides, organic manures, and sewage sludge (4). Worldwide, NPS pollutants are recognized as *the* major contributors to surface and groundwater contamination (5), with agriculture as the single greatest contributor of NPS pollutants (6). Agricultural activities result in the movement of NPS pollutants from the soil surface into rivers and streams via runoff and erosion, and into subsurface soil and groundwater via leaching through the vadose zone (i.e., the portion of the soil extending from the soil surface to the groundwater table). Figure 1 reflects the worldwide extent of human-induced degradation of soil by region and by cause over the period 1945 to the late 1980s.

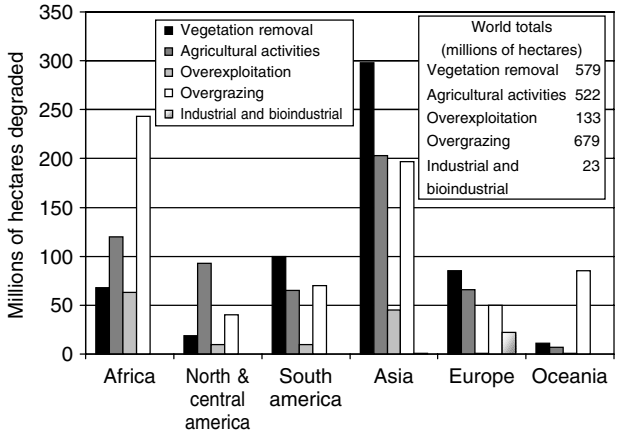


Figure 1. Human-induced soil degradation by region and by cause from 1945 to the late 1980s. *Source:* Ref. 7. With permission.

The world's population has doubled since 1950 and is expected to range from 8 to 12 billion in 2050. Barring unexpected technological breakthroughs, sustainable agriculture is viewed as the most viable means of meeting the food demands of the projected world's population. The concept of sustainable agriculture is predicated on a delicate balance of maximizing crop productivity and maintaining economic stability while minimizing the utilization of finite natural resources and the detrimental environmental impacts of associated NPS pollutants. Assessment of NPS pollutant impacts on soil-groundwater systems at local, regional, and global scales is a key component to achieving sustainable agriculture. Assessment provides the means (1) to establish the true extent of the NPS-pollution problem, (2) to evaluate mitigating management practices and regulatory policies, and (3) to predict future potential problems. The distinct advantage of prediction is that it can alter the occurrence of detrimental conditions before they occur. The reasons for modeling NPS pollutants in the vadose zone are (1) to increase the understanding of cause-and-effect relationships of spatiotemporal processes occurring in soil systems and (2) to provide a cost-effective means of synthesizing the current level of knowledge into a useable form for making environmental policy decisions (8,9).

MULTIDISCIPLINARY NATURE OF MODELING NPS POLLUTANTS IN THE VADOSE ZONE

Modeling NPS pollutants in the vadose zone is a complex environmental problem that requires a multidisciplinary, systems-based approach taken within a spatial context with an awareness of scale (10). The formidable barriers to modeling NPS pollutants are the consequence of the complexities of geographic scale and position; the complexities of the physical, chemical, and biological processes of solute transport in porous media; and the spatial complexities of the soil media's heterogeneity. The knowledge, information, and technology needed to address each of these issues crosses several subdisciplinary lines, including classic and spatial statistics, remote sensing, geographic information systems (GIS), surface and subsurface hydrology, soil science, and space science. Spatial statistics is useful in dealing with the uncertainty and variability of spatial information (11); remote sensing provides measurements of physical, chemical, and biological properties needed in environmental models (12); GIS is a means of organizing, manipulating, storing, and displaying spatial data (13); and water flow and solute transport models developed within soil science and hydrogeology are the tools for simulating future scenarios to assess potential temporal and spatial changes (2,14). Precise geographic location and areal extent are captured with the space science technology of the global positioning system (GPS).

COMPONENTS OF A NPS POLLUTANT MODEL

Modeling the fate and movement of NPS pollutants in the vadose zone is a spatial problem well suited

for the integration of a deterministic solute transport model with a GIS. A GIS characteristically provides a means of representing the real world through integrated layers of constituent spatial information. To model NPS pollution within the context of a GIS, each transport parameter or variable of the deterministic transport model is represented by a three-dimensional layer of spatial information. The three-dimensional spatial distribution of each transport parameter/variable must be simulated, measured, or estimated, which creates a tremendous volume of spatial information because of the complex spatial heterogeneity exhibited by the numerous physical, chemical, and biological processes involved in solute transport through the vadose zone. GIS serves as the tool for organizing, manipulating, and visually displaying this information efficiently.

The essential components of modeling NPS pollutants consist of (1) a *model* of solute transport and/or accumulation, (2) input and parameter *data* for the model, and (3) a *GIS* to handle the input, manipulation, and output of spatial data. Figure 2 shows the interaction among these three basic components based on flow of information.

Because of the complex spatial heterogeneity of the vadose zone, a variety of sophisticated techniques are useful as tools to deal with the vicissitudes of soil (Fig. 2). Fuzzy logic theory provides a means of handling vague and imprecise data whether as a means to characterize map units or transitional boundaries between map units (16,17). Fractal geometry with its scale independence may offer a means of bridging a variety of gaps related to spatial variability from determining the predictability of complex spatial phenomena such as solute transport to relating difficult-to-measure soil hydraulic properties to other soil variables available from soil surveys (18). Geostatistics is useful in interpolating sparse spatial data and providing associated uncertainty (19). Hierarchical theory establishes an organizational hierarchy of pedogenetic modeling approaches and their appropriate scale of application (20,21). Wavelet analysis provides a means of determining spatial scales and the dominant processes at those scales (22,23). Neural networks and transfer functions provide a means of deriving complex hydraulic parameters from easily measured data (24). Digital terrain or digital elevation models (DEM) provide spatial geomorphologic information. Uncertainty analysis serves as a means of establishing the reliability of simulated model results based on model errors and data uncertainties (25).

Data

The effectiveness of a model to simulate a practical application is highly dependent on how well model inputs and model parameters are identified. Basically, three sources of input and parameter data for NPS pollutant models exist (15): (1) measured data, (2) estimated data, and (3) existing data. Each source of data carries distinct advantages and limitations.

A review of current measurement techniques to determine flow-related properties of subsurface porous media and soil physical properties is provided by Dane and Molz (26) and Topp et al. (27), respectively. Although direct measurement of transport parameters and variables is the most reliable means of obtaining accurate information for modeling purposes, it is also the most labor intensive and costly. A quick and easy means of obtaining these measurements is crucial to the cost-effective modeling of NPS pollutants. Remote sensing and noninvasive measurement techniques have the greatest potential for meeting the thirst for measured spatial data.

Corwin (28) provided a cursory review of some instrumental techniques developed for the remote and noninvasive measurement of variables and parameters found in transport models for the vadose zone. The review covers geophysical resistivity methods, aerial photography, x-ray tomography, ground-penetrating radar, magnetic resonance imaging, microwaves, multispectral imagery, thermal infrared imagery, and advanced very-high-resolution radiometry (AVHRR). Barnes et al. (12) provided a more

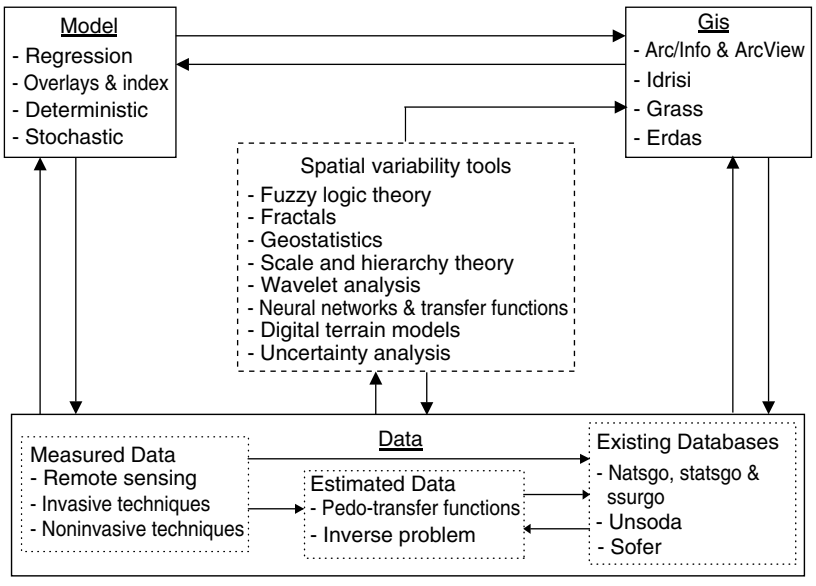


Figure 2. Integrated components of a GIS-based NPS pollutant model system. Arrows show the flow of information. Modified from Ref. 15. With permission.

recent review of remote- and ground-based sensor technology for mapping soil properties.

Even though considerable progress has been made over the past decade, the remote sensing instrumentation needed to measure *all* parameters and variables in even the simplest of transport models, for the vadose zone is not available or even on the drawing board. In most cases, remote sensing provides measurements of only the top few centimeters; consequently, it suffers from a lack *of depth information* needed in modeling the vadose zone. Noninvasive techniques such as electromagnetic induction (EMI) can provide information down to several meters in depth, but these techniques generally require measurements taken at or near the soil surface and their measurement volume is limited to tens of cubic meters or less. Nevertheless, geospatial measurements of apparent soil electrical conductivity (EC_a) with EMI is currently the most widespread and reliable means of characterizing the spatial variability of a variety of physicochemical properties in the vadose zone including salinity, texture, water content, cation exchange capacity (CEC), organic matter (OM), and bulk density (29). Furthermore, in most cases, the parameters measured by remote sensing and noninvasive techniques are often not directly applicable to solute transport models. For instance, the use of EMI to measure soil salinity is not a direct measure of salinity in the soil solution, but rather it measures EC_a, which includes the conductivity of both the solid and liquid phases, thereby requiring ground-truth soil samples for calibration.

The extreme spatiotemporal variability and the nonlinearity of many soil processes make parameterization of landscape-scale models a daunting task. The inability of remote measurement techniques to meet the demand for spatial and temporal parameter and input data has resulted in the development of transport parameter estimation techniques that estimate parameters by fitting data or are based on the formulation of transfer functions. Inverse modeling is a powerful and practical means of estimating flow and transport parameters for landscape-scale solute transport models using advanced optimization algorithms. Transfer functions relate readily-available and easy-to-measure soil properties to more complex transport variables/parameters needed for simulation.

Corwin et al. (15) provide a referenced list of the estimation methods for many common parameters in solute transport models of the vadose zone. The most common transfer function, the pedo-transfer function (PTF), uses particle-size distribution, bulk density, and soil organic-carbon content to yield soil-water retention or unsaturated hydraulic conductivity functions. Rawls et al. (30) provide a review of soil-water retention estimation methods. Reviews of methods of estimating soil hydraulic parameters for unsaturated soils have been written by van Genuchten et al. (31).

In most instances, limited resources do not permit the measurement or even estimation of needed input or parameter data. In these instances, the use of existing data is crucial. Existing soil databases for the United States include SSURGO (State Survey Geographical Database; http://www.ncg.nrcs.usda.gov/ssurgo.html), STATSGO (State Soil Geographical Database; http://www.ncg.nrcs.usda.gov/statsgo.html), and NATSGO (National Soil Geographical Database; http://www.ncg.nrcs.usda.gov/natsgo.html). SSURGO (map scale ranges from 1:12,000 to 1:63,360) is a county-level database, and it is the most detailed GIS database available from NRCS. STATSGO (map scale 1:250,000) is the state-level database designed for state, large watershed, and small river basin purposes. NATSGO (map scale 1:7,500,000) is the national soil database whose map units are defined by major land resource area (MLRA) and land resource region (LRR) boundaries.

The problem with the use of generalized rather than measured data has been associated uncertainties. Loague et al. (32) extensively reviewed the uncertainty associated with the use of an existing database for non-point source groundwater vulnerability and concluded that assessments based on this type of data are relegated to guiding data collection strategies rather than their intended purpose of groundwater vulnerability assessment. Measured input data that captures natural variability both in space and time is essential for diminishing uncertainty in simulations.

GIS

A GIS is defined by Goodchild (33) as a "general-purpose technology for handling geographic data in digital form with the following capabilities: (i) the ability to preprocess data from large stores into a form suitable for analysis (reformatting, change of projection, resampling, and generalization), (ii) direct support for analysis and modeling, and (iii) postprocessing of results (reformatting, tabulation, report generation, and mapping)." In the context of NPS pollutant modeling, a GIS is a tool that characterizes the full information content of the spatially variable data required by solute transport models. The advantages of GIS include (1) ease of data retrieval; (2) ability to discover and display information gained by testing interactions between phenomena; (3) ability to synthesize large amounts of data for spatial examination; (4) ability to make scale and projection changes, remove distortions, and perform coordinate rotation and translation; and (5) capability to discover and display spatial relationships through the application of empirical and statistical models (34). The principal benefit of coupling GIS to subsurface hydrologic models is to enable the models to deal with large volumes of spatial data that geographically anchor many environmental processes.

Model

A review of GIS-based NPS pollutant modeling in the vadose zone has been presented by Corwin et al. (15). To date, most models of NPS pollutants in the vadose zone have used deterministic models of solute transport coupled to a GIS (15,28). However, a growing recognition exists that stochastic approaches may offer the most viable means of modeling an NPS pollution (35).

The use of deterministic transport models with GIS has been justified on practical grounds based on availability,

usability, widespread acceptance, and the assumption that a heterogeneous medium macroscopically behaves like a homogeneous medium with properly determined parameters and variables. The philosophy of modeling NPS pollutants in the vadose zone with a one-dimensional deterministic model of solute transport is based on the representation of physical, chemical, and biological properties influencing transport in the vadose zone with a distributed parameter structure. The validity of the assumption that a heterogeneous medium macroscopically behaves like a homogeneous medium depends on whether spatial domains can be defined and characterized that behave as stream tubes or "representative element volumes" (REV).

Three categories of deterministic models have been coupled to GIS to simulate NPS pollution in the vadose zone: regression models, overlay and index models, and transient-state solute transport models (15). Regression models have generally used multiple linear regression techniques to relate various causative factors to the presence of an NPS pollutant. These causative factors have included soil properties or conditions related to groundwater vulnerability or to the accumulation of a solute in the soil root zone. Overlay and index models refer to those models that compute an index of NPS pollutant mobility from a simple functional model of steady-state solute transport. Two types of overlay and index models have been developed: property-based and process-based. Property-based index models are established on a hydrogeologic setting (e.g., DRASTIC) or NPS pollutant properties (e.g., GUS). Process-based index models are founded on the characterization of transport processes (e.g., Rao's attenuation factor model). Overlay and index models have been used largely to assess groundwater pollution vulnerability to pesticides and nitrates. Transient-state, process-based solute transport models include deterministic models capable of handling the movement of a pollutant in a dynamic flow system. Transient-state, process-based models describe some or all of the processes involved in solute transport in the vadose zone: water flow, solute transport, chemical reactions (adsorption-desorption, exchange, dissolution, precipitation, etc.), root growth, plant-water uptake, vapor phase flow, degradation, and dispersion/diffusion.

Jury (36) pointed out that the difficulty of constructing a three-dimensional model of chemical transport as a consequence of field variability has two significant implications: (1) Any hope of attempting to estimate a continuous spatial pattern of chemical transport must be abandoned; and (2) a possibility exists of extreme deviations from average movement so that significant concentrations of chemical may flow within relatively small fractions of the total cross-sectional area, which may be nearly impossible to detect from point measurements. The latter implication has fostered the development of stochastic solute transport models for the vadose zone as opposed to deterministic models.

Two distinct stochastic approaches are currently in use for dealing with the spatial variability encountered in modeling NPS pollutants in the vadose zone: geometric scaling and regionalized variables. Jury (36) indicates that geometric scaling uses specific "standardized variables to scale the differential equations describing transport and relates the standardized variables to some measurable or definable property of each local site of a heterogeneous field." Once the variables are defined, the onerous task of characterizing the variability is reduced to determining the statistical and spatial distribution of these scaling parameters. In contrast, Jury (36) explains that the regionalized variable approach regards the "various parameters relevant to a field-wide description of transport as random variables characterized by a mean value and a randomly fluctuating stochastic component."

In comparison with deterministic models, the coupling of a stochastic solute transport model to GIS is less explored. In a paper discussing the potential compatibility of stochastic transport models with GIS, Jury (35) suggested that stochastic-convective stream tube modeling seems the most compatible with GIS because it "utilizes a relatively simple local process driven by parameters that might be associated with soil morphological features, and could be integrated up to a large scale by simple arithmetic averaging over the local sites." A stochastic stream tube model is made up of parallel, noninteracting one-dimensional soil columns whose properties are locally homogeneous, but vary from one soil column to the next. The collection of all stream tubes constitutes the field-, basin-, or regional-scale area being represented. This approach is in essence the same approach that has been undertaken in the past where deterministic piston-flow local transport models have been coupled to soil survey information; only now there is an associated stochastic component of information. Jury (35) warns that the challenge of this approach will be "to develop a reasonable local-scale model whose parameters can be related to identifiable local-scale features."

CONSIDERATION OF SCALE WHEN MODELING NPS POLLUTANTS

Scale, as used in soil science and hydrology, refers to the "characteristic length in the spatial domain" and to the "characteristic time interval in the temporal domain" (37). So, even though space and time are continuous, only a discrete set of scales is of interest based on specific features that make them of particular use or interest (37). The existence of a hierarchy of scales has been postulated to relate to spatial or temporal features of systems of interest (see Fig. 3).

Temporal and spatial scales dictate the general type of model. The consideration of scale in model development requires observed information for the real system being modeled at the spatial and temporal scales of interest, which is to say that microscopic-scale models developed in the laboratory are not appropriate for macroscopic-scale applications, and vise versa.

Models of solute transport in the vadose zone exist at all scales. A hierarchical depiction of the scales from molecular to global showing the relationship between scale and model type is depicted in Fig. 3. An important consideration in model conceptualization is for the model to account for the predominant processes occurring at the

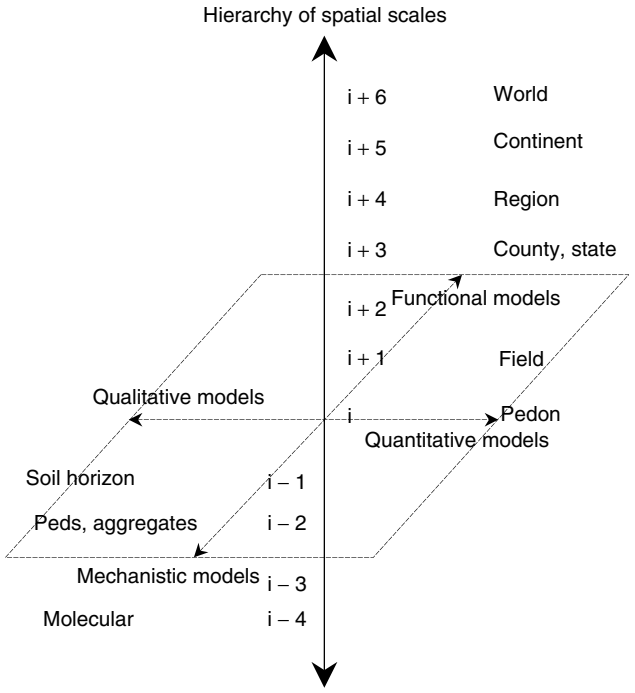


Figure 3. Organizational hierarchy of spatial scales pertinent to NPS pollutant models. *Source:* Ref. 21. With permission.

spatial and temporal scales of interest, which complies with the guideline of parsimony. Qualitatively speaking, as spatial scale increases, the complex local patterns of solute transport are attenuated and dominated by macroscale characteristics. For this reason, mechanistic models are used more frequently at the (i) to $(i - 4)$ scales, whereas functional models are more often applied to scales ranging from $(i + 1)$ to $(i + 6)$. The stochastic application of deterministic models is found at the $(i + 1)$ scale, and stochastic models generally are used at $(i + 1)$ and $(i + 2)$ scales. Statistical models are applied most often at the larger scales, $(i + 3)$ to $(i + 6)$.

The relevance of temporal domain is also a consideration not to be overlooked. Larger spatial scales appear more constant because the rapid dynamics of the lower scales are disregarded (20). For this reason, time steps of functional models can expand over days, such as the time between irrigation or precipitation events, whereas the time steps of mechanistic models characteristically extend over minutes.

The integration of solute transport models of the vadose zone into a GIS provides the ability to dynamically describe NPS pollutant transport at a range of spatial scales allowing the user to rapidly scale "up" and "down." However, this integration introduces incompatibilities between the model and data and raises basic questions regarding (1) the compatibility of the model with input and validation data, and (2) the relevance of the model to the applied spatial scale. Wagenet and Hutson (38) addressed the issue of scale dependency and proposed three scale-related factors to consider when applying GIS-based solute transport models to the simulation of NPS pollutants in soils: (1) the type of model (i.e., functional or mechanistic) must consider the scale of application, and the nature of the available data at that scale; (2) sampling and measurement of input and validation data must be spatially consistent with the model; and (3) measurement and monitoring methods must be relevant at the temporal domain being modeled.

FUTURE DIRECTION

Beven (39) asserts that the real constraint on predictability by landscape-scale environmental models is not the detail of the model structure, but rather the ability to spatially and temporally characterize the variability of model inputs and parameters. Among the various techniques for characterizing the spatial variability of model inputs (e.g., electromagnetic induction, ground penetrating radar, time domain reflectometry, remote imagery, etc.), electromagnetic induction will be the most useful in the short term (29), whereas greater future potential exists for hyperspectral imagery, which is in its infancy for soil and plant science applications.

BIBLIOGRAPHY

1. Corwin, D.L. and Wagenet, R.J. (1996). Applications of GIS to the modeling of non-point source pollutants in the vadose zone: A conference overview. *J. Environ. Qual.* **25**: 403–411.
2. Corwin, D.L. and Loague, K. (In press). Multidisciplinary approach for assessing subsurface non-point source pollution. In: *Soil-Water-Solute Processed in Environmental Systems: An Integrated Approach*. J. Alvarez-Benedi and R. Munoz-Carpena (Eds.). CRC-Press, Boca Raton, FL.
3. Duda, A. and Nawar, M. (1996). Implementing the World Bank's water resources management policy: A priority on toxic substances from nonpoint sources. *Water Sci. Technol.* **33**: 4–5, 45–51.
4. Pimental, D. (Ed.). (1993). *World Soil Erosion and Conservation*. Cambridge University Press, Cambridge, UK.
5. Duda, A.M. (1993). Addressing nonpoint sources of water pollution must become an international priority. *Water Sci. Technol.* **28**: 1–11.
6. Humenik, F.J., Smolen, M.D., and Dressing, S.A. (1987). Pollution from nonpoint sources: Where we are and where we should go. *Environ. Sci. Technol.* **21**: 8, 737–742.
7. World Resources Institute. (1998). *World Resources 1998–99: A Guide to the Global Environment*. Oxford University Press, New York.
8. Beven, K.J. (1989). Changing ideas in hydrology—the case of physically-based models. *J. Hydrol.* **105**: 157–172.
9. Grayson, R.B., Moore, I.D., and McMahon, T.A. (1992). Physically-based hydrologic modeling—II. Is the concept realistic? *Water Resour. Res.* **26**: 2659–2666.
10. Corwin, D.L., Loague, K., and Ellsworth, T.R. (1999). Advanced information technologies for assessing nonpoint source pollution in the vadose zone: Conference overview. *J. Environ. Qual.* **28**: 357–365.
11. Cressie, N.A.C. (1993). *Statistics for Spatial Data*. Wiley-Interscience, New York.
12. Barnes, E.M. et al. (2003). Remote- and ground-based sensor techniques to map soil properties. *Photogramm. Eng. Remote Sens.* **69**(6): 619–630.
13. Burrough, P.A. (1996). Opportunities and limitations of GIS-based modeling of solute transport at the regional scale. In:

Applications of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone. D.L. Corwin and K. Loague (Eds.). SSSA Special Publication No. 48, Soil Science Society of America, Madison, WI, pp. 19–38.

14. Skaggs, T.H. and Leij, F.J. (2002). Solute transport: Theoretical background. In: *Methods of Soil Analysis: Part 4—Physical Methods*. J.H. Dane and G.C. Topp (Eds.). SSSA Book Series No. 5, Soil Science Society of America, Madison, WI, pp. 1353–1380.
15. Corwin, D.L., Vaughan, P.J., and Loague, K. (1997). Modeling nonpoint source pollutants in the vadose zone with GIS. *Environ. Sci. Technol.* **31**: 8, 2157–2175.
16. Altman, D. (1994). Fuzzy set theoretic approaches for handling imprecision in spatial analysis. *Int. J. Geogr. Inf. Syst.* **8**(3): 271–289.
17. Zhu, A.-X. (1999). Fuzzy inference of soil patterns: Implications for watershed modeling. In: *Assessment of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin, K. Loague, and T.R. Ellsworth (Eds.). American Geophysical Union, Washington, DC, pp. 135–150.
18. Crawford, J.W., Baveye, P., Grindrod, P., and Rappoldt, C. (1999). Application of fractals to soil properties, landscape patterns, and solute transport in porous media. In: *Assessment of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin, K. Loague, and T.R. Ellsworth (Eds.). American Geophysical Union, Washington, DC, pp. 151–164.
19. Bourgault, G. et al. (1997). Geostatistical analysis of a soil salinity data set. *Adv. Agron.* **58**: 241–292.
20. O'Neill, R.V. (1988). Hierarchy theory and global change. In: *Scales and Global Change*. Rosswall et al. (Eds.). Scientific Committee on Problems of the Environment (SCOPE), John Wiley & Sons, New York, pp. 29–45.
21. Hoosbeek, M.R. and Bryant, R.B. (1993). Towards the quantitative modeling of pedogenesis: A review. *Geoderma* **55**: 183–210.
22. Lark, R.M. and Webster, R. (1999). Analysis and eleucidation of soil variation using wavelets. *Eur. J. Soil Sci.* **50**: 185–206.
23. Lark, R.M., Kaffka, S.R., and Corwin, D.L. (2003). Multiresolution analysis of data on electrical conductivity of soil using wavelets, *J. Hydrol.* 272, 276–290, 2003.
24. Wösten, J.H.M. and Tamari, S. (1999). Application of artificial neural networks for developing pedotransfer functions of soil hydraulic parameters. In: *Assessment of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin, K. Loague, and T.R. Ellsworth (Eds.). American Geophysical Union, Washington, DC, pp. 235–242.
25. Loague, K. and Corwin, D.L. (1996). Uncertainty in regional-scale assessments of non-point source pollutants. In: *Applications of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin and K. Loague (Eds.). SSSA Special Publication No. 48, Soil Science Society of America, Madison, WI, pp. 131–152.
26. Dane, J.H. and Molz, F.J. (1991). Physical measurements in subsurface hydrology. In: *Reviews of Geophysics*. Supplement, U.S. National Report to International Union of Geodesy and Geophysics 1987–1990, American Geophysical Union, Washington, DC, pp. 270–279.
27. Topp, G.C., Reynolds, W.D., and Green, R.E. (Eds.). (1992). *Advances in Measurement of Soil Physical Properties: Bringing Theory into Practice*. SSSA Special Publication No. 30, Soil Science Society of America, Madison, WI.
28. Corwin, D.L. (1996). GIS applications of deterministic solute transport models for regional-scale assessment of non-point source pollutants in the vadose zone. In: *Applications of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin and K. Loague (Eds.). SSSA Special Publication No. 48, Soil Science Society of America, Madison, WI, pp. 69–100.
29. Corwin, D.L. and Lesch, S.M. (In press). Apparent soil electrical conductivity measurements in agriculture. *Comput. Electron. Agric.*
30. Rawls, W.J., Gish, T.J., and Brakensiek, D.L. (1991). Estimating soil water retention from soil physical properties and characteristics. *Adv. Soil Sci.* **16**: 213–234.
31. van Genuchten, M.Th., Leij, F.J., and Lund, L.J. (Eds.). (1992). Indirect Methods for Estimating the Hydraulic Properties of Unsaturated Soils. *Proc. Int'l. Workshop, Riverside*, CA, Oct. 11–13, 1989, University of California, Riverside, CA.
32. Loague, K. et al. (1996). Uncertainty of groundwater vulnerability assessments for agricultural regions in Hawaii: A review. *J. Environ. Qual.* **25**(3): 475–490.
33. Goodchild, M.F. (1993). The state of GIS for environmental problem-solving. In: *Environmental Modeling with GIS*. M.F. Goodchild, B.O. Parks, and L.T. Steyaert (Eds.). Oxford University Press, New York, pp. 8–15.
34. Walsh, S.J. (1988). Geographic information systems: An instructional tool for earth science educators. *J. Geogr.* **87**(1): 17–25.
35. Jury, W.A. (1996). Stochastic solute transport modeling trends and their potential compatibility with GIS. In: *Application of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin and K. Loague (Eds.). SSSA Special Publication No. 48, Soil Science Society of America, Madison, WI, pp. 57–67.
36. Jury, W.A. (1986). Spatial variability of soil properties. In: *Vadose Zone Modeling of Organic Pollutants*. S.C. Hern and S.M. Melancon (Eds.). Lewis Publishers, Chelsea, MI, pp. 245–269.
37. Baveye, P. and Boast, C.W. (1999). Physical scales and spatial predictability of transport processes in the environment. In: *Assessment of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin, K. Loague, and T.R. Ellsworth (Eds.). *Geophysical Monograph* 108, American Geophysical Union, Washington, DC, pp. 261–280.
38. Wagenet, R.J. and Hutson, J.L. (1996). Scale-dependency of solute transport modeling/GIS applications. *J. Environ. Qual.* **25**(3): 499–510.
39. Beven, K.J. (2002). Towards an alternative blueprint for a physically-based digitally simulated hydrologic response modeling system. *Hydrol. Process.* **16**(2): 189–206.

MODELING TECHNIQUES FOR SOLUTE TRANSPORT IN GROUNDWATER

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INTRODUCTION

Groundwater constitutes an important component of water supply systems for domestic use, industry, and

agriculture. Due to increased use regularly above sustainable levels, groundwater quality often deteriorates. Contaminants in groundwater systems are introduced by hazardous industrial wastes, leachate from landfills, oil spills, agricultural activities, sites of radioactive waste repositories, and other sources. In most cases, the source of contamination is aboveground, and the contaminants pass through the unsaturated zone on their way to the saturated region.

The fundamental processes that govern solute mobility in groundwater have been studied and reasonably well understood for some time. Solute migration results from a variety of coupled physical, chemical, and biological processes. Owing to the complexities of natural soils and solute–soil–fluid interactions and frequently changing field conditions, modeling solute transport involves some degree of approximation. However, the modeling framework must retain the important aspects of real phenomena. It is also necessary for a reliable/realistic model to answer several relevant questions, such as, what is the purpose of the predictive calculations, what types of environments can be modeled, what level of precision is expected, and what are the advantages and disadvantages of the developed approach. To answer these questions while developing a model for solute movement in the subsurface, many issues must be considered. Table 1 presents some examples of such issues.

Soil is a porous medium, composed of solid and void sections (Fig. 1). The void portion that forms the *effective pore space* is made up of many interconnected channels through which fluid convection takes place. The usual way of modeling solute transport in soil has been to adopt a macroscopic approach where the flow variables are averaged over a *representative elementary volume* (REV) or *representative elementary area* (REA), depending on the dimensionality of the problem domain (1–3). The length scales of REV and REA are selected so that they represent soil heterogeneity. They are much larger than the pore scale but much smaller than the main physical domain. They are determined under the assumption that the solid matrix is distributed uniformly throughout the porous medium domain and is present in each REV or REA. Furthermore, it is assumed that the specific surface of the solid matrix is larger than that of the void portion in a REV or REA.

Convection of a solute in soil takes place due to fluid movement through its pores. As this transport occurs, in most cases, the carrier fluid is a multiphase/multifluid medium (a mixture) that can be miscible or immiscible. If two or more miscible fluids occupy the void space, even if they occupy different regions in the domain initially, they ultimately produce a multicomponent mixture due to gradients (e.g., diffusive and dispersive effects) prevailing over the fluid components. In the case of immiscible fluid flow, distinct layers are observed and interphase mass transfer among the fluid components takes place. Therefore, modeling immiscible multifluid convection of a solute requires more rigorous approaches. Models of single-phase flow can be considered a limiting case of multiphase flow phenomena. The main interest in a single-phase model lies in its simplicity and the methods developed for it which can be extended to multiphase transport mechanisms. Greenkorn (4) and Nield and Bejan (5) have given good descriptions of multicomponent, multiphase flow through porous media. Numerous other studies have also been devoted to modeling two-phase (the simplest multiphase case) or multiphase flow phenomena in soil/porous media (6–9).

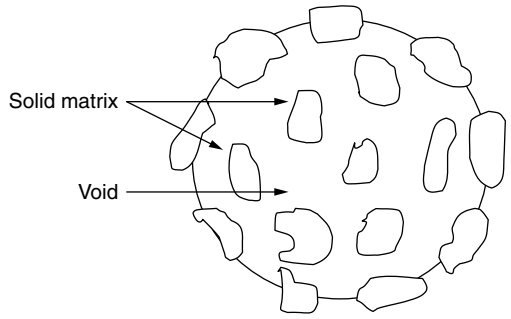


Figure 1. A representative elementary volume (REV) showing solid and void matrices in a porous medium.

Good management of water resources requires the ability to forecast the response of the managed system, for example, an aquifer, to planned operations such as pumping, recharging, and controlling conditions at aquifer boundaries. Any planning of mitigation, cleanup, or control measures requires forecasting the path and fate of contaminants in both the unsaturated and the saturated aquifer. The preferred tool for prediction is a numerical model that simulates the groundwater flow and pollutant movement and any chemical transformation. The construction of good models should be based on a thorough understanding of what happens within the modeled domain and on its boundaries, including chemical and biological processes. We need the ability to express this information as well-posed mathematical statements and, eventually, as a solvable numerical model. The model developed can be solved by employing a suitable numerical technique and appropriate computer programs. Many such programs for flow and solute transport in the subsurface are now available. This article introduces the fundamental concepts for modeling solute transport in groundwater systems. These are particularly useful for developing any remediation method for a contaminated subsurface.

SCALES OF OBSERVATION

Four spatial scales of observation have been suggested for describing solute transport phenomena in the subsurface:

1. The molecular scale, where materials are viewed as a discrete collection of molecules
2. The microscale or pore-scale, which describes solute behavior within a single pore in a porous medium
3. The macroscale or core-scale, where porous medium properties such as porosity, fluid phase saturation, and permeability can be described as continuous functions of space
4. The megascale, which is the scale of a system.

Table 1. Some Important Issues Involved in Solute Mobility in Groundwater Systems

S.N.	Issues	Details	Remarks
1.	Sources of pollutants/chemicals/solute in the ground	1. Hazardous and toxic waste disposal sites 2. Possible leaks in the compartments in ground used for storing toxic chemicals 3. Groundwater movement 4. Interphase mass transfer from air to soil 5. Dry deposition of contaminants from polluted air 6. Wet deposition on land 7. Accidental release of chemicals in the environment	Along with sources of pollutants, the amount of substance available in soil is equally important
2.	Properties of solute	1. Molecular structure 2. Vapor pressure 3. Water solubility 4. Absorption spectra 5. Particle size of particulate matter 6. Rate constants for its various reactions in the aquatic environment 7. Reactive or nonreactive 8. Life of the solute in the environment or its stability 9. Toxicological characteristics of the solute	
3.	Form of the pollutant in the environment	1. Dissolved in water 2. As suspension or colloid 3. As ions 4. As particulate matter	
4.	Direction of flow	1. One-dimensional (1-D) 2. Two-dimensional (2-D) 3. Three-dimensional (3-D)	In almost all cases, flow takes in a three-dimensional domain, but, for ease of modeling, a simpler geometry is often assumed
5.	Nature of transport mechanism	1. Saturated flow (single-phase flow) 2. Unsaturated flow (e.g., vadose zone) 3. Two-phase flow 4. Multiphase flow (more than two phases)	
6.	Soil type	1. Homogeneous soil 2. Heterogeneous soil (e.g., randomly heterogeneous, fractured media) 3. Layered soil and the no. of layers 4. Aggregated soil composed of large lumps	
7.	Soil characteristics	1. Porosity 2. Permeability 3. Dispersibility 4. Tortuosity 5. Density 6. Capillarity 7. Connectivity 8. Moisture content 9. Surface area 10. Depth 11. pH 12. Turbulence 13. Temperature 12. Absorption spectra 13. Proportion of diffusible ion	

Table 1. (*Continued*)

S.N.	Issues	Details	Remarks
8.	Transport and fate mechanisms in the soil	1. Diffusion: random motion of ions, atoms, molecules in all phases 2. Hydrodynamic dispersion: primarily from the complexities of the pore system 3. Adsorption: the passage of chemical species from one bulk phase to the surface of another where it accumulates without penetrating the structure of the second 4. Ion exchange 5. Hydrolysis 6. Photolysis 7. Volatilization 8. Microbial activity in the soil, e.g., anaerobic reaction 9. Relative velocity of a chemical with respect to moving water—sometimes the moving contaminants may be retarded with respect to moving water in soil for the following reasons: (a) ionic exchange reaction (b) precipitation and dissolution reaction (c) generation of insoluble complexes (d) formation of colloids followed by flocculants	
9.	Significance of groundwater	1. Inflow, outflow, downflow, and overflow of water from a control volume of soil 2. Infiltration and percolation of surface water 3. Level of groundwater table rises from rainfall 4. Groundwater draft from pumping of water 5. Carrying capacity of solute in groundwater	

To design soil and groundwater remediation techniques and to make reliable predictions about the efficiency of these techniques, it is necessary to identify and understand flow and transport processes on a smaller (e.g., pore scale) scale and to describe their manifestation on a larger scale (e.g., core scale). The connection of a smaller scale to a larger scale can be understood by a suitable upscaling technique. The choice of an appropriate upscaling method generally depends on the scale of observation because the relative importance of the dominant forces (e.g., capillary, viscous, and gravitational effects) may change with change in the averaging scale.

In principle, the mathematical model that describes the transport of an extensive quantity of a fluid or solid phase through a porous medium (mass balance equations for the transported quantities considered constitutive relations, initial conditions within the phase, and boundary conditions on the surface that bounds that phase) can be stated at every point within the phase considered. This description is said to be on the microscopic level, as we focus our attention on what happens at a (mathematical) point within the phase considered in the domain. Although the transport problem can be stated as a well-posed model, it is difficult to solve on this scale because the detailed geometry of the surface that bounds the phase is not known or is too complex. It is also very difficult to measure the values of variables at points within a phase to validate a flow or transport model and to determine the model parameters. As a consequence, the complete description and solution of a transport problem on a microscopic level is still unavailable.

To circumvent these difficulties, the transport problem is transformed from a microscopic to a macroscopic level, at which the problem is reformulated in terms of average values of the microscopic values. The average values are measurable quantities. We refer to this approach, employed in many branches of science, as the continuum approach.

SUBSURFACE HETEROGENEITY CHARACTERIZATION

The most typical features of groundwater systems are the spatial heterogeneity of the media and the temporal variability of the flow and transport properties. Moreover, these processes occur on multiple of scales. The mathematical descriptions of these processes on different scales are not necessarily similar. Scaling theories have

been developed that attempt to quantify the links among process descriptions on various scales. However, due to spatial heterogeneity and temporal variability and the high nonlinearity of hydrologic processes, developing appropriate scaling rules is not trivial. Sometimes, new governing equations and constitutive relations to describe the flow and transport processes in groundwater have to be identified. This may yield a number of upscaled parameters in the governing equations that may have to be measured directly or indirectly. These parameters are either new, meaning they exist on only the larger scale or are averages of small-scale parameters. Questions that may arise in this regard are (1) how can parameter values measured on a small scale (e.g., laboratory experiments) be translated to effective values on a larger scale? (2) how can effective parameters of the larger scale be measured directly? (3) how can small-scale heterogeneities be accounted for in large-scale descriptions of hydrologic systems? (4) how can the large-scale behavior of a system be downscaled to its behavior on a smaller scale?

During the last 60 years, some methods have been developed to describe spatial heterogeneities in the subsurface. These methods cannot generate actual heterogeneity patterns, but they provide a theoretical basis for understanding the effects of heterogeneities and any coupled processes therein on flow and transport processes. Three types of methods have evolved:

1. descriptive methods
2. process-based methods
3. stochastic methods

Each method has its own limitations in theory and application. The descriptive method is limited mostly to large-scale solute transport problems. It cannot describe local variations in hydraulic permeability (K) and is not transferable to deterministic numerical models for flow and transport calculations. Process-based models cannot recreate the depositional faces or the experimental values of hydraulic permeability (K) at observation points. This method also requires data that are often not available, for example, sedimentation and erosion rates, and turbidity factors. Further, process-based models are computationally inefficient in computer time and storage and are highly sensitive to initial and boundary conditions. Interpretation and validation of results are therefore very subjective. Stochastic models are based on the principles of geostatistics and work well in theory. For example, they honor known data and their locations and patterns of spatial variability. Data for these models can be obtained from boreholes, soil survey maps, or any other sampling methods. However, they require an enormous amount of observational data for calculating the spatial statistics of the K distribution, and these data are generally lacking, especially in lateral directions. Therefore, one question that frequently arises in using stochastic models is, how can we estimate spatial variability in three directions from vertical data sets? Therefore, even with available methods, it is still difficult to create a reliable 3-D model that honors the important heterogeneous features at a given location.

An alternative to these approaches for characterizing heterogeneity is to use a Markov-chain approach. This is a hybrid method of deterministic and stochastic models. The earliest attempt to apply Markov chains was used to synthesize stratigraphic sequences in the vertical direction (10). However, the approach was not directed toward extension to multidimensions, and it was not used in real field situations for a long time. Later, a methodology (11) for characterizing subsurface heterogeneity based on a two-dimensional extension of the original one-dimensional Markov chain theory was developed. This model, called the coupled Markov-chain (CMC) model (11), couples two chains for 2-D problems and three chains for 3-D problems. For example, for a 2-D problem, the first chain describes the sequence in lithologies in the vertical direction, and the second chain describes the sequences of variation in the lithological structure in the horizontal direction. The two chains are coupled in the sense that a state of a cell in the domain is dependent on the state of two cells, the one on top and the other on the left of the current cell. This dependence is described in terms of transition probabilities from the two chains. The CMC is a general technique that can produce a variety of heterogeneous patterns that can be stationary or nonstationary in statistical sense.

GOVERNING MODEL EQUATIONS

The equations governing fluid flow and solute transport in groundwater are based on the principles of mass, momentum, and energy conservation. They can be expressed in two different formulations based on the dependent variables used: first, vorticity stream-function equations that are derived by incorporating the definitions of vorticity and stream-functions; second, primitive variable formulations that are expressed in terms of pressure and velocity or mass and momentum of the fluid particles. Furthermore, the governing equations of the fluid flows can be classified mathematically as elliptic, hyperbolic, or parabolic equations. Based on the physical problem under consideration, these model equations can be solved either in rectangular or curvilinear coordinate frameworks.

The use of the vorticity stream-function formulation is most commonly found in one- and two-dimensional cases. Although it is possible to extend vorticity-stream functions to 3-D domains, they give rise to many complications and are not often recommended (12).

Primitive variable formulations can be expressed in either conservative or nonconservative forms, which in turn can be dimensional or nondimensional. The conservative forms of equations derived are based on the assumption that the fluid model is fixed in space. Hence, new fluid particles interact across the domain boundaries as the fluid flows in and out. For nonconservative forms, the observer is assumed to move with the frame of the fluid particles. In other words, the equations are formulated based on a moving coordinate system. Therefore, for a nonconservative system, there is no interaction of fluid elements across boundaries. For a complete discussion

of conservative and nonconservative forms of equations, readers are referred to Anderson (13).

Governing equations can also be expressed in either Eulerian or Lagrangian forms. These two formulations are similar to conservative and nonconservative equations, respectively, because they assume that the fluid model is either fixed in space or moving with the flowing fluid. However, as Abbott and Basco (14) have described, important differences exist between Eulerian and conservative forms. Similar differences are also applicable to nonconservative and Lagrangian formulations. An important characteristic of Eulerian equations is that the accelerations of fluid particles form substantial or total derivatives of each velocity component. They are expressed in terms of continuous spatial velocities and pressures. Therefore, when the flow variables are discontinuous, this formulation suffers serious drawbacks. Conservative approaches remove such limitations because they are formulated by assuming mass and momentum of the fluid particles as the dependent variables and as functions of space and time. They are represented as integral forms. This makes any discontinuity of the flow variables irrelevant in the computational domain. Conservative approaches, therefore, provide a more general way of formulating fluid flow phenomena.

The primary issue that comes up in formulating groundwater flow problems is selection of proper mathematical forms for the governing equations. Solute transport in porous domains can be represented by the convective dispersion equation (Eq. 1). The velocity profiles can be obtained by solving a suitable flow equation, for example, the Darcy or Brinkman equation. Equation 1 does not include any source/sink terms, which might become evident if there are any reactions in subsurface flow problems.

Solute Transport Equation

$$\text{Convective dispersion equation: } \frac{\partial C}{\partial t} + \overline{\nabla}.(C\mathrm{v}) = \overline{\nabla}.(D\overline{\nabla}\overline{v}) \tag{1}$$

D in Eq. 1 is the dispersion coefficient tensor and can be represented as

$$D = \begin{bmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{bmatrix} \tag{2}$$

where D_{xx}, D_{yy}, and D_{zz} are the principal components of the dispersion coefficient tensor in the x, y, and z directions.

Flow Equations

Various linear and nonlinear relationships describe flow behavior in the subsurface (5). The two most popular flow equations are the Darcy (Eq. 3) and the Brinkman (Eq. 4) equations.

Assuming that the fluid is incompressible and neglecting any body forces, the governing momentum balance equations can be written as

$$\text{Darcy's equation: } \overline{\nabla}P = -\frac{\mu}{\overline{\overline{K}}}\overline{v} \tag{3}$$

$$\text{Brinkman equation: } \overline{\nabla}P = -\frac{\mu}{\overline{\overline{K}}}\overline{v} + \mu'\overline{\nabla}^2\overline{v} \tag{4}$$

K in Eqs. 3 and 4 represents anisotropic soil permeability and is a second-order tensor that can be represented as

$$K = \begin{bmatrix} K_{xx} & 0 & 0 \\ 0 & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{bmatrix} \tag{5}$$

where K_{xx}, K_{yy}, and K_{zz} are the principal components of the permeability tensor in the x, y, and z directions. Hence, the diagonal form of the anisotropic permeability is a special case which occurs when the coordinate axes coincide with the normal axes of K. In general, these components are functions of the fluid and material properties. Due to the varying range of particle sizes and shapes and complex fluid–solid interactions in field conditions, there is a lack of theoretical corelations for estimating the permeability in the subsurface.

If the soil is isotropic, then,

$$K_{xx} = K_{yy} = K_{zz}$$

Equations 3 and 4 are coupled with the continuity equation (Eq. 6), and then solved to determine the unknown field variables, velocities and pressures.

For an incompressible fluid and nondeformable porous medium, the continuity equation for conservation of mass can be written as

$$\text{Continuity equation: } \overline{\nabla}.\overline{v} = 0 \tag{6}$$

NUMERICAL TECHNIQUES FOR SOLVING GOVERNING MODEL EQUATIONS

There are mainly five different numerical approaches for modeling solute transport problems in groundwater: the finite-difference, finite-element, finite-volume, boundary-element, and spectral-expansion. They have been employed for solving many different complex fluid problems with reasonably good success (15–19). Each method was developed to handle a specific problem, to eliminate the limitations of an existing technique, or simply, as a variant form. For example, the finite-element method was developed mainly because of its ability to cope with complex geometry. Similarly, the spectral method was developed as a variant of the finite-element method (15) to enhance the accuracy of solutions. The techniques have their own advantages and disadvantages, and many similarities and dissimilarities exist among their concepts and procedures. Comparison among these methods has been made by Hirsch (16), Versteeg and Malalasekera (17), Comini et al. (18) and Garg (19), among many other authors. The choice of the technique to be used in modeling depends on all these criteria, apart from its applicability to the particular problem.

Finite-Difference Method

The procedure for deriving finite-difference equations consists of approximating the derivatives in the differential equations via a truncated Taylor series expansion. Let us consider the grid points shown in Fig. 2. For grid point

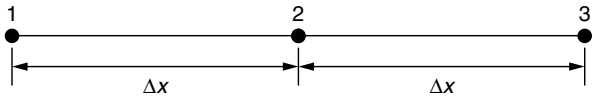


Figure 2. Computational grid for a Taylor series expansion.

2, located midway between grid points 1 and 3 such that $\Delta x = x_2 - x_1 = x_3 - x_2$, the Taylor series expansion gives

$$\varphi_1 = \varphi_2 - \Delta x \left(\frac{d\varphi}{dx}\right)_2 + \frac{1}{2}(\Delta x)^2 \left(\frac{d^2\varphi}{dx^2}\right)_2 - \dots \quad (7)$$

$$\varphi_3 = \varphi_2 + \Delta x \left(\frac{d\varphi}{dx}\right)_2 + \frac{1}{2}(\Delta x)^2 \left(\frac{d^2\varphi}{dx^2}\right)_2 + \dots \quad (8)$$

Truncating the series just after the third term and adding and subtracting the two equations, we obtain

$$\left(\frac{d\varphi}{dx}\right)_2 = \frac{\varphi_3 - \varphi_1}{2\Delta x} \quad (9)$$

$$\left(\frac{d^2\varphi}{dx^2}\right)_2 = \frac{\varphi_1 + \varphi_3 - 2\varphi_2}{(\Delta x)^2} \quad (10)$$

Substituting such expressions in the differential equations leads to a finite-difference equation, which can be cast in matrix notation and then solved using matrix solvers. For advanced literature on finite-difference methods, readers may refer to (20–23).

Finite-Element Method

This method is based on the principles of variational calculus. The differential equation to be solved can be represented as

$$L(\varphi) = 0 \quad (11)$$

Further, we assume an approximate solution for the dependent variable $\overline{\varphi}$ that contains a number of undetermined parameters, such as $a_0, a_1, a_2, \dots, a_m$:

$$\overline{\varphi} = a_0 + a_1 x + a_2 x^2 + \dots + a_m x^m \quad (12)$$

Substituting $\overline{\varphi}$ into the differential equation leaves a residual R, defined as

$$R = L(\overline{\varphi}) \quad (13)$$

We wish to make this residual small over the entire computational domain, and hence it can be proposed that

$$\int WR\, dx = 0 \quad (14)$$

where W is a weighting function and the integration is performed over the computational domain. By choosing a succession of weighting functions, we can generate as many equations as are required for evaluating the parameters. For simple regular grids, the equations derived by using the finite-difference and finite-element methods are identical. The computational meshes are generally more refined in the areas of rapid change of dependent variables. For complex problems, the finite-element method has several advantages. First, the boundary conditions are handled naturally by this method in contrast to the finite-difference method, where special formulas must be developed for the boundaries in many instances. Second, inhomogeneities and anisotropies can be taken into account easily. Moreover, the size and shape of the elements can be varied readily, and for curved geometries, the concept of isoparametric mapping can be employed to yield robust solutions. This method, developed by Zienkiewicz (24–27), was applied to structural engineering problems, and later on, was extended to subsurface hydrology.

Finite-Volume Method

The primary steps involved in the finite-volume method are grid generation to divide the domain into discrete control volumes. The governing equations are then integrated over the control volume to yield a set of discretized equation at nodal points. The integral form of the equations allows for discontinuities inside the fixed volume unlike the differential forms of governing equations, which assume that the flow properties are differentiable, hence continuous. This consideration becomes useful when dealing with flow problems that have real discontinuities encountered in subsurface flow. For a detailed text on the finite-volume method, refer to (17).

Boundary-Element Method

The boundary-element method is derived by discretizing an integral equation defined on the boundary of the domain and relates the boundary solution to the solution at points in the domain. The integral equation is commonly referred as the boundary integral equation (BIE) and the method as the boundary-element method (BEM). An integral equation formulated on the boundary can be derived only for certain classes of PDEs. Hence, the BEM is not widely applicable compared to the finite-element and finite-difference methods. The advantages of the boundary-element method are that only the boundary of the domain needs to be discretized. The dimension of the problem is effectively reduced. For example, an equation governing a three-dimensional region is transformed into one over its surface. When the domain is exterior to the boundary, as in potential flow past an obstacle, the extent of the domain is infinite, and the equation governing the infinite domain is reduced to an equation over the boundary. Thus it results in a numerical method that is easier to use and more computationally efficient than the competing methods. One can refer to (28) and (29) for detailed information on the BEM.

Spectral Expansion Method

Spectral methods are algorithms for solving certain classes of PDEs using the fast Fourier transform. Finite-difference, finite-element, and spectral methods can be distinguished on the basis of weighting functions used in the mathematical formulations. In the finite-difference method, the trial functions are polynomials of low order; in the finite-element method, they are local smooth

functions (i.e., polynomials of fixed/higher order), whereas in spectral methods, they are global smooth functions such as Fourier series expansions. All spectral methods are based on the complete family of global smooth functions. Detailed discussions on the development of various spectral expansion techniques based on selecting different weighting functions can be found in (30–32).

CONCLUSIONS

The study of solute transport in groundwater systems is a multidisciplinary subject because it integrates the principles of engineering, pure science subjects, for example, applied mathematics, chemistry and physics and, other life science subjects, for example, biology. The physical, chemical, and biological mechanisms that govern solute transport in the subsurface interact in a highly complex manner, and elucidating the important or dominant control mechanisms that govern transport processes can be highly nonintuitive. On the other hand, without thorough knowledge of the governing processes and their interactions, accurate prediction and control of solute migration is severely restricted. For this reason, many experiments on both laboratory and field scales have been attempted. The knowledge gained from such experiments (benefits) is clearly evident in the scientific literature now. However, it is also pivotal to place experimental work within a consistent and coherent theoretical framework to interpret the results obtained and direct further experimental work appropriately. By examining a system in terms of suitable equations with well-defined parameters, a mathematical model can help to provide a route to such a framework.

In the text presented, the important concepts related to modeling solute migration in groundwater systems have been presented. We have discussed the various scales of observation over which solute migration may take place. The ways to characterize the ubiquitous media heterogeneities in the subsurface have been briefly mentioned. Basic equations that govern solute transport behavior in the subsurface and numerical methods to solve them have been presented. These are far from exhaustive analyses. However, it is envisaged that the text gives an overview of various basic underlying concepts for modeling solute transport in groundwater.

NOMENCLATURE

C	Solute concentration
D	Dispersion coefficient tensor
D_{xx}	x component of the dispersion coefficient tensor
D_{yy}	y component of the dispersion coefficient tensor
D_{zz}	z component of the dispersion coefficient tensor
K	Permeability tensor
K_{xx}	x component of the permeability tensor
K_{yy}	y component of the permeability tensor
K_{zz}	z component of the permeability tensor
P	Pressure
t	Dimensional time
v	Velocity vector
xx	x coordinate
yy	y coordintate
zz	z coordinate
Φ	Variable
μ	Fluid viscosity
μ'	Effective fluid viscosity

BIBLIOGRAPHY

1. Chinanzvavana, S., Grosshandler, W.L., and Davis, D.C. (1986). *Trans. ASAE* **29**(6): 1797–1801.
2. Jo, J.C., Shin, W.K., and Choi, C.Y. (1999). *Numerical Heat Transfer Part B* **36**: 95–113.
3. Kazmierczak, M., Poulikakos, D., and Pop, I. (1986). *Numerical Heat Transfer* **10**: 517–571.
4. Greenkorn, R.A. (1983). *Flow Phenomena in Porous Media*. Marcel Dekker, New York.
5. Nield, D.A. and Bejan, A. (1992). *Convection in Porous Media*. New York
6. Slattery, J.C. (1970). *AIChE J.* **16**(3): 345–352.
7. Madsen, J.H. and Jensen, K.H. (1992). *J. Hydrol.* **135**: 13–52.
8. Butts, M.B. and Jensen, K.H. (1996). *J. Hydrol.* **183**: 101–116.
9. Wang, C.Y. (1997). *Numerical Heat Transfer Part B* **31**: 85–105.
10. Krumbein, W.C. (1967). *Fortran computer programs for Markov chain experiments in geology: Computer contribution 13*. Kansas Geological Survey, Lawrence, KS.
11. Elfeki, A.E., Dekking, F.M., Bruining, J., and Kraaikamp, C. (2002). Influence of fine-scale heterogeneity patterns on large-scale behaviour of miscible transport in porous media. *Pet. Geoscience* **8**: 159–165.
12. Hoffman, K.A. and Chiang, S.T. (1993). *Computational Fluid Dynamics for Engineers*. Engineering Education System, Wichita, KS, Vols. I and II.
13. Anderson, J.D., Jr. (1995). *Computational Fluid Dynamics: The Basics with Applications*. McGraw-Hill, New York.
14. Abbott, M.B. and Basco, D.R. (1989). *Computational Fluid Dynamics—An Introduction for Engineers*. Longman Group, Harlow, UK.
15. Peyrot, R. and Taylor, T.D. (1983). *Computational Methods for Fluid Flow*. Springer, Berlin.
16. Hirsch, C. (1990). Numerical computation of internal and external flows. Vol. 2. *Computational Methods for Inviscid and Viscous Flows*. John Wiley, Chichester, UK.
17. Versteeg, H.K. and Malalasekera, W. (1995). *An Introduction to Computational Fluid Dynamics: The Finite Volume Method*. Wesley Longman, Essex, UK.
18. Comini, G., Malisan, M., and Manzan, M. (1996). *Numerical Heat Transfer Part B* **29**: 43–60.
19. Garg, V.K. (1998). *Applied Computational Fluid Dynamics*. Marcel Dekker, New York.
20. Shaw, F.S. and Southwell, R.V. (1941). *Proc. R. Soc.* **A178**: 1–17.
21. Forsythe, G.E. and Wasow, W.R. (1960). *Finite Difference Methods for Partial Differential Equations*. John Wiley & Sons, New York.
22. Richtmeyer, R.D. and Morton, K.W. (1967). *Difference Methods for Initial Value Problems*. Wiley-Interscience, New York.
23. Saulyev, V.K. (1964). *Integration of Equations of Parabolic Type by the Method of Nets*. G.J.Tee (Trans). Macmillan, New York.

24. Zienkiewicz, O.C. and Cheung, Y.K. (1967). *The Finite Element Method in Structural and Continuum Mechanics*. McGraw-Hill, London.
25. Zienkiewicz, O.C. and Taylor, R.L. (1997). *The Finite Element Method: The Basis*. Vol. 1. Butterworth Heinemann, Oxford.
26. Zienkiewicz, O.C. and Taylor, R.L. (1998). *The Finite Element Method: Solid Mechanics*. Vol. 2. Butterworth Heinemann, Oxford.
27. Zienkiewicz, O.C. and Taylor, R.L., (2000). *The Finite Element Method: Fluid Dynamics*. Vol. 3. Butterworth Heinemann, Oxford.
28. Chen, G. and Zhou, J. (1992). *Boundary Element Methods*. Academic Press, San Diego, CA.
29. Hall, W.S. (1994). *The Boundary Element Method*. Kluwer Academic, Dordrecht, the Netherlands.
30. Gottlieb, D. and Orszag, S.A. (1977). *Numerical Analysis of Spectral Methods*. Society for Industrial and Applied Mathematics, Philadelphia, PA.
31. Canuto, C., Hussaini, M.Y., Quarteroni, A., and Zang, T.A. (1988). *Spectral Methods in Fluid Dynamics*. Springer-Verlag, Berlin.
32. Mercier, B. (1989). *An Introduction to the Numerical Analysis of Spectral Methods*. Springer-Verlag, Berlin.

AMBIENT GROUNDWATER MONITORING NETWORK STRATEGIES AND DESIGN

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WHY CREATE AN AMBIENT GROUNDWATER NETWORK?

Expanding populations and associated development are creating greater water demands worldwide. Groundwater is increasingly being used to meet these needs because surface water sources are often over-appropriated, heavily polluted, or are preserved for their ecological benefits. With significant future groundwater withdrawal increases, the long-term sustainability of groundwater resources is a vital issue. Yet even where there appears to be sufficient groundwater supplies to provide for irrigation, municipal, domestic, livestock, industrial, and/or mining purposes, the quality of this resource may limit the applications for which it can be used.

Groundwater quality can be negatively impacted by a variety of physical features and cultural activities that are not always easily discerned by empirical observations. The detection and continued monitoring of groundwater quality constituents and contaminants requires expensive field sampling operations and laboratory analyses. Once deterioration of groundwater quality begins, it may be difficult to reverse, and treating the impacted water can be prohibitively expensive.

Assessing groundwater is a challenging endeavor as the resource resides beneath the land surface, available only for examination at limited sites where wells or springs are located. It is a complex, large-scale, three-dimensional resource that has a high degree of spatial variability (3). To meet these challenges are the benefits supplied by ambient groundwater monitoring, characterization, and assessment networks that address these groundwater quantity and quality concerns. The term "ambient" refers to broad-scale or basinwide conditions not associated with a specific point source, facility, or property. The term "monitoring" refers to point measurement of water level or water quality conditions of groundwater sites, and "characterization" is the description and interpretation of the hydrogeologic setting where the groundwater occurs. Finally, the term "assessment" is used to describe efforts that combine both characterization and monitoring (3).

An ambient network is a proactive strategy that uses groundwater monitoring and characterization along with scientific methods and hydrologic models to assess holistically the groundwater of a given area, usually a defined hydrologic basin. Ambient networks are designed to identify regional changes in groundwater levels and/or degradation of groundwater quality such as occurs from widespread nonpoint sources of pollution or a high density of point sources. Information gleaned from an ambient network includes determining where groundwater levels are fluctuating, locating areas of poor water quality, and identifying spatial and temporal water quality patterns. When correctly designed, the data collected in ambient monitoring programs can be statistically analyzed to make broad statements about the groundwater of a basin that have a known degree of confidence using a relatively small number of investigated sites. Several states such as Arizona and Idaho (1) have redesigned their ambient networks to reflect a statistical, rather than subjective, selection of sites. Others such as Minnesota (2) initiated new ambient networks because the previous design failed to meet objectives.

Although planning and implementing ambient networks is not inexpensive, their costs may be considered relatively minor compared to the hydrologic information they can provide when properly designed and executed. On a regional scale, such networks can determine whether aquifers are in hydrologic equilibrium at current pumping levels, which areas should not be used for municipal or domestic uses without treatment, and whether groundwater quality is being impacted over time by anthropogenic activities. On a more localized scale, networks provide valuable background groundwater level and quality information for site-specific hydrologic studies and projects that may involve remediating contaminated sites or siting production wells. Finally, networks will assist in various surface water investigations because discharges from groundwater systems often sustain river base flow and often directly influence the quality of riparian and wetland ecosystems (3).

OVERVIEW

At their zenith, ambient groundwater networks balance sometime divergent entities such as science and art, theoretical statistical considerations and pragmatic field decisions, and precise analytical laboratory tests and empirical field observations, to assess best the groundwater of a specified area. These networks provide a structured yet flexible framework from which to survey a large basin which, if

desired, then can transit into smaller, localized networks to examine groundwater concerns in more specific areas.

CONCEPTUAL STRATEGIES AND DESIGNS—GENERAL OVERVIEW

When creating an ambient groundwater network, attention should focus on adhering to the general principles of probability sampling, so that inferences can then be made about the total population from data collected on the sampled population (4). Thus, statements of the network's goals and methods and which randomized site selection will be used, should be included in the planning. Four different strategies for creating an ambient network are detailed: simple random monitoring, stratified random monitoring, random monitoring within grid cells, and transect monitoring. Each strategy has various strengths and weaknesses but each method should be considered a tool to focus objectives of the study and to minimize potential sources of error rather than to dictate rigid rules blindly (4).

Simple Random monitoring

The easiest method of implementing an ambient groundwater monitoring network is simple random selection of monitoring sites within a basin. This network design is created by random selection, using either a computer or table of random numbers, in which a subset sample of sites is selected for monitoring. This design has the benefit that every potential groundwater monitoring site has an equal chance of being selected for the network. However, this design has the major drawback of being unlikely to achieve a set of monitoring sites that are spatially distributed throughout the basin. Commonly, potential measurement sites are clustered in areas of extensive groundwater development, which may lead to biases in the data.

Stratified Random Monitoring

Stratified random monitoring is a viable alternative to simple random monitoring, particularly where information is available to subdivide a basin into subunits that are likely to be more homogenous than the basin as a whole. The information used to subdivide the basin can be somewhat subjective, though stratification tends to be most effective when the subunits are very dissimilar from one another in combination with minimal variability within each subunit. Stratified random monitoring might be used when, for example, a basin has three distinct physiographic areas, and each has a different land use. These areas include an upland area primarily used for low-intensity grazing, a valley primarily used as farmland irrigated by surface water, and a mesa primarily used for farmland irrigated by groundwater. In this scenario, an important facet of the ambient groundwater monitoring network would be to distinguish water level and quality differences among the areas. Each subunit is then monitored individually by simple random selection, and monitoring sites are equally divided among the subunits. The goal of this monitoring strategy continues to be overall assessment of the basin, but an important factor is the assessment of each individual subunit. Idaho uses stratified random monitoring for its ambient network by dividing the state into 22 subareas characterized by fairly homogenous hydrogeology (1).

Random Monitoring Within Grid Cells

The most common method of implementing an ambient groundwater monitoring network is overlaying a grid on the basin (or other area of hydrologic interest), and randomly monitoring a site within each cell created by the grid. The systematic element requires that the selected sites be spatially distributed throughout the area; the random element ensures that every well within a cell has an equal chance of being monitored. The systematic grid monitoring strategy is especially effective in relatively homogenous areas as a tool to distribute sample sites adequately spatially.

More sophisticated systematic grid monitoring models aided by computer software may divide the basin into equal area cells so that each contains three random sample points (5). The random points are designated primary, secondary, and tertiary, respectively. An appropriate well or spring is then located within a specified radius of the primary sample point to monitor. If no appropriate groundwater sample site can be found near the primary point, a similar process is used for the secondary point and then the tertiary point, if necessary. If no appropriate groundwater sites can be located around any of these three random points, then any appropriate well or spring within the cell can be randomly selected for monitoring.

Random monitoring using grid cells can be adapted to more complex or comprehensive groundwater assessments. Basins that have several overlying aquifers (for example, an upper, unconfined aquifer above a lower, confined aquifer) would require selecting two random sites for monitoring within each cell to characterize each aquifer. One random site should be a deep well screened only in the lower aquifer, and the other site should be a shallow well whose depth does not exceed the upper aquifer's thickness. Wells should be avoided that have the possibility of being screened in both aquifers, as this would provide an unknown mix of groundwater. Even if only a single aquifer is spatially located within a cell, two wells pumping water from different depths (deep and shallow) could be monitored to examine for variability in groundwater levels and constituent concentrations with groundwater depth. In the perfect scenario, the shallow well could be pumping water from just below the water table to provide data on the water quality of the recharge percolating through the vadose zone.

Transect Monitoring

Transect monitoring is an especially useful design in basins that consist of steep river valleys. Most water development in these basins occurs along the flat river floodplain; minimal groundwater monitoring opportunities lie in the surrounding uplands. Transect monitoring requires selecting sites from each aquifer along, as close as possible, a straight line perpendicular to the river valley. For example, sites could be monitored

at high elevation mountain hardrock, in the upland basin-fill aquifer, and finally along the floodplain aquifer. Each of these transects would allow the opportunity to examine groundwater evolution flow paths from the basin's highest recharge points down to the valley floor. A final groundwater evolution flow path is then examined along the floodplain aquifer from the most upgradient site to the most downgradient site in the basin.

Transitional Subunit Monitoring

Any of the ambient groundwater network designs described can be adjusted to examine for targeted objectives within the basin. A higher density of monitored sites could be established for preselected areas that have, as previously shown in the hydrologic literature, the potential to impact either groundwater levels or quality. Preselected sites include, but are not limited to, clusters of large capacity production wells, confined animal feedlots, mines, landfills, irrigation districts, and residential areas that have a high density of septic systems for wastewater disposal. Other activities that also have a good probability of impacting groundwater may be found in the hydrologic literature. For these targeted subunit studies, care should taken to monitor groundwater at shallow sites both upgradient and downgradient of the preselected site.

Transitional subunit monitoring may also be used to define the extent of sampling sites better in the ambient network that have either dramatic groundwater level changes and/or constituent concentration statistical outliers. This additional monitoring will assist in determining if the randomly selected site is characteristic of the area. A groundwater level outlier might indicate that the well, is tapping a shallow, perched aquifer instead of the regional aquifer. For a constituent concentration outlier, it might indicate that the well is not representative of the area because of construction flaws such as a cracked casing or an improper surface seal that could allow impacted surface flow down the well casing.

MONITORING SITE SELECTION

An important consideration when establishing an ambient network is the type of well to use for monitoring. The preferable option is to construct new wells throughout the system. This allows the major benefit of control over their location, depth, screened opening, pump type, and other characteristics. The downfalls of this option include locating suitable well sites and the major expense of drilling, developing, and the upkeep of the wells. Even if funding allows establishing the wells, finding suitable well sites might not be easy. Preferable sites for wells are public lands, including road rights-of-way to obtain unlimited access. However, it may be difficult to find public lands in all areas where ambient network wells should be established. Selecting groundwater monitoring sites on private property with the land owner's permission allows a wider range of potential well sites. However, this option has the downfall of potentially being denied access to the well at a later date by the present or future, property owner.

Using preexisting private wells also has a number of advantages and disadvantages; the major factor is significantly less initial cost to establish an ambient monitoring network. No well drilling, development, or upkeep costs are required because wells are already in place, maintained by an outside party. The disadvantages are that there is no control over well characteristics. There is also no guarantee that the well will continue in operation for monitoring in the future. Even if the current well owner is very positive about involvement in the ambient network, a future property owner could have a different position.

Preexisting wells may generally be divided into two groups. High capacity wells typically consist of those used for municipal, mining, and irrigation purposes. Low capacity wells typically consist of those used for domestic, stock, and monitoring purposes. Other potential groundwater monitoring sites include naturally flowing springs. There are many advantages and disadvantages of using each type of well in an ambient network (Table 1).

In order to minimize potential biases in well selection, the most pragmatic approach for choosing wells for the network is to use a mix of high and low capacity wells that supply groundwater for different purposes. Care should be taken to select wells that are only screened in a single aquifer and have the most complete well characteristic data available. Using both high and low capacity wells should result in a mix of deep and shallow wells that will provide for a more complete assessment of the basin. Generally, public water supply wells are monitored under state and/or federal regulations which may make them generally more amenable to additional sampling. However, other high capacity wells such as which supply irrigation or mining uses or low capacity wells may have never been previously sampled. Selecting these wells could result in obtaining important hydrologic information not previously known about the area of interest.

If some funding is available for well drilling, very shallow monitoring wells often are a good choice to construct for several reasons. Foremost, such wells would indicate what type of impacts the aquifer might be receiving from recharge through the vadose zone. Because they are screened near the top of the water table. Also, because of their shallow depth and associated lesser cost, more monitoring wells could be drilled than other types of deeper wells.

MONITORING SITE INVENTORY

A site inventory is created to collect and document information for each well or spring selected or constructed for the ambient network. The site inventory contains important hydrologic information including, but not limited to, well location, owner, water use, well depth, screened interval, pumping depth, field measurements (water level and physical parameters such as temperature, pH, and specific conductivity), sampling permission forms, prior sampling measurements, and miscellaneous field activities and observations. A preprinted field sheet should be c-cated on which much of the above information can be added should be created, so that items are not overlooked in the field. Consistent field measurement and sampling protocols must be adhered to.

Table 1. Advantages and Disadvantages of Various Types of Wells for Ambient Groundwater Networks

Well Type	Advantages	Disadvantages
	High-Capacity Production Wells	
All	– easy to purge	– might not have flow rate controls making sampling for volatile constituents difficult
	– provide a more complete measure of groundwater quality throughout depth	– because of high pumping rates may draw water from more than the aquifer the well is screened in
Irrigation	– may pump constantly during the crop's growing season	– might have only seasonal use – turbine pump oil can cause contamination – can cause contamination when used for chemigation without antisiphon devices
Mining	– may pump constantly	
Municipal	– long-term access frequently possible	– wells producing water not meeting standards might be abandoned
	– might have extensive historical water quality data	– must sample before any chlorination
	Low-Capacity Production Wells	
All	– might lack well construction information	– susceptible to local impacts such as septic systems
Domestic	– often are more shallow wells	– may have water taps after storage or pressure tanks
Monitor	– often screened near the water table to investigate aquifer recharge	– may have been originally installed to monitor some sort of contamination
Stock	– often located in areas devoid of other types of wells	– often are windmills which can be difficult to purge adequately in calm weather
	Other Groundwater Sites	
Springs	– often located in mountainous areas devoid of any wells	– may flow only seasonally or during wet periods – may not have a clearly demarcated point of emergence.

MONITORING MEASUREMENTS AND SAMPLES

To determine what measurements and samples to collect for the monitoring network, the cost of each must be weighed against how valuable the information potentially gained from it is. One viewpoint is that much of the cost of an ambient network consists of salaries, travel expenses, and sampling equipment. As such, as wide a variety of groundwater data as possible should be collected at the monitoring site, which is an especially persuasive argument during the initial monitoring, when establishing baseline conditions. However, it might not be fiscally or scientifically prudent to collect certain types of samples where there is an extremely remote possibility of detecting the contaminants. As an example, collecting samples to be analyzed for organic contamination such as pesticides or volatile organic compounds in relatively pristine areas might not be the best use of scarce resources, as these tests are relatively expensive.

Baseline data collected at ambient network sites may include, but are not limited to, the following types of samples: inorganic constituents (physical parameters, major ions, nutrients, and trace elements), isotopes (oxygen, hydrogen, tritium, and others), radiochemistry (especially in areas of granite geology or mining activity), radon gas, volatile organic compounds, and pesticides. In addition, on-site measurements of groundwater depth, temperature, pH, specific conductivity, dissolved oxygen, alkaling and redox can be determined using portable instruments. Bacteria can be sampled but it may be of limited value for long-term trend analyses because microbiological contamination in groundwater is often transient and subject to a variety of changing environmental conditions, including soil moisture and temperature.

During selection of sample types to collect for the ambient network, adequate quality assurance/quality control procedures and samples should be integrated into work plans and activities. Quality assurance data validation tests may include cation–anion balances, specific conductivity–total dissolved solids ratios, hardness (lab-calculated), pH (field-lab), specific conductivity (field-lab), and groundwater temperature–groundwater depth. Quality control samples may include, but should not necessarily be limited to, travel blanks, equipment blanks, replicate samples (both duplicates and splits), and spiked samples.

AMBIENT NETWORK SIZE

The various conceptual designs are efficient methods for characterizing groundwater because they require monitoring relatively few sites to make valid statistical statements with a known degree of confidence about the conditions of a large basin. Each design will characterize the overall basin, though the density of monitoring will depend on scientific and fiscal factors. Obviously, funding has a critical influence on the density of monitoring. When possible, a network size of 30 sites is desired as this is

often large enough for a normally distributed population to be recognized as such (4).

Hydrologic factors also provide some measurement of optimal monitoring density. The hydrologic complexity of the basin and the variability of historical groundwater information are important components to consider when planning an ambient network. The hydrologic complexity of a basin is influenced by factors such as the number of aquifers, surface water features such as rivers and lakes, and the presence of high water use activities such as irrigation districts, mining and milling operations, or large urban areas. The variability of historical groundwater data can be judged qualitatively by examining the variation in groundwater levels, the types of dominant water chemistries present, and the number of trace elements detected. More extensive quantitative analyses should also be conducted which can include determining constituent concentration means and standard deviations to gauge the variability of groundwater quality in the basin.

MONITORING FREQUENCY

Once the ambient network has been established and the baseline data have been collected, it should be determined how frequently it will be monitored and what types of data will be collected. Measurement of groundwater levels should be tied to both the overall extent, and to recent changes in, the water development of the basin. Groundwater quality typically varies spatially more than temporally because of the insulating effect of the soil and vadose zone. Therefore, except in very shallow wells, it is typically unnecessary to resample wells frequently because rarely do constituent concentrations change significantly over periods of a few years. A quantitative method of determining the frequency is to examine previous groundwater quality studies in the basin covered by the ambient network. If wells or springs common to both are established, the constituent concentrations can be examined for significant statistical differences that are unlikely to occur by chance. The time period between the previous study and the baseline monitoring of the ambient network can establish the frequency needed for sampling. If new development has occurred in the basin that could potentially impact groundwater, this time period should be shortened to account for these recent influences.

In select areas of very shallow groundwater, monitoring should be seasonal. Particularly susceptible to seasonal fluctuations are perched aquifers of little storage capacity. Impacts such as high runoff from wet winters or irrigation recharge during an agricultural growing season may be reflected in high seasonal variability in both groundwater depth levels and constituent concentrations.

EFFECTIVELY USING DATA FROM AN AMBIENT NETWORK

Hydrologic data obtained from an ambient network should be used for a variety of purposes to make the investment in a program of this type as valuable and cost-effective as possible. If the ambient network is created and data collected without any subsequent assessment, the program should not be considered successful in accomplishing its goals. A common problem is adequately planning, developing, and monitoring an ambient network without the subsequent dedication to analyzing and interpreting the data and producing readable, scientifically valid reports that can be used by hydrologists, planners, and others interested in groundwater information.

Data collected from an ambient network should be used for a multitude of purposes. Most simply, efficient and accessible data storage and retrieval is a necessity for others seeking information from the ambient network, which should be as convenient as possible; potentially the data should be available electronically over the Internet. The potential audience for the ambient network data is wide and includes hydrologists, planners, real estate professionals, and anyone using groundwater.

Data from the ambient network should be examined for both spatial and temporal patterns. Empirical observations and qualitative methods are often successfully used to examine groundwater data. However, so that the hydrologist remains unbiased, statistical methods should also be used to examine the data. Groundwater data can be divided among various components of the basin to examine for statistically significant correlations. Aquifers, geologic types, watersheds, land uses, recharge zones, and fault zones are just some of the potential components used in examining for groundwater quality patterns. The ambient network becomes a powerful predictive tool when significant relationships are revealed between groundwater quality concentrations and physical or cultural features. At this point, the groundwater quality of unmonitored areas is predictable with a known degree of confidence based on statistically significant patterns revealed by the ambient network.

Finally, the data, spatial and temporal patterns and the interpretations of these patterns should be woven into a readable, scientifically valid report. Two versions could be produced: an in-depth report designed for hydrologists who require comprehensive groundwater information on a basin and a short fact sheet designed for a more casually interested audience. Both published reports should be widely disseminated among both the hydrologic community and the area of interest as well as be available on the Internet.

BIBLIOGRAPHY

1. Neely, K.W. (1994). *Idaho Statewide Ground Water Quality Monitoring Program Network Design*. Idaho Department of Water Resources, Boise, ID, p. 7.
2. Myers, G., Magdalene, S., Jakes, D., and Porcher, E. (1992). *The Redesign of the Ambient Ground Water Monitoring Program*. Minnesota Pollution Control Agency, St. Paul, MN.
3. Pitz, C.F. (2003). *Strategic Recommendations for Groundwater Assessment Efforts of the Environmental Assessment Program*. Washington State Department of Ecology, Olympia, WA.
4. Alley, W.M. (1993). *Regional Ground-Water Quality*. Van Nostrand Reinhold, New York.
5. Scott, J.C. (1990). *Computerized Stratified Random Site-Selection Approaches for Design of a Groundwater Quality Sampling Network*. U.S. Geological Survey Water-Resources Investigations Report 90–4101, Oklahoma City, OK.

MTBE

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Methyl tertiary-butyl ether (MTBE) is a synthetic compound that was developed as a solution to the problem of air pollution from vehicle emissions. MTBE was originally added to gasoline as a fuel oxygenate in approximately 1979 to reduce air emissions and make the fuel burn cleaner, allowing more complete combustion in internal combustion engines. The concept was to improve air quality by producing fuels that were more readily oxidized and decrease the resulting tropospheric ozone production. In the late 1980s, the U.S. EPA supported the use of fuel oxygenates in reformulated gasoline to achieve air quality goals.

MTBE, a byproduct of gasoline refining, was inexpensive, and readily available nationwide. Ironically, the use of this air-saving gasoline additive has taken its toll on groundwater and surface water resources throughout the nation. Life-cycle studies were not performed on MTBE and ultimately, leaks and spills of gasoline containing MTBE from underground tanks and pipelines have leaked into the groundwater. In addition, incomplete combustion of gasoline containing MTBE by two- and four-stroke engines in water skis and boats has allowed the release of MTBE into surface waters.

MTBE is an ether whose general chemical formula is $C_5H_{12}O$ and structural formula is $CH_3OC(CH_3)_3$ or $(CH3)_3COCH_3$ (1). (See Fig. 1). MTBE is highly soluble in water, more than 75 times more so than many other gasoline compounds. 250,000 MTBE-contaminated sites throughout the nation have been identified. A January 16, 2000, more than airing of the "60 Minutes" television program on MTBE highlighted the problem for a national audience, although the problem of MTBE and water resources had been known for a few years to water professionals and regulators.

PERSISTENCE IN GROUNDWATER

Sampling of groundwater in California and other states has shown that MTBE is more persistent and more mobile than many other fuel compounds.

TASTE AND ODOR

A taste and odor like turpentine has made MTBE-contaminated groundwater sources at levels exceeding the taste and odor threshold unusable for human consumption. Supplying bottled water for impacted areas and/or other large-scale treatment or water importation options will be expensive and will continue into the future. Blending clean water with MTBE-impacted water will also continue.

HEALTH RISK

Although MTBE is considered a potential health risk, there is inadequate evidence that MTBE causes cancer in humans. The strong odor and taste of MTBE at relatively low concentrations would make drinking of large amounts of high-level MTBE contaminated water unlikely, thus reducing the potential for exposure and resulting human health risks from MTBE. MTBE is not listed as a human carcinogen by the U.S. National Toxicology Panel, the California Proposition 65 Committee, or the International Agency for Research on Cancer. Limited evidence from an older Italian MTBE rodent study indicated that MTBE caused cancer in the experimental animals when administered in unrealistic doses hundreds of times greater than probable human exposure. California, a state that has the most MTBE cases, has a primary MCL of 13 μg/L and a secondary MCL (taste and odor threshold) of 5 μg/L (2).

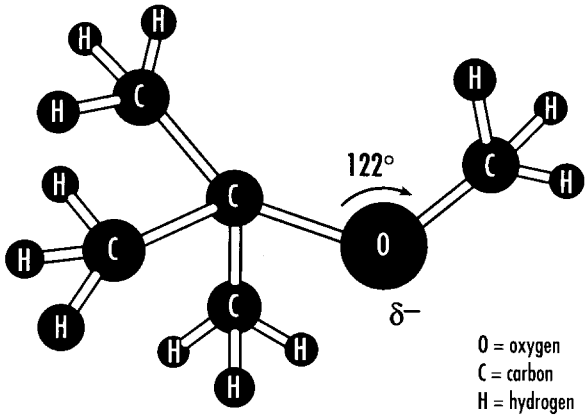


Figure 1.

FATE AND TRANSPORT

The MTBE issue is a chemical handling problem associated with gasoline leaking from underground storage tanks, leaking pipelines, and surface spills or from small gasoline engine equipment. Even though the majority of underground tanks in this country have been upgraded, the amount of MTBE already released with gasoline into the environment is so large that the problem of degraded drinking water sources may persist for decades. Compared to other fuel compounds, MTBE adsorbs to soils much less and dissolves in groundwater at much higher concentrations.

Due to these characteristics, MTBE migrates much faster and further in groundwater than equal amounts of other gasoline compounds. According to Wilson (2), MTBE often appears to move out ahead of a BTEX plume. The explanation is based on differences in the extent of adsorption to the aquifer materials. As the fraction of organic carbon in the aquifer sediment increases, benzene and other gasoline compounds adhere more to aquifer sediments than MTBE. Therefore, an aquifer with a high fraction of organic carbon (0.1%) would have a retardation index for MTBE and benzene, at 1.6 and 2.9, respectively (3). These differences help to explain the variations in contaminant transport rates.

GROUNDWATER INVESTIGATION

The investigation of a groundwater resource impacted with MTBE requires more detailed and more rapid sampling of soil and groundwater than other fuel-impacted sites due to the potential for faster and deeper migration of MTBE compared to other gasoline compounds. The presence of other oxygenates should also be tested at all sites containing MTBE. Some brands of gasoline contain tertiary-butyl alcohol (TBA) as an additive. As TBA is a biological breakdown product of MTBE, TBA should also be analyzed at sites containing MTBE.

REMEDIATION

MTBE is an ether compound and was considered very different from gasoline. Some investigators originally thought MTBE was a recalcitrant compound. MTBE remediation has improved after years of research in the laboratory and numerous field case studies. The same technologies that are used to treat fuel hydrocarbons have, in general, been used successfully to treat MTBE. Due to the chemical characteristics of MTBE, the cost of remediation or clean up of the contaminant is equal to or more expensive than that for other gasoline related chemicals, such as benzene, toluene, ethylbenzene, and xylenes. New technologies have improved the remediation efficiency and cost. MTBE remediation has been documented using a variety of *in situ* technologies, including, but not limited to, chemical oxidation (Fenton's chemistry and ozone) and bioremediation. Enhanced *in situ* bioremediation using various delivery systems for oxygen and peroxygens effectively reduce MTBE in groundwater. *Ex situ* technologies include pump and treat systems and soil vapor extraction systems, as well as dual-phase extraction with appropriate surface treatments and destruction. Virgin coconut shell carbon has been documented for MTBE remediation. Due to the high mobility of MTBE in the environment, rapid implementation of source control is the key to remediation of sites impacted with MTBE. More detailed MTBE information and case studies are contained in Moyer and Kostecki (4).

AIR POLLUTION

The effectiveness of MTBE in reducing air pollution in recent years is suggested, but uncertain. Reformulated gasoline containing MTBE may be related to some of the improvement in air quality, however, various conflicting air studies exist. Part of the improvement may be attributable to newer and more efficient vehicle engines with computer-controlled ignition. Replacements for MTBE must be evaluated carefully as to their fate and transport once released into the subsurface. Life-cycle studies focusing on the potential release into the air, soil, and groundwater should be performed prior to introducing any new chemicals into a product as widely used as gasoline.

BIBLIOGRAPHY

1. Motzer, W. (2001). Physical and chemical properties of MTBE. In: *MTBE: Effects on Soil and Groundwater Resources*. J. Jacobs, J. Guertin, and C. Herron (Eds.). CRC Press/Lewis, Boca Raton, FL.
2. US EPA. (March 2004). Available: http://www.epa.gov/swerust1/mtbe/mtbemnp.pdf.
3. Wilson, J. (2003). Fate and transport of MTBE and other gasoline compounds. In: *MTBE Remediation Handbook*. E. Moyer and P. Kostecki (Eds.). Amherst Scientific, Amherst, MA, pp. 19–61.
4. Moyer, E. and Kostecki, P. (2003). *MTBE Remediation Handbook*. Amherst Scientific, Amherst, MA, p. 670.

READING LIST

California Dept. of Health Services. Available: http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/MtBE/MtBEindex.htm.

California State Resources Control Board's Draft Guidelines on MTBE contains technical documentation on MTBE fate and transport in the subsurface. Available: http://www.swrcb.ca.gov/cwphome/ust/MtBE_finaldraft.doc.

Diaz, A. and Dragus, D.L. (Eds.). (2002). *Oxygenates in Gasoline, Environmental Aspects*. American chemical society ACS symposium series #799, Washington, DC, p. 310.

Environmental Behavior and Fate of MTBE. Available: htttp://water.wr.usgs.gov/MtBE/fs20396/.

Jacobs, J., Guertin, J., and Herron, C. (Eds.). (2000). *MTBE: Effects on Soil and Groundwater Resources*. CRC Press/Lewis, Boca Raton, FL, p. 264.

USGS has a reference site for MTBE. Available: http://water.wr.usgs.gov/MtBE/.

LIMITING GEOCHEMICAL FACTORS IN REMEDIATION USING MONITORED NATURAL ATTENUATION AND ENHANCED BIOREMEDIATION

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In Situ Monitored Natural Attenuation (MNA) and enhanced bioremediation are affected by a variety of limiting factors, including the availability of a terminal electron acceptor (TEA), macronutrients (nitrogen and phosphate), as well as an energy source (carbon). The TEA for aerobic degradation is limited to oxygen. For anaerobic degradation, TEA processes include denitrification using nitrate (NO_3^-), manganese reduction using manganese dioxide (MnO_2), iron reduction using bioavailable iron that includes the hydroxide form ($Fe(OH)_3$), sulfate reduction using the sulfate ion (SO_4^{2-}), and methanogenesis using carbon dioxide (CO_2) (1).

Macronutrients are measured in the laboratory as nitrogen in the form of ammonia or nitrate and orthophosphate. Nutrients, although important, are not

as critical as depletion of the TEA. The energy source is the carbon in the hydrocarbons or chlorinated solvents that act as food for the microbes.

Monitored Natural Attenuation occurs when these processes are believed to be occurring on their own without additives. Natural attenuation frequently starts on many hydrocarbon sites, but the aerobic degradation process frequently stops or slows down considerably because of the limiting factors of oxygen and nutrient depletion. Enhanced bioremediation and Monitored Natural Attenuation have been described in detail in numerous volumes, including (1) and (2).

Aerated water at one atmosphere and at room temperature usually has about 8.0 mg/L dissolved oxygen. Although groundwater may have about 8 mg/L near the recharge area, oxygen depletion starts to occur as the oxygen is consumed by the chemical and biological processes that use up the oxygen. To measure these demands, laboratories measure solid or sediment oxygen demand. For dissolved oxygen demand, chemical oxygen demand and a subset, the biological oxygen demand, are typically analyzed. The biological oxygen demand is commonly evaluated as a 5-day analysis originally designed for sewer treatment plants.

To support aerobic biodegradation of petroleum hydrocarbons, aerobic processes are less than optimal when the dissolved oxygen is below 2 to 4 mg/L (3); at this oxygen level, facultative anaerobes may become active. At this stage of oxygen depletion, if a biodegradation process is to be used for the complete remediation of the site, enhanced bioremediation may be used. Enhanced bioremediation is designed wherein oxygen and sometimes nutrients are delivered into the subsurface through wells, well points, borings, or trenches. The delivery of oxygen depends on the oxygen form. Oxygen comes in many forms and can be added using a variety of techniques. Some of the more common forms of oxygen used for enhanced bioremediation include gas phase oxygen (O_2) or ozone (O_3), liquid oxygen sources such as hydrogen peroxide (H_2O_2), and solid oxygen sources including magnesium peroxide (MgO_2) and calcium peroxide (CaO_2). Some of these compounds are chemical oxidizers and, above certain threshold concentrations, can kill microbes in the pore space of the injection area during the process of releasing the contained oxygen. After the reactions occur, microbial populations can increase greatly from populations in more isolated areas of the mineral matrix.

In theory, oxygen levels of at least 3 to 3.5 times that amount of subsurface petroleum mass are required for complete mineralization of the hydrocarbon. Complete mineralization is the converting of the hydrocarbon to carbon dioxide and water:

$$\text{Benzene: } C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3H_2O \text{ (3.1 oxygen requirement)}$$

For anaerobic TEAs used to treat chlorinated solvents by reductive dehalogenation, one common method of TEA replenishment is to add a carbon source such as liquid molasses, lactic acid, cheese whey, or gases such as propane that also contain a large number of hydrogen atoms. In the process of the biological breakdown of the introduced chemical, hydrogen is liberated in the process. The hydrogen is used as the electron donor and the liberated carbon is used as a food source, along with the carbon-based contaminant. For petroleum hydrocarbons and some xenobiotics, such as MTBE ferric iron or sulfate, salts can be added to stimulate anaerobic biooxidation.

NUTRIENTS

Nutrient levels can be at well below reporting levels. The carbon:nitrogen:phosphorus ratios necessary to enhance biodegradation occur in the optimal range of 100:10:1 to 100:10:0.5, depending on the chemical contaminant, microbes, and other site-specific conditions (3). In some instances, anaerobic biooxidation processes may be inhibited because of the lack of trace nutrients. In these cases, native sulfate will be present in the groundwater and possibly iron. Continued use of these native inorganic TEAs can be stimulated by the addition of critical nitrogen and phosphate as trace nutrients.

SOIL MOISTURE

Soil moisture content in the unsaturated zone may be related to precipitation in the region and the retention capacity of the shallow soil. Soil moisture content of 75 to 90 percent of field capacity is considered optimal for aerobic microbial activity (4).

TEMPERATURE

Temperature has been seen as a limiting factor for biological degradation of hydrocarbons. Microbial growth rate is a function of temperature. Subsurface microbial activity has been shown to decrease significantly at temperatures below 10 °C and essentially to cease activity below 5 °C. From 10 °C to 45 °C, the rate of microbial activity typically doubles for every 10 °C increase in temperature (3). Typical soil microbial activity will slow as the temperatures reach 55 °C and will reach a steady state determined by the capacity to flush heat from the system. In cases where the load of petroleum hydrocarbons is high, the thermodynamics of the heat transport may be the rate-limiting factor rather than any biogeochemical process.

One case adjacent to the Yuba River near Donner Pass in California (7,000 feet above mean sea level) and another at South Lake Tahoe area in Nevada were evaluated for total heterotrophic plate counts and specific hydrocarbon microbial degraders. In both cases, plate counts were well below 100 colony forming units per gram of dry soil. Temperature of the water was seen as the limiting factor.

Assessment procedures must be completed that will, support the reliance on the MNA or enhanced bioremediation process by proving natural attenuation is taking place, defining the site-specific natural attenuation mechanisms, quantifying the kinetics of the process and providing an estimated time for cleanup, and insuring that the site-specific conditions will not allow unacceptable offsite migration of the contaminant plume. Given the above

information, a governing regulatory body can support a decision for an MNA solution. The purpose of this article is to examine conditions under which the biological component of natural attenuation is inhibited or terminated, because of toxicity from heavy metals or certain hydrocarbons from the impacting contaminants, other compounds associated with the contaminants (at nonregulated levels), or compounds associated with the native groundwater.

The effect of toxicity on the MNA process is seen in three areas. First is a simple inhibition of activity. The microbial population continues to function, but at a rate that is slower than what would occur under normal conditions.

Second is a complete cessation of biological degradation activity. The bacteria are killed outright or, more commonly, they enter into a vegetative static state in which they are metabolically inactive. However, if the offending toxic material is removed from the system, bioactivity can resume.

Third is interference with degradational activity that is specifically focused on a contaminant of concern, which is more subtle, but particularly important to the MNA process. The overall microbial activity is not inhibited, just degradation of the contaminant. This problem is more often seen in systems where xenobiotic hydrocarbons are the targets of cometabolically generated degradation enzymes. In these cases, it is common for attenuation of the xenobiotic to take place after all of the other "natural" hydrocarbons have been consumed.

To evaluate the impact of toxicity, it is important to understand the mechanisms by which substances are toxic to microorganisms or interfere with the degradation process. The following bacteria cell components or processes are sensitive to toxic effects from the listed compounds:

- The bacterial cell wall can be totally destroyed by heavy metals, phenols, and alcohols.
- The permeability of the cell wall can be fatally increased by phenolic compounds, alcohols, detergents, and quaternary ammonium compounds.
- The alteration of interior proteins (destroying their cellular function) is caused by halogens, phenols, and alcohols.
- Interference with the action of intercellular enzymes will stop metabolic activity. Compounds toxic via this effect include cyanide, strong oxidants (chlorine, etc.), phenols, metals, and metalloids.
- Interference with nucleic acid synthesis can prevent bacterial reproduction; heavy metals can act in this fashion. Environmental conditions also play a role in the impact that toxic materials have, particularly for metals. Toxicity of metals is governed by concentration, chemical form of the metal, pH and Eh of the environment, the type of microbial system involved (i.e., aerobic or anaerobic), and potential for adaptation of the bacteria. Toxic forms of metals include soluble salts and anionic complexes. Insoluble salts, oxides, or even elemental forms are not necessarily toxic. The best method to evaluate groundwater for the presence of potentially toxic metals is to collect and test filtered water samples.

Effect of pH

Bacteria are sensitive to pH conditions. Most bacteria that are indigenous to groundwater systems and functional in the MNA process thrive in the pH range of 6.3 to 7.5. An anthropogenic pH lower than 5.0 is inhibitory or toxic from the pH effects alone. In cases where native groundwater has lower pH, the indigenous bacteria will have likely adapted to that specific condition, which is the case in lignite-rich areas of east Texas where it is common for the native groundwater pH to be as low as 4.5. Lower pH will cause an increase in soluble metal concentrations, including metals that may be native to the aquifer matrix.

REDOX Conditions

Oxidation-reduction (Redox) potential largely impacts the consortia of bacteria that will be active and the electron acceptor available to be used by the system. Almost any range of Eh conditions has the potential to offer effective biodegradation. However, some anaerobic systems are more sensitive to toxic compounds.

Toxicity Issues

Some naturally occurring metals and compounds, as well as man-made pollutants, have contributed to minimizing or stopping *in situ* biodegradation processes. As a general rule, heavy metals in excess of 2,500 mg/L are too toxic for microbial populations (5).

These toxic elements and compounds affect bacteria consortia and bacterial adaptability at the site. There are substances or compounds commonly found at contaminanted sites that have proven to be toxic to microbial populations. In instances where a concentration range is given, the low value represents inhibition of microbial activity, and the high value represents a concentration that will kill or stop microbial activity.

Copper may be the heavy metal with the highest toxicity with regard to the impact on the *in situ* biological degradational process. It is extremely toxic, inhibitory at low concentrations, and can interfere with the cometabolic degradation of chlorinated solvents at the lowest end of this range.

CONCENTRATION RANGES FOR SELECTED TOXIC SUBSTANCES

Copper 0.01 to 20 mg/L
Zinc 0.3 to 10 mg/L
Cadmium 0.1 to 20 mg/L
Chromium 25 mg/L - Inhibition
Nickel 25 mg/L - Inhibition
Lead 900 mg/L - Inhibition
Cobalt 0.3 to 10 mg/L
Mercury 0.01 to 20 mg/L
Methanol 90 mg/L - Inhibition
Isopropanol 55 mg/L - Inhibition
Acetone 75 mg/L - Inhibition
Pentachlorophenol 1 to 200 mg/L
TNT 10 to 100 mg/L
Cyanide 10 to 150 mg/L

Petroleum Hydrocarbons

The components of common petroleum hydrocarbons become inhibitory when soluble concentration ranges reach 200 to 500 mg/L. The upper range for lethal toxicity verges on 50,000 mg/L or free product, in which electron acceptor transport is more an issue than chemical toxicity. Evidence exists that methanogenesis may be inhibited by some constituents in crude oil.

Chlorinated Hydrocarbons

Most chlorinated solvents (also called chlorinated hydrocarbons) become inhibitory to microbes when soluble concentrations of these compounds are in the 100 to 500 mg/L range. They become toxic at concentrations around 1,000 mg/L, because of chemical attack on cell wall lipids. Chlorinated solvent concentrations in excess of 7,000 mg/L are inhibitory or toxic to microbial populations (5).

A baseline of total heterotrophic colony forming units and specific hydrocarbon degraders is useful prior to recommending natural or enhanced bioremediation at appropriate sites. If heterotrophic microbial population count is low (below 1,000 CFU per gram of dry soil), an assessment screen for compounds toxic to bacteria may be useful.

If toxic compounds are found, it may be necessary to perform some level of bench scale testing to quantify the toxic effect of suspect compounds. This assessment process is still a much less expensive procedure than the typical "pump and treat" active groundwater remediation projects. In some situations, pH amendments or other geochemical treatments can modify toxic conditions in the subsurface.

Monitored Natural Attenuation, enhanced aerobic bioremediation, and stimulated anaerobic biooxidation are likely to continue into the future. The first two are commonly used remedial approaches to obtain site closure for hydrocarbon-impacted properties where remediation time can be lengthy, the latter is a rapidly developing new tool for those processes. The costs of bioremediation can be significantly lower than pump and treat or other active and more aggressive remedial approaches. Assessing the limiting factors and performing geochemical studies help set baseline levels and allow for the monitoring of contaminant degradation over time.

Dissolved oxygen and nutrients are commonly depleted early on, so the use of enhancements to optimize subsurface conditions are frequently used. The power of nutrient stimulation to exploit native sulfate and iron for anaerobic biooxidation or the supplement of sulfate or iron salts for further stimulation of anaerobic biooxidation lies in the fact that the amendments are water soluble at relatively high concentrations and, in most instances, are also conservatively transported. They do not react until present with the utilizing bacteria and the impacting hydrocarbon. Sites using MNA as the sole remedial method to obtain site closure to low residual contaminant levels are not that common. Regardless of the biological method used, *in situ* bioremdiation methods are effective, but generally work on a slow time scale, with the results being observed over many months or years.

BIBLIOGRAPHY

1. Suthersan, S.S. (2002). *Natural and Enhanced Remediation Systems*. CRC Press/Lewis Publishers, Boca Raton, FL, p. 419.
2. Wiedemeier, T., Rafai, H., Newell, C., and Wilson, J., (1999). *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, New York.
3. United States Environmental Protection Agency (USEPA). (2004). Enhanced Aerobic Bioremediation. In: *How to Evaluate Alternate Cleanup Technologies for Underground Storage Tank Sites; A Guide for Corrective Action Plan for Regulators*. EPA 510-R-04-002, Washington, DC.
4. United States Environmental Protection Agency (USEPA). (2004). Monitored Natuaral Attenuation. In: *How to Evaluate Alternate Cleanup Technologies for Underground Storage Tank Sites; A Guide for Corrective Action Plan for Regulators*. EPA 510-R-04-002, Washington, DC.
5. United States Environmental Protection Agency (USEPA). (2004). In-Situ Groundwater Bioremediation. In: *How to Evaluate Alternate Cleanup Technologies for Underground Storage Tank Sites; A Guide for Corrective Action Plan for Regulators*. EPA 510-R-04-002, Washington, DC.

NITRATE CONTAMINATION OF GROUNDWATER

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Groundwater supplies drinking water for half of the people in the country and represents the total water supply for many of the western states. Numerous contaminants are anthropogenic, including petroleum products, chlorinated solvents, and pesticides, but nitrate contamination can be either natural or man-made and is one of the most common chemical contaminants of groundwater. Nitrate levels in uncontaminated groundwater are generally less than 2 mg/L, but levels have been increasing during the past five to six decades in areas where contamination has occurred.

Nitrate nitrogen is predominantly the product of the microbial decomposition of nitrogenous material, and almost all nitrogen reactions in soil and groundwater are the result of microorganisms. Through decomposition, nitrogenous matter is converted to ammonia (NH_3) which is first oxidized to nitrite (NO_2^-) followed by further oxidation to the production of nitrate (NO_3^-); both are accompanied by the production of nitrogen gas (N_2). Nitrate serves as a nutrient for the production of plant life that is consumed by living animal matter, which produces wastes products and, upon death, completes the nitrogen cycle by creating nitrogenous matter.

Sodium and calcium nitrate add nitrogen directly to the soil resulting in valuable fertilizers. A large natural

deposit of sodium nitrate in Chile served as a major source of nitrogen fertilizer. Geologically deposited nitrate can also be found in the San Joaquin Valley in California, Runnels County, Texas, and shale in Montana and South Dakota.

Although the degradation of plant materials can account for small amounts of nitrate in groundwater, most results from the application of fertilizers to agricultural land, parks, lawns, and golf courses. Other sources include animal wastes, seepage from septic tanks, the application of sewage and sludge to the land, precipitation, geological deposits, and biological fixation. Canter and Knox (1), for example, estimate that one trillion gallons of septic-tank waste are released to the subsurface annually. According to Nolan et al. (2), 11.5 million tons of nitrogen as fertilizer in used in agriculture annually in the United States where the production of commercial fertilizer has increased by a factor of 20 between 1945 and 1985. Manure from farm animals accounts for an estimated 6.5 million tons of nitrate annually, and that from the atmosphere is about 3.2 million tons.

Nitrates are the cause of methemoglobinemia which is also referred to as blue baby disease and nitrate cyanosis in infants. Nitrates are reduced to nitrites in the intestinal tract and absorbed into the blood. The nitrites combine with hemoglobin which deprives organs and tissues of oxygen, resulting in cyanosis which causes a blue color of the skin. Nitrates in drinking water have also been linked to non-Hodgkin's lymphoma. Other health related problems may include impairments to the nervous system and birth defects (3). The U.S. Public Health Service established drinking water standards for nitrate in 1946 at a limit of 10 mg/L expressed as nitrogen and 45 mg/L expressed as nitrate.

Generally, nitrate contamination is pervasive at shallow depths in the vadose zone. For this reason, drinking water from rural water districts or other public water supplies is less likely to contain high nitrate concentrations because of the depth of the wells and steps taken to prevent contamination from sources near the surface such as septic tanks. When water is pumped from greater depths, it is also more likely to have a low oxygen concentration that results in possible denitrification. Rural wells, on the other hand, are usually completed at shallower or depths in areas where sources of contamination, such as septic tanks, fertilizers, or manure from feedlots or holding pens, are more likely. When obtaining water from a domestic well, care should be given to ensure that the screen is placed as deep as is practicable for that location, that the upper casing is properly sealed, and that the wellhead is elevated and protected by a concrete pad and is in a secure enclosure. In a study by Schubert et al. (4), it was found the most likely scenario for exposure to high nitrates in drinking water involved families living on farms supplied by old, shallow wells. In such cases, the water should be tested periodically for nitrates as well as bacteria.

BIBLIOGRAPHY

1. Canter, L. and Knox, R.C. (1984). *Evaluation of Septic Tank System Effects on Ground Water Quality*. EPA-600/2-84-107.
2. Nolan, B.T., Ruddy, B.C., Hitt, K.J., and Helsel, D.R. (1997). Risk of nitrate in groundwaters for the United States—A national perspective. *Environ. Sci. Technol.* **31**: 2229–2236.
3. Keeney, D. (1986). Sources of nitrate to ground water. *CRC Crit. Rev. Environ. Control* **16**: 257–304.
4. Schubert, C., Knobeloch, L., Kanarek, M.S., and Anderson, H.A. (1999). Public response to elevated nitrate in drinking water wells in Wisconsin. *Arch. Environ. Health* **54**(4): 242–247.

TREATMENT FOR NITRATES IN GROUNDWATER

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INTRODUCTION

Nitrate is a naturally occurring compound that forms in the soil when nitrogen and oxygen combine. Small amounts of nitrate are normal, but excess amounts can pollute supplies of groundwater.

Drinking water high in nitrate is potentially harmful to human and animal health. Nitrate (NO_3) is a naturally occurring form of nitrogen (N) that is very mobile in water. It is essential for plant growth and is often added to soil to improve productivity. Water moving down through soil after rainfall or irrigation carries dissolved nitrate with it to groundwater. In this way, nitrate enters the water supplies of many homeowners who use wells or springs (1).

Sources of Nitrate Pollution in Water

Common sources of nitrogen in the soil are fertilizers, livestock waste, and septic systems. Excess nitrate in the soil is most often found in rural and agricultural areas. Nitrate travels easily through the soil and is carried by rain or irrigation water into groundwater supplies. Wells that tap groundwater may be affected. Shallow wells, wells in sandy soil, or wells that are improperly constructed or maintained are more likely to have nitrate contamination.

The distribution of nitrate contamination in the United State is widespread. It constitutes the largest amount of pollutant released into the environment. The following references describe the extent of nitrate pollution (1–3).

Agricultural runoff and seepage into the groundwater occurs wherever fertilizer is applied. The denitrification of nitrate effluent into the Mississippi River is what caused the 'dead zone' of the Gulf of Mexico area along the coast of Texas and Louisiana downstream from the Mississippi River estuary. Shallow groundwater in the farming states, Illinois, Ohio, Indiana, Iowa, and Minnesota, is heavily polluted with nitrate. Large cattle feedlots, dairy farms, and orchards in California, Kansas, and Illinois release large amounts of nitrate into shallow groundwater. Nitrate pollution in groundwater is a worldwide problem.

Nitrate Properties in Groundwater

The following references provide in-depth properties of nitrate physical chemistry, natural degradation processes, and migration phenomenon (4–7).

Health Effects of Nitrate/Nitrite in Water

Infants under 6 months of age are susceptible to nitrate poisoning. Bacteria that live in the digestive tracts of newborn babies convert nitrate to nitrite (NO_2). Nitrite then reacts with hemoglobin, which carries oxygen in blood, to form methemoglobin. Methemoglobin cannot carry oxygen, thus the affected baby suffers oxygen deficiency. The resulting condition is referred to as methemoglobinemia, commonly called "*blue baby syndrome*." The most noticeable symptom of nitrate poisoning is a bluish skin coloring, called cyanosis, particularly around the eyes and mouth. A baby with bluish skin should be taken to a medical facility immediately and tested for nitrate poisoning. The blood sample of an affected baby is chocolate brown instead of the normal bright red due to lack of hemoglobin. Methemoglobinemia is relatively simple to treat, and, in most reported cases, the affected baby makes a full recovery. Within several months after birth, the increasing level of hydrochloric acid in a baby's stomach kills most of the bacteria that convert nitrate to nitrite. By the age of 6 months, the digestive system is fully developed, and the risk of nitrate-induced methemoglobinemia is greatly reduced.

Water quality standards for human consumption have been set at 10 milligrams of nitrate-nitrogen per liter of water (10 mg/L NO_3-N). This level of nitrate-nitrogen is equivalent to 45 mg/L of nitrate (NO_3). When reading laboratory reports of water quality, be sure to note whether reported values are for nitrate-nitrogen or nitrate. Note that 1 mg/L equals 1 ppm (parts per million). Most reported cases of blue baby syndrome due to contaminated water have occurred when infant formula was prepared using water that contained more than 40 mg/L NO_3-N. Consumption of high-nitrate water by pregnant women and nursing mothers is not as likely to be harmful to babies as direct consumption. The health effects in these cases are not completely understood, so it is recommended that pregnant women and nursing mothers limit nitrate consumption. Possible connections between nitrate and other health problems such as nervous system disorders, cancer, and heart damage are not well documented and are currently being researched.

Ruminant animals (cattle and sheep) and infant monogastrics (baby pigs and baby chickens) are also susceptible to nitrate poisoning because of bacteria living in their digestive tracts. Horses, even though they are monogastric, are susceptible to nitrate poisoning throughout their lives. Livestock may be exposed to large quantities of nitrate in their feed as well as in contaminated water. Animals that are treated in time can recover fully from nitrate poisoning. Scientific studies indicate that water that contains more than 25 mg/L NO_3-N can be harmful to animals.

Water Use Criteria for NO_3/NO_2 in Water

The U.S. Environmental Protection Agency (EPA) has established the maximum contaminant level (MCL) for nitrate at 10 milligrams per liter (mg/L). In addition, EPA established an MCL for nitrite at 1 mg/L.

Water quality standards for human consumption have been set at 10 milligrams of nitrate-nitrogen per liter of water (10 mg/L NO_3-N). This level of nitrate-nitrogen is equivalent to 45 mg/L of nitrate (NO_3). The presence of high nitrate levels may indicate that other, more serious contaminants may also be entering your water supply. Nitrate and coliform bacteria concentrations are commonly used to indicate well water contamination by surface waters. Water with nitrite (NO_2) levels of 1 ppm or more also is not recommended for human consumption.

These guidelines will help you interpret the results of your water test. Be careful when interpreting different lab results. Nitrate can be measured as NO_3 or as NO_3-N, and the results mean very different things (Table 1).

Nitrate is colorless and odorless. The surest way to tell if you have nitrate in your water is to have it tested. If your water comes from a public water supply, such as a city supplier, it is tested regularly to ensure that it meets safe drinking water standards. If your water comes from a private well, you are responsible for testing it and ensuring that it is safe to drink.

Table 1. Guidelines for Drinking Water

Measured Level (mg/L)	Interpretation NO_3
0–44	Below the drinking water standard. The nitrate level is safe for humans and livestock.
45–176	Higher than the drinking water standard. The water should not be consumed by infants 6 months of age or younger or by pregnant or nursing women. It may be acceptable for adults and livestock, though it is not recommended.
176+	Significantly higher than the drinking water standard. The water should not be consumed. Install a water treatment system or use bottled water for drinking and cooking.
Measured Level (mg/L)	**Interpretation NO_3-N**
0–9	Below the drinking water standard. The nitrate level is safe for humans and livestock.
10–39	Higher than the drinking water standard. The water should not be consumed by infants 6 months of age or younger or by pregnant or nursing women. It may be acceptable for adults and livestock, though it is not recommended.
40+	Significantly higher than the drinking water standard. The water should not be consumed. Install a water treatment system, or use bottled water for drinking and cooking.

Water Testing Frequency

Unfortunately, nitrate is only one of several possible contaminants in well water, which is why water districts recommend that well users conduct comprehensive tests of their water supplies every 1 to 3 years, or more frequently if the taste, odor, or appearance of the water changes, or if you have specific health concerns.

Preventive Measures for Nitrate/Nitrite Pollution

Septic systems, animal waste, and fertilizer are all potential sources of nitrate contamination. Water that comes into contact with a source of nitrate can carry that contamination through the soil and into the groundwater supply. Follow these guidelines to reduce the risk of nitrate contamination:

1. Proper well location: Wells should be located uphill (up-gradient) and at least 100 feet away from septic tanks, leach fields, animal confinement areas, and fertilized areas.
2. Proper well construction: Make sure your well casing extends above the ground, and construct an earth berm around the well to divert surface runoff away from the wellhead. Also, make sure your well has at least a 50 feet deep annular seal (grouting around the outside of the well casing) and an intact concrete slab on the wellhead.
3. Operate your septic system correctly: Maintaining your septic system regularly will help avoid system failure, which can lead to water contamination, the spread of disease, and the need for costly repairs. Follow these guidelines:

Do not run heavy vehicles over the area above your septic tank, drain pipes, or leach field.

Avoid planting trees or shrubs near drain pipes or the leach field. Roots can clog the lines.

Do not dispose of chemicals or nonbiodegradable materials in your toilet or drain.

Conserve water.

Install a lint trap on your washing machine.

Hire a reputable contractor to pump out your septic tank every 2 to 3 years.

If you have two leach fields, switch them every year.

4. Reduce your use of fertilizer: Use lawn and garden fertilizers only when necessary and always according to the manufacturer's instructions. Farmers can use management practices that are both environmentally and economically sound.

BIOLOGICAL DENITRIFICATION

Biodenitrification will probably be a very common technology used to comply with nitrate/nitrite regulation (8).

The demonstration project has developed a two-stage *ex situ* anoxic biofilter biodenitrification process. The process is fixed film bioremediation, using biocarriers and specific bacteria to treat nitrate-contaminated water. Unique to the process is a patented mixed bed reactor that retains the biocarrier within the system, thus minimizing solids carryover. Fixed film treatment allows rapid and compact treatment of nitrate with minimal byproducts. Methanol is added as a source of carbon for cell growth and for metabolic processes that remove free oxygen. The resulting oxygen-deficient environment encourages the bacteria to consume nitrate. Methanol is also important to ensure that conversion of nitrate proceeds to produce nitrogen gas rather than the more toxic nitrite intermediate.

The mechanism for anoxic biodegradation of nitrate consists of two sequential denitrification reactions. Oxygen must be consumed to a dissolved oxygen concentration of <1 mg/L. In the first denitrification step, the bacteria are forced to substitute the nitrate as the electron acceptor and the nitrate is reduced to nitrite. In the second step, the nitrite is further reduced to nitrogen gas. Nitrite production is an intermediate step, and there is no a priori reason to assume that the second reaction is at least as fast and/or favored as the first reaction in the presence of a specific bacterial population. Consequently, any evaluative scheme must establish that there is no buildup of nitrite, particularly because the nitrite-nitrogen maximum contaminant level (MCL) is only 1 mg/L, one-tenth that of nitrate. High concentrations of nitrate and high nitrate/methanol ratios may also affect the concentration of residual nitrite in a particular process configuration.

A simplified process diagram of the treatment system used during the demonstration is composed of two major components: a biodenitrification system and a polishing or posttreatment system. The biodenitrification system is intended to convert nitrates in the groundwater to nitrogen, thus reducing nitrate concentrations. The posttreatment system destroys or removes intermediate compounds generated during the biological breakdown of nitrate and removes bacteria and suspended solids that are not attached to the biocarrier. The posttreatment system can also incorporate treatment for other contaminants, such as VOCs, that may be in the influent.

Biodenitrification is conducted in two reactors, R1 and R2, respectively. The major part of the oxygen removal step is conducted in R1 where aerobic bacteria reduce the dissolved oxygen levels of the influent. Methanol is metered to the tank to encourage the bacteria to begin consuming nitrate. The resulting oxygen-deficient water is pumped from the bottom of R1 to the bottom of R2, which is densely packed with biocarrier media (1 cm) that have the appearance of small foam cubes. A patented mixing apparatus within R2 directs the incoming water into a circular motion, thus ensuring intimate contact with the biocarrier. Within R2, the majority of denitrification occurs by anaerobic bacteria that are continually fed methanol and populate on the large mass of biocarrier media. After a sufficient retention time, depending on concentration and goal, denitrified water drains by gravity to an overflow tank, which allows for continuous and smooth transfer to the posttreatment system and removal of entrained bacteria and media.

Depending on the presence of other contaminants, the posttreatment system consists of a series of varying

sized filters downstream of one or more contaminant-specific treatment units. For instance, ozonation may be used to oxidize any residual nitrite to nitrate and to deactivate/destroy all residual biological materials leaving the biodenitrification unit. If VOCs are present, an air stripper and/or carbon adsorption unit can be used. If state regulations require chlorination of drinking water, then chlorine can be added as a posttreatment or directly to the overflow tank immediately following denitrification.

Waste Applicability

Anoxic biodenitrification using one or more biocarriers should be applicable to industrial wastewaters and leachate from commercial, industrial, and hazardous waste sites containing various nitrate concentrations, as well as for treatment of groundwater (the medium treated during the demonstration). The presence of other contaminants could play a significant role in the effectiveness and viability of the overall treatment system. For example, if volatile chlorinated hydrocarbons are present along with nitrate, a postnitrate treatment system (e.g., carbon filters) may be necessary to remove those compounds to acceptable levels.

Demonstration Results

A site demonstration of the biodenitrification system was conducted at the location of a former public water supply well in Bendena, Kansas. This study, from May until December of 1999, was conducted in cooperation with the Kansas Department of Health and Environment (KDHE). The KDHE provided a small building and necessary utilities for the EcoMat systems. In addition, the state is analyzing water samples independently.

The demonstration focused on treating contaminated water from the Bendena Rural Water District No. 2 Public Water Supply (PWS) Well No.1. This former railroad well, constructed in the early 1900s, was at one time the sole source of water for the town of Bendena. The primary contaminant in the water is nitrate from uncertain sources ranging from 20 to 130 mg/L. Low concentrations of VOCs, particularly carbon tetrachloride (CCl_4), in the groundwater, ranging from 2 to 31 g/L, are a secondary problem.

The main goal of the study was to demonstrate that its biodenitrification system could reduce incoming nitrate-N in excess of 20 mg/L to a combined nitrate plus nitrite concentration below 10 mg/L. A second goal of the study was to demonstrate that the posttreatment system used would produce treated water that would meet applicable drinking water standards with respect to nitrate-N and nitrite-N; and that the final effluent would not have turbidity greater than 1 NTU, detectable levels of methanol (1 mg/L), increased levels of biological material or suspended solids, and a pH in the acceptable 6.5 to 8.5 range.

To evaluate both the biodenitrification system and the posttreatment system adequately, water samples were collected from four specific points along the entire process, which were (1) an influent sample point between PWS #1 and R1, (2) a partial treatment sample point between R1 and R2, (3) an intermediate effluent sample point between the biodenitrification system and the posttreatment system, and (4) a final effluent sample point downstream of the posttreatment system. To ensure a statistically adequate number of samples, an average of 30 influent and 30 effluent samples were collected for each of four separate sampling episodes. Over an approximate seven and one-half month period, EcoMat operated its system at a flow between 3 and 8 gallons per minute. Results from the biodenitrification process were encouraging when the entire system was operating at optimal performance. In those instances where the final combined nitrate-nitrite effluent concentration was above the regulatory limit, operating problems (mostly mechanical) were suspected as the primary cause.

REVERSE OSMOSIS TREATMENT

Reverse osmosis (RO) systems can often improve the quality of water. Reverse osmosis water treatment has been used extensively to convert brackish water or seawater to drinking water, to clean up wastewater, and to recover dissolved salts from industrial processes. It is becoming more popular in the home market as homeowners are increasingly concerned about contaminants that affect their health and about nonhazardous chemicals that affect the taste, odor, or color of their drinking water. People considering the installation of a water treatment system to reduce toxic chemicals should first have their water tested to determine how much, if any, hazardous compounds are in the water. Public water supplies are routinely monitored and treated as required under the federal Safe Drinking Water Act and state regulations. Private water systems should be tested at the owner's initiative based on knowledge of land use and contamination incidents in the area (9).

Reducing Contaminants through RO

Reverse osmosis reduces the concentration of **dissolved solids**, including a variety of ions and metals and very fine suspended particles such as asbestos, that may be found in water. An RO device may be installed following a water softener to reduce the concentration of sodium ions exchanged for hardness ions. RO also removes nitrate (NO_3^-), arsenic (As), chromium (Cr), certain organic contaminants, some detergents, and specific pesticides.

The Reverse Osmosis Process

In reverse osmosis, a cellophane-like membrane separates purified water from contaminated water. An understanding of osmosis is needed before further describing RO. Osmosis occurs when two solutions containing different quantities of dissolved chemicals are separated by a semipermeable membrane that allows only some compounds to pass through. Osmotic pressure of the dissolved chemical causes pure water to pass through the membrane from the dilute to the more concentrated solution. In reverse osmosis, water pressure applied to the concentrated side forces the process of osmosis into reverse. Under enough pressure, pure water is "squeezed" through the membrane from the concentrated to the dilute side. Salts dissolved in water as charged ions are repelled by

the RO membrane. Treated water is collected in a storage container. The rejected impurities on the concentrated side of the membrane are washed away in a stream of wastewater, not accumulated as on a traditional filter. The RO membrane also functions as an ultrafiltration device, screening out particles, including microorganisms, that are physically too large to pass through the membrane's pores. RO membranes can remove compounds in the 0.0001 to 0.1 micron range (thousands of times smaller than a human hair).

Design of an RO System

Although the reverse osmosis process is simple, a complete water treatment system is often complex, depending on the quality of the incoming water before treatment and the consumer's needs. Most home RO systems are point-of-use (POU) units placed beneath the kitchen sink to treat water used for cooking and drinking. Point-of-entry (POE) systems that treat all the water entering the household are more expensive to purchase and operate than POU systems.

A typical home reverse osmosis system consists of pretreatment and posttreatment filters as well as an RO membrane, flow regulator, storage container for the treated water, and dispensing faucet. The pressure for RO is usually supplied by the feed line pressure of the water system in the home, but a booster pump may be needed to produce an adequate volume of treated water. A sediment prefilter is essential for removing relatively large sand grains and silt that may tear or clog the RO membrane or clog a pump or flow regulator. Water softeners are used in advance of the RO system when household water is excessively hard. If the water is chlorinated or contains other oxidizing chemicals such as bromine, an activated carbon prefilter is needed to protect membranes sensitive to these chemicals.

To remove certain pesticides and organic solvents, activated carbon (AC) posttreatment must be included in the system. A standard AC filter positioned after the storage tank removes compounds that cause unpleasant taste and odors, including those from the tank or plastic tubing, just before water is dispensed. To remove high levels of organic chemicals such as trihalomethanes, volatile organic chemicals, and chloramines, an additional prolonged contact carbon filter (PCCF) is placed between the RO membrane and the storage tank. Combining an activated carbon filter with RO expands the range of chemicals the system can remove. Furthermore, AC treatment is improved because RO removes compounds that adversely affect AC adsorption.

The storage tank, tubing, and dispensing faucet should be made of plastic, stainless steel, or other nontoxic materials. The low pH and mineral content of RO-treated water may corrode copper pipes and allow lead to leach into the drinking water from brass components.

RO Membrane Materials

The most common RO membrane materials are polyamide thin film composites (TFC) or cellulosic types [cellulose acetate (CA), cellulose triacetate (CTA), or blends]. Very thin membranes are made from these synthetic fibers. Membrane material can be spiral-wound around a tube, or hollow fibers can be bundled together, providing a tremendous surface area for water treatment inside a compact cylindrical element (Fig. 1). Hollow fiber membranes have greater surface area (and therefore greater capacity) but are more easily clogged than the spiral-wound membranes commonly used in home RO systems.

The flux, or capacity, of the RO membrane indicates how much treated water it can produce per day. Typically, RO membranes for home systems are rated in the range of 10 to 35 gallons per day. Thus, under standard operating conditions it could take from 2 to 6 hours to fill a two and-a-half-gallon storage tank. CA/CTA membranes have adequate capacity for most households, but TFC membranes should be used if large volumes of treated water are needed.

RO membranes are rated for their ability to reject compounds from contaminated water. A rejection rate (% rejection) is calculated for each specific ion or contaminant as well as for reduction of total dissolved solids (TDS). It is important that consumers know their specific requirements for water quality when buying a system. For example, high rejection rates are essential when high nitrate or lead concentrations in the water must be brought below the EPA maximum contaminant or action levels.

Efficiency of RO Systems

The performance of an RO system depends on membrane type, flow control, feed water quality (e.g., turbidity, TDS, and pH), temperature, and pressure. The standard at which manufacturers rate RO system performance is 77 °F, 60 pounds per square inch (psi), and TDS at 500 parts per million (ppm). Only part of the water that flows into an RO system comes out as treated water. Part of the water fed into the system is used to wash away the rejected compounds and goes down the drain as waste. The recovery rate, or efficiency, of the system is calculated by dividing the volume of treated water produced by the volume of water fed into the system. If not properly designed, RO systems can use large quantities of water to produce relatively little treated water. Most home RO systems are designed for 20 to 30% recovery (i.e., 2–3 gallons of treated water are produced for every 10 gallons put into the system). Home RO systems can operate at higher recovery rates, but doing so may shorten membrane life. The flow regulator on the reject stream must be properly adjusted. If the flow is slow, the recovery rate is high, but RO membranes are easily fouled if concentrated impurities are not washed away quickly enough. If the flow is too fast, the recovery rate is low and too much water goes down the drain. Overall water quality affects the efficiency of an RO system and its ability to remove specific contaminants. The higher the TDS, the lower the recovery rate of treated water. The amount of treated water produced decreases by 1 to 2% for every degree below the standard temperature of 77 °F. An RO system supplied with well water at a temperature of 60 °F produces only three-quarters of the volume it would produce at 77 °F. For an RO system to function properly, there must be enough water pressure. Although most home RO systems are

rated at 60 pounds per square inch, the incoming feed line pressure of many private water systems is less than 40 psi. The RO system must work against back pressure created in the storage tank as it fills with water and compresses the air in the tank. The RO device must also overcome osmotic pressure, bonding between water molecules and dissolved impurities; the higher the TDS level, the greater the osmotic pressure. The net water pressure at the RO membrane can be calculated by subtracting back pressure and osmotic pressure from feed line pressure. If the net water pressure at the membrane is lower than 15 psi, treated water production is less efficient and contaminant rejection rates are lower. Auxiliary pumps can be added to the treatment system to boost pressure and improve the quality and quantity of water produced. High-quality RO systems have valves that shut off the flow whenever storage tank pressure reaches two-thirds of the feed pressure; at that point, low net water pressure can result in low rejection rates. In some systems, once the storage tank is filled, surplus treated water is discarded; water loss from such units is frequently excessive. A system that automatically shuts off when the pressure on the tank reaches a given level saves water.

Maintenance of an RO System

An RO system must be well maintained to ensure reliable performance. Clogged RO membranes, filters, or flow controls decrease water flow and system performance. If fouling is detected in early stages, the membrane can often be cleaned and regenerated. The cleaning procedure varies depending on the type of membrane and fouling. Completely clogged or torn RO membranes must be replaced. In addition, pre- or postfilters must be replaced once a year or more often, depending on the volume of water fed through the system and the quality of the feed water. Damage to RO membranes cannot be seen easily. The treated water must be analyzed periodically to determine whether the membrane is intact and doing its job. Many systems now have a built-in continuous monitor that indicates a high TDS level, a sign that the system is not operating properly. It may also be necessary to test regularly for specific health-related contaminants such as nitrates or lead. Microorganisms, dead or alive, can clog RO membranes. To prevent biofouling, RO units must be disinfected periodically with chlorine or other biocides provided by the manufacturer. Continuous chlorination can be used with cellulosic membranes to protect the system from biofouling and eliminate the particle-trapping slime that worsens other forms of fouling such as scaling. Chlorine and other oxidizing disinfectants are harmful to thin film composite membranes. If the feed water is chlorinated, an activated carbon unit must be used to remove the oxidizing chemicals before they reach the TFC membrane. Activated carbon (AC) prefilters should not be used on nonchlorinated water supplies because they provide a place for microorganisms to multiply and lead to increased biofouling of the RO membrane surface. It is important to replace AC filters periodically following the manufacturer's instructions, especially after an extended shutdown period during which microorganisms can flourish.

Choosing an RO System

Homeowners who are thinking about buying reverse osmosis systems should determine their initial water quality and their goals in adding water treatment systems. RO removes many inorganic impurities from drinking water, especially nitrate. Its effectiveness depends not only on the type of membrane but on feed water quality, temperature, pressure, and flow control, as well as the type and concentration of specific contaminants to be removed. A typical RO system consists of a sediment filter, pump, reverse osmosis membrane, flow regulator, storage tank, final activated carbon filter (for taste and odors), and dispensing faucet. An AC prefilter is sometimes needed for dechlorination. RO is commonly used to treat only the water used for drinking and cooking at the point of use rather than at the point of entry for all household use. RO membrane types vary in their ability to reject contaminants and differ in capacity (the volume of treated water produced per day). Water pressure is an important factor in determining the RO system's rejection rate, capacity, and recovery rate (amount of treated water produced per amount of feed water used). Maintenance of an RO system is essential for reliable performance. High levels of TDS and microorganisms in the system are commonly the cause of fouled membranes. Treated water should be monitored for TDS and the level of any specific contaminants that may affect health.

A list of home water treatment devices certified by various state Department of Health Services can be found on their web sites.

INNOVATIVE *IN SITU* TREATMENT

The following are advanced studies for *in situ* groundwater treatment containing nitrate.

Metallic Ion Treatment

Metallic iron was selected as a new reductant for chemically reductive removal of nitrate from water in this study (10). The effect of pH on the reduction rate and products of nitrate was investigated using a fixed dosage of iron powder (size: 80 mesh) of 12 mol-Fe:mol-N^{-1} under acidic (pH = 2–5) and aerobic conditions. The reduction of nitrate by metallic iron was a pseudo-first-order reaction under our experimental conditions. The reduction rate of nitrate increased with decreasing pH of the reaction solution, and the pseudo-first-order reaction rate constants were 0.49, 0.40, 0.05, and 0.01 h^{-1} at pH = 2, 3, 4, and 5, respectively. The reduction products of nitrate were ammonia and nitrogen gas, and their yields were strongly affected by pH. The yields of nitrogen gas were 30, 31, and 45% at pH = 3, 4, and 5, respectively, but no formation of nitrogen was found at pH = 2. It was also demonstrated that the indirect reduction of nitrate by hydrogen generated from the reaction between protons and metallic iron may be a major mechanism for the reduction of nitrate under the experimental conditions.

Wetland Treatment

Constructed wetlands have become popular, mainly for polishing wastewater effluent (11). In the arid southwest,

where natural wetlands have all but disappeared, constructed wetlands can be a significant wildlife attractant. In our arid climate, wildlife enhancement can be considered an "intermediate" use of wastewater before it is discharged or recharged to aquifers. Despite the widespread popularity of wetlands, our understanding of the biogeochemical transformations occurring in wetlands is lacking. Furthermore, the "black box" design approach commonly used for designing treatment wetlands is archaic.

The C:N Ratio as a Design Guideline. Baker also evaluated the effect of hydraulic loading rate (HLR) and carbon addition (chopped up cattails that were "fed" to the microcosms once a week) on nitrate removal in microcosms that received water containing 30 mg NO_3-N/L. We found that the "critical" C:N ratio for denitrification was 5:1 and that the denitrification rate constant varied linearly with carbon addition.

As wetlands are inherently well suited for nitrate removal (carbon supplied by plants; anoxic mats), potential N removal rates are much higher for wetlands receiving nitrate than for wetlands receiving nonnitrified wastewater. Nitrate treatment wetlands could have broad application for treating irrigation return flow, remediating nitrate-contaminated aquifers, and removing nitrate in nitrified wastewater effluents prior to recharge.

Model of N and C Transformations in Wetlands. During 1996, nitrogen transformations were studied in a wetland receiving lagoon effluent in Kingman, Arizona. In this study, various N species (SON, PON, ammonium, nitrate) were measured for 10 months at 13 locations along the longitudinal axis of the wetland. On average, the wetland removed 75% of input N. Effluent TN levels were consistently <15 mg/L and NO_3-N was always <10 mg/L. In the same study, it was found that effluent DOC concentrations represent the balance between the degradation of DOC in wetland inflow (lagoon effluent) and DOC produced by decomposition of plants.

Low-Tech Wastewater Reuse System. Others have studied the potential for using wetlands as part of a low-tech approach to treat and recharge wastewater in small towns in the United States and Mexico that have limited water supplies and must recycle wastewater if they continue to grow. Proposed systems would treat effluent from an existing aerated lagoon in a wetland; the effluent from the wetland would then be infiltrated through the soil to recharge groundwater. The lagoon would provide most of the BOD and SS removal. Further removal of SS, BOD (and DOC), and most of the N removal would occur in the wetland. Infiltration would remove additional DOC and filter most pathogens. Finally, we developed an integrated design concept that incorporates a "plug flow" component to assure high-level treatment and more natural components (pools; riparian areas) for wildlife habitat.

In Situ Iron Filing Curtain Treatment of Nitrate Contaminated Agricultural Runoff

The common agricultural practice of overapplying slow-release nitrate-based chemical fertilizers, such as ammonium nitrate, and livestock waste disposal practices can result in substantial levels of nitrate (NO_3^-) concentrating in agricultural water runoff that enters streams, rivers, and groundwater aquifers. In many agriculturally intensive regions, the groundwater nitrate concentration exceeds human drinking water standards. These agricultural regions quite often face restricted land development opportunities as strict government nitrate approval criteria are often imposed on developers to ensure that the problem is not worsened by adding new residential and commercial sources of potential nitrate contamination. Beyond the immediate human health impacts, nitrate-laden agricultural runoff that enters rivers and lakes also represents a significant contributor to excessive growth of algae blooms that can negatively impact these ecosystems.

In recognition of these impacts, a passive reactor system for containing and treating nitrate-contaminated agricultural runoff has been developed. Nitrate-laden runoff is gravity conveyed by land drain pipes or ditches to a collection reservoir. The contained runoff is then further gravity fed through a reactor system that is kept under anaerobic conditions and uses a reactive porous carbonaceous medium to convert the nitrates to a less harmful form of nitrogen. In most practical applications of the technology, the low-cost and easily constructed reservoir and reactor system can be passively connected to the end of an existing farm field drainage tile system without any requirement for pumping or chemical addition equipment and without maintenance requirements for many years after installation.

A small-scale field test was completed during June 1991 to May 1992, the results of which were documented in a paper accepted by the *Journal Contaminant Hydrogeology* (7/93). More recently, the technology has been commercially applied at several other sites in Ontario. Canadian patent #2068283 has issued, and the technology is available for licensing in Canada. U.S Patent #5,330,651 has been issued, and the technology is licensed in the U.S to Lombardo Associates Inc. (www.lombardoassociates.com), Contact:

G.G.H. Gray, Director
gghgray@uwaterloo.ca July 2002.

In Situ Electrokinetic Treatment

Electrokinetic treatment of nitrate, chromium, arsenic, and manganese may provide a cost-effective solution (12).

The electrokinetic treatment process involves applying direct current (dc) in a medium (soil and water). The flow of electrons from anode to cathode creates a migration of cations in the medium toward the cathode. The electrolysis of water creates a higher pH and oxidizes the metal or reduces the valence of the metal which renders the metal into a nontoxic form near the cathode. Clayey material may show a dramatic increase in cation exchange capacity under a high pH near the cathode. The proposed electrokinetic process can be applied both *in situ* and *ex situ*. Figure 1 presents a more realistic distribution of the various valence states of metals under the proposed *in situ* electrokinetic influence.

Besides the treatment of the metals, the beneficial side effects of the *in situ* EK treatment are as follows:

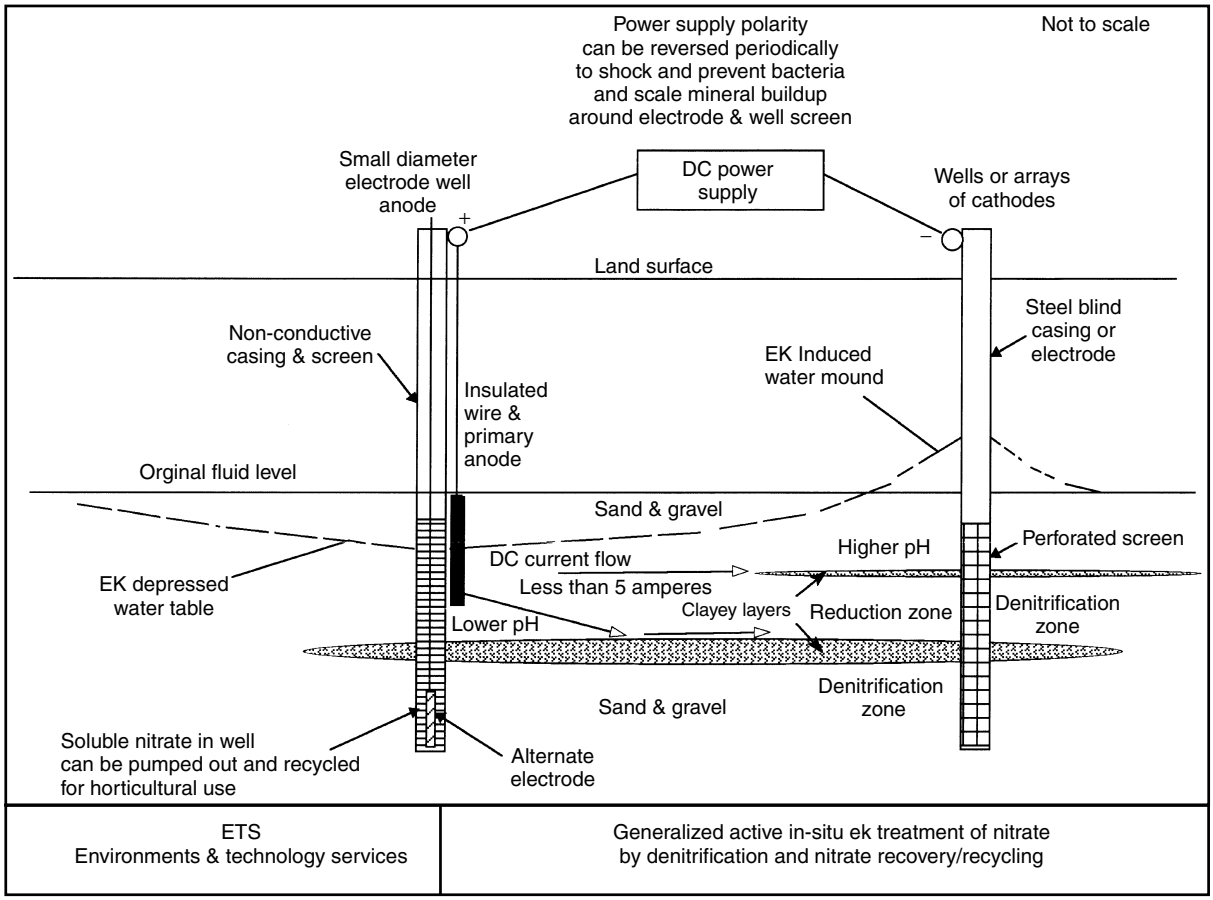


Figure 1. Generalized active *in situ* EK treatment of nitrate by denitrification and nitrate recovery/recycling.

1. The well itself is set up as cathode, so iron bacteria will not live on the surface of the well casing and perforation because of the high pH.
2. The electrokinetically induced water migration toward the cathode (well) may induce an increase in hydraulic head thus increasing well yield.

No large-scale treatment has been tried on nitrate, chromium, arsenic, and manganese in a saturated medium to date. There are many successes of the proposed EK process in the laboratory and in soil. However, we have successfully demonstrated the electrokinetic control of nitrate, selenium, and boron in clayey saturated media at two sites in the Panoche Irrigation District, Central Valley, California. We believe that the same EK control can be applied to nitrate because of the similarity of the electrochemical processes (Fig. 1).

Due to the simplicity of the cathode and anode setup, we believe that the proposed EK processes will prove very cost-effective. In particular, the proposed *in situ* EK treatment (once set up) is permanent. It has a one time capital cost and minimum long-term maintenance costs. The continuous operating electricity demand will not exceed 50 amperes at 30 to 100 Vdc or 1500 w to 5000 watts per site.

BIBLIOGRAPHY

1. Jennings, G.D. and Sneed, R.E. (1996). *Nitrate in Drinking Water*.
2. Downes, C.J. (1985). *Groundwater Quality*. Wiley, New York, Chap. 7, Fig. 7.4, p. 102.
3. Pye, V.I. and Kelley, J. (1984). *The Extent of Groundwater Contamination in the United States*. National Academy Press, Washington, DC, pp. 23–33.
4. Devinny, J.S. et al. (1990). Subsurface migration of hazardous wastes. In: *Microbiology of Subsurface Wastes*. Van Nostrand Reinhold, New York, pp. 116–141.
5. Freeze, A.R. and Cherry, J.A. (1979). *Groundwater*. Chap. 2: Physical Properties, pp. 15–79; Chap. 9.3: Hydrochemical Behavior of Contaminant–Nitrogen, pp. 413–416, Prentice-Hall, Englewood Cliffs, NJ.
6. Hem, J.D. (1989). *Study and Interpretation of the Chemical Characteristics of Natural Water—Occurrence of Nitrogen in Water*. US Geological Survey Water-Supply Paper 2254, pp. 125–126.
7. Zuane, J.D. (1997). *Handbook of Drinking Water Quality*.
8. EPN. Superfund Innovative Technology Evaluation Demonstration Bulletin Biological Denitrification Process - EcoMat, Inc. EPA/540/MR-01/501.
9. Kneen, B., Lemley, A., and Wagenet, L. (1995). *Reverse osmosis treatment of drinking water*. Fact Sheet 4. Cornell Cooperative Extension, New York State College of Human Ecology.
10. Hu, H.-Y. et al. (2001). Reductive treatment characteristics of nitrate by metallic iron in aqueous solution. *J. Chem. Eng. Jpn.* **34** (9): 1097–1102.

11. Gerke, S., Baker, L., and Xu, Y. (2001). Sequential model of nitrogen transformations in a treatment wetland receiving lagoon effluent. *Water Res.* **35** (16): 3857–3866.
12. Lehr, J.H. (Ed.). (2001). *Standard Handbook of Environmental Health, Science and Technology*. Chapters 14.4 & 14.6 on Bioremediation & Electrokinetic Treatment of Hazardous Wastes by Walter W. Loo, MacGraw-Hill, New York.

NONPOINT SOURCES

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In recent years, it is being recognized that the nonpoint sources of water pollution have greater importance than point sources, which is due in part to the continuing efforts to reduce pollution from point sources during the past few decades, as well as recognition that nonpoint sources, such as storm water, may contain harmful contaminants. Modern agriculture has also relied, among other things, on heavy use of fertilizers and pesticides. This has largely occurred without any serious regard to the environmental consequences, especially pollution of both surface and groundwater resources. Chemicals (fertilizers and pesticides) applied in agroecosystems invariably enter the hydrologic cycle and contaminate both surface and groundwater resources. Nutrients and pesticides, particularly, are of major concern because of eutrophication and toxicity. Nutrients and pesticides are transported from cropland either by being absorbed onto eroded soil particles or dissolved in runoff water, which has increased the need to identify and quantify major sources of nutrients and pesticides deposited within river systems. In this article, some basic concepts of nonpoint source pollution, including the effects and extent of pollution in surface and groundwater bodies, pollution control measures, monitoring and modeling approaches, and management options are presented.

INTRODUCTION

The assessment of nonpoint source (NPS) pollution is a perfect example of a spatially and temporally complex, multidisciplinary environmental problem that exists on multiple scales. Nonpoint source pollution accounts for more than 50% of total water quality problems. In many areas, nonpoint source pollution, such as runoffs from cropland, urban storm water, strip mining, and construction sites are becoming major water quality problems (1). Agriculture is often considered the largest contributor to nonpoint source pollution of both surface and subsurface systems. It is mainly responsible for degrading river water quality by generating runoff from animal husbandry units, which contain predominantly organic compounds from the use of mineral fertilizers and chemical pesticides.

The problem of NPS pollution is being recognized and systematically studied in Western countries (2–8) this is not so in developing countries where agricultural pollution is usually complicated by urban and industrial pollution (9). The factors that influence nonpoint source pollution include soil erosion, sedimentation, and erosion of stream banks; washing out nutrients and organic material from livestock wastes and agricultural land; storm runoff from urban areas; and atmospheric deposition. Adsorption to the surface of sediment particles provides a mechanism for transporting many contaminants derived from agricultural fertilizers, pesticides, and industrial wastes. Deposition of sediments carrying such loads in a channel or on a flood plain can have detrimental consequences for ecology and agriculture. The sediment released into a river system can promote channel instability and cause bed degradation.

In most cases, the sources and concentrations of nonpoint source pollutants result from land use interactions with the transport system. It is a source transport problem in which the hydrologic cycle provides the transport processes to move pollutants from the source to groundwater, a stream, or a reservoir. Nonpoint sources can be urban, industrial, or agricultural pollutants that are distributed over the surface. The mode of transport is the flow of water across the soil surface and in stream channels and reservoirs or the flow of water through the soil profile.

The problem of nonpoint source pollution does not involve only the traditional pollution parameters such as suspended sediment, biochemical oxygen demand (BOD), and dissolved oxygen (DO). Some of the most serious nonpoint pollution problems do not have a parallel in the traditional point source oriented environmental pollution control area. These problems include nutrients (nitrogen and phosphorous); PCB (polychlorinated biphenyl) contamination; acid rain; and pesticide contamination of surface water, groundwater bodies, and aquatic biota.

In recent years, exponential growth in population and fragmentation of farm families have caused a reduction in land holding size, consequently forcing the farmers toward intensive cultivation (10) that leads to increased soil and nutrient loss. According to Wollast (11), the increase in the dissolved nitrogen flux in rivers represents 30% of the nitrogen fixed annually by humans in combustion processes and fertilizer production. For phosphorous, the increase is only 15% of the total phosphorous mined annually. The increased biological activity due to the entry of N and P in rivers had led in some cases to anoxia and consequent fish mortality.

To understand the nitrogen and phosphorous concentrations in surface waters, one should always take into account factors such as current and historic nutrient inputs to agricultural land from fertilization and atmospheric deposition, soil type, hydrology, historical landuse, and climatic conditions. Preferential flow also plays an important role in the subsurface losses of nutrients in many soils, especially after longer periods of drought.

Various pathways are involved in transporting N and P into a river system. Depending on the pH and temperature of soils, NH_4^+ and NO_3^- ions are produced in a watershed through ammonification and nitrification

of organic matter and are mobilized into rivers through runoffs. The weathering of apatitic rocks is the major natural source of PO_4^{3-}. Rain is a source of dissolved N and S. N, P, and S from fertilizer application, sewage, and nonpoint source runoff contribute significant quantities of dissolved species of N, P, and S near human habitation.

Modern high yielding crops generally require adding fertilizers, which can be inorganic or organic. Annual uptake efficiencies by crops are relatively poor, approximately 50% and 20% for N and P, respectively (12,13). Fertilizer application rates have increased considerably during the last two–three decades (14), which has resulted in the possibility of increased NO_3-N losses from terrestrial systems into watercourses through surface runoff and/or by leaching through the soil profile (15). The relative contribution of individual sources and processes to N and P losses varies spatially and temporally; it is greatly influenced by climatic and management factors.

As per the National Water Quality Inventory Report, nonpoint agricultural pollution significantly affects water quality in 68% of the drainage basins in the United States (16). It has been reported that agricultural pollution contributes 60% of the BOD, 64% of suspended solids, and 76% of total phosphorous discharged into water resources (17).

In the Great Lakes region (18,19), the phosphorous contribution from nonpoint sources represents roughly 50% of the total load to Lakes Superior, Huron, and Erie and exceeds municipal and industrial point sources. The balance is due to atmospheric fallout and shoreline erosion. Phosphorous is the limiting nutrient for controlling eutrophication of most of the Great Lakes. More than 90% of the total loading to Lakes Superior, Michigan, Huron, and Ontario originates from nonpoint sources. In addition, the International Joint Commission research (19) has found that diffuse sources, including atmospheric inputs, account for the major loading of PCBs and organic chemicals to the lakes.

Several articles discuss the urgent need for and the problems of controlling nonpoint sources of water pollution from agriculture, and others evaluated the economic aspects of controlling NPS pollution. Wallace et al. (20) presented an example of a point-NPS trading framework developed to help a discharger comply with load allocation constraints in the Minnesota River. Hoag and Hughes-Popp (21) compared the theory of pollution credit trading and its application in the Tar-Pamlico nutrient-trading program in North Carolina, where point-NPS trading is possible. The article evaluated transaction costs, number and relative discharge of participants, abatement costs, enforcement costs, trading ratio, and loading limits and identified factors that encourage or discourage trades.

SURFACE WATER PROBLEMS

In recent years, it is being recognized that nonpoint sources of water pollution have greater importance than point sources. Several studies on the nutrient levels in surface waters from agricultural watersheds have been conducted in Pennsylvania, Maryland, Delaware, North Carolina, Colorado, Denmark, and Wisconsin (22). Increased nitrogen concentrations were correlated with a greater portion of cropland area in several Chesapeake Bay watersheds (23,24), whereas phosphorus concentrations did not correlate with land use. Sediments in agricultural drainage basins were reportedly enriched with phosphorous in Delaware's Inland Bays (25,26). Deletic and Maksimovic (27) studied the water quality of storm runoff at two experimental catchments in Belgrade, Yugoslavia, and Lund, Sweden. Rai and Sharma (28) made a comparative assessment of runoff characteristics under different land use patterns within a Himalayan watershed and reported that a large quantity of sediments leaves the watershed through its rivers.

Heathwaite and Johnes (29) studied the contribution of nitrogen and phosphorous from agricultural catchments by monitoring the chemical composition of these nutrients in agricultural runoff for both surface and subsurface flow pathways. In another publication, Heathwaite et al. (30) studied the role of nitrogen and phosphorous as key nutrients that determine the trophic status of water bodies. The paper primarily focuses on results from North America and Europe, particularly for the United Kingdom where a wide range of data exists. It is reported that, in general, N and P concentrations have increased dramatically (>20 times background concentrations) in many areas and causes vary considerably, ranging from urbanization to changes in agricultural practices. Johnes and Heathwaite (31) also modeled the impact of agriculture on the nitrogen and phosphorous loading in the surface waters of two contrasting agricultural catchments.

The concentrations of pesticides in surface waters in agricultural watersheds were monitored in Arkansas (32), Nebraska (33), Idaho and Wyoming (34), California (35), and France (36). The pesticides detected include Metolachlor, atrazine, norflurazon, cyanazine, simazine, isoproturon, and organophosphate in varying concentrations. Several studies have also been carried out to evaluate the impact of pesticides on management practices (37–40).

Laroche et al. (41) used model HSPF to study the transport of pesticides on a 78-ha watershed in the province of Quebec, Canada. Pesticide concentrations were measured at the outlet of the watershed from February to November 1993. This short period of time allowed calibrating the pesticide component but precluded verification. Variations of atrazine concentration were well simulated by the Hydrological Simulation Program FORTRAN (HSPF), simulated concentrations were in the same range as observed values, and peak concentrations occurred at the same time.

Surface water-quality impacts of urban and industrial land uses were monitored in Texas (42), Utah (43), North Carolina (44), South Africa (45), and Singapore (46). Results from these studies indicated that urban land uses contribute varying levels of metals, bacteria, sediment, nutrients, and organic chemicals to surface waters. Line et al. (44) showed that metal concentrations in runoff from industrial sites varied significantly for various categories of businesses. Regarding sources of nutrients in urban areas, Linde and Watschke (47) reported that, on average, 11% of applied phosphorus and 2% of applied nitrogen were

detected in runoff from turf grass plots, whereas 14% of phosphorus and 3% of nitrogen were detected in leachate.

Bouraoui and Diallaha (48) developed a nonpoint source pollution management model (Answers-2000) to simulate long-term average annual runoff and sediment yield from agricultural watersheds. The model is based on the event-based Answers model and is intended for use without calibration. Wong et al. (49) developed a land use runoff model for Santa Monica Bay using a geographic information system (GIS) coupled with an empirical runoff model. The GIS/model has simple data requirements compared to more complex models that require routing information and is useful for predicting receiving water loading on an annual basis or for single storms.

GROUNDWATER PROBLEMS

There is wide concern in developed countries that groundwater resources are deteriorating in the long term, both in quantity and quality. Groundwater pollution is a major concern mainly because of the implications for human health when it is used for drinking water. Many of the most serious sources of health risk, such as bacterial and viral infection and toxic metals, do not have a specific agricultural origin. However, nitrates, as a cause of methaemoglobinaemia, and pesticides, which have a suspected disturbingly wide array of health effects, have largely agricultural origins and are a major concern.

Concentrations of nitrogen in groundwater are an important concern because a large number of people use groundwater as their drinking water supply. In addition, much of the nitrogen entering our streams and lakes comes from nitrates in groundwater. When urea is applied as a deicing agent during the winter, large concentrations of ammonium are observed at all soil depths; however, over time, the ammonium is oxidized to nitrate, which leaches into the groundwater (50).

Nolan et al. (51) prepared national maps of groundwater vulnerability to nitrate contamination for the United States using different input parameters (population density and the amount of nitrogen contributed by fertilizer, manure, and atmospheric sources) and aquifer vulnerability (soil drainage characteristics and the ratio of woodland acres to cropland acres in agricultural areas). In England and Wales, 125 groundwater sources supplying 1.8 million people had nitrate concentrations exceeding 50 mg/L (52).

Unfortunately, very little has been done in India to carry out well-planned primary field studies to assess the impact of nonpoint source pollution. Agarwal et al. (53) reviewed the status of the diffuse agricultural nitrate pollution of groundwater in India and reported that nitrate levels in groundwater across vast agricultural areas can be correlated with intensive irrigated agriculture, corresponding use of nitrogenous fertilizers, and groundwater development. It is further reported that diffuse agricultural pollution has already endangered the safety of potable groundwater for future generations in both rural and urban areas.

In recent years, there has been a considerable rise in the number of reported incidents of pesticide contamination in groundwater due to excessive use of pesticides in agriculture. Monitoring of pesticides in central South Dakota indicated that the movement of pesticides is controlled primarily by the geological and chemical characteristics of the medium and pesticides (54). Milde et al. (55) reported the occurrence of 22 different pesticides in 34 locations in the United States and Europe. In Britain, the most extensive survey of pesticides in surface waters and groundwaters has taken place in the Anglian region where herbicide usage on cereals has been the greatest.

Milde et al. (55) stated that the main factors influencing the contamination potential of any pesticide are molecular structure, formulation, metabolism, water solubility, adsorption by soil, the retardation factor, and resistance to chemical and biochemical degradation. The time, quantity, and frequency of application, as well as the local hydrogeologic and meteorologic conditions, also affect the quantity of pesticides that reach the water table. Kolpin et al. (56) found that 70% of all 106 municipal wells sampled were contaminated by pesticides and that the different types of aquifers affected pesticide leaching differently.

Numerous workers have studied the processes that affect the movement of pesticides into groundwater. Sorption of pesticides on different types of colloids and subsequent movement of these colloids through the soil profile were studied, and the researchers found almost no increase in the transport of atrazine (57). When fluxes of pesticides from a stream bed were measured, it was found that pesticide fluxes of atrazine were two to five orders of magnitude greater in the stream bed than fluxes of atrazine through agricultural fields (58). Guo et al. (59) found that the concentration of organic matter in the soil profile affects the transport of atrazine through the soil profile. Kolpin (60) studied the effects of land use on concentrations of agricultural chemicals and reported that the concentrations of atrazine and nitrate were positively correlated with the amount of irrigated land area and that alachlor was inversely related to the amount of highly erodible land.

Loague and Corwin (61) presented a regional-scale assessment of nonpoint source groundwater contamination, and Takarate et al. (62) studied the effect of hydrology, vegetation, and substrate on the spatial and temporal variations of nutrient concentrations in the groundwater of a flood plain. It is reported that on the regional scales associated with NPS agrochemical applications, there are staggering data management problems in assessing potential groundwater vulnerability. Geographical information system (GIS) is a timely tool that greatly facilitates the organized characterization of regional-scale variability. The strengths and weakness of using GIS in regional-scale vulnerability assessments (owing to both data and model errors) have also been discussed. A regional GIS-driven integrated assessment approach is discussed, which is based upon cost–benefit analysis and incorporates both physical and economic factors that can be used in a regulatory decision process.

POLLUTION CONTROL MEASURES

Concern for nonpoint source pollution in integrated water quality management has been growing recently. Such

sources are likely to be more critical in developing countries, where agriculture and rural habitats are still dominant. The term pollution control refers to regulation of pollutants from individual outfalls or nonpoint sources, including urban developing lands, feedlots, agricultural areas, and other pollution generating land uses. The purpose of all pollution control programs is to protect the capacity of surface waters to assimilate pollution without damage or impairment of their use, to protect shellfish and wildlife, to preserve or restore the aesthetic and recreational values of surface waters, and to protect humans from adverse water quality conditions (63).

Water quality management deals with all aspects of water quality problems for all beneficial uses of water or lands from which pollution originates, whereas pollution control is mostly understood as the safe disposal of wastewater and its treatment. Water quality and pollution are determined by comparing measured physical, chemical, biological, microbiological, and radiological parameters to a set of standards and criteria.

The water quality standards used presently by water pollution engineers and scientists as well as pollution abatement authorities throughout the world are either stream standards or effluent standards. The effluent standards, which determine how much pollution can be discharged from municipal and industrial wastewater sources, are of lesser importance in nonpoint source pollution control and management. Performance standards, the equivalent of effluent standards to control pollution from lands, have been used by some local authorities to control pollution from subdivisions, construction areas, and mining. The stream standards can be related to the protection of aquatic habitat and biota and/or to intended downstream use of water.

Nutrient Control

The control of nutrients is an important issue throughout the world, both from a public health perspective and to keep natural waters free from eutrophication. The most widely used water quality standard for nitrate is the 50 mg/L limit adopted by the WHO as a precautionary level to safeguard babies from the risks of contracting methaemoglobinaemia (64). Most national authorities regard the 50 mg/L concentration as a realistic target in relation to eutrophication and, therefore, programs aimed at controlling eutrophication often use this value as an EQS. Whereas there are techniques available to remove nitrate from drinking water after it has been abstracted, the eutrophication problem is universally dependent on the control of nitrate sources.

An added and unexpected health implication related to eutrophication exists, particularly in lakes. In a number of countries in the world, the phenomenon of excessive growth of blue-green algae has caused concern where recreational pursuits take place on the lakes and also where the water is withdrawn for public supply, which is due to the recognition that such algae produce a number of toxins, which, if ingested, can cause liver damage. There are a number of well-documented cases where animals are known to have died as the result of drinking water heavily laden with these algae and, for this reason alone, nutrient control is justified.

The reduction of nitrogen and phosphorous from agriculture relies upon changes in farming practices because they give rise to diffuse sources. Plowing of grassland and other crops, particularly during autumn, leads to the release of large quantities of soil nitrogen and, therefore, a general move toward permanent pasture regimes assists in lowering nitrate leaching. When this is not possible, the use of short-term rotational crops to take up nitrogen followed by their harvesting and subsequent removal from the catchment is helpful. Animal wastes should be used carefully, avoiding overuse and direct runoff into watercourses, but wherever possible they should be used in place of synthetic fertilizers. Spreading of cattle manure and liquid sludge should be banned when aquifers are being replenished by rains. A manuring season should be prescribed for main crops depending on monsoon and crop patterns in different regions. The use of biofertilizers and green manures should be encouraged, and research needs to be undertaken to improve their quality and efficiency. Use of all types of fertilizers should be carefully controlled and matched to crop requirements.

One of the most important aspects of controlling phosphorous inputs from agriculture is the need to prevent erosion from field surfaces. Phosphates tend to bind to soil particles which, washed from fields into watercourses, become a source of phosphate in suspended form and in deposited sediments. Sediments act as a long-term source of phosphate by releasing it (i.e., by redissolution) under certain environmental conditions. Physical removal of the sediment layer to remove the bound phosphate from the catchment has been tried in a number of locations around the world. Some success has been achieved in lowering phosphate levels in the Norfolk Boards in England by a combination of diverting effluents containing phosphorous out of the area, phosphorous stripping at sewage treatment works, and by dredging 1 m of sediment. Concentrations below the target of $100\ \mu g\ L^{-1}$ of phosphorous were reached (65).

In addition to agricultural sources, phosphate occurs in sewage effluents as a result of its use in detergents. Control of phosphate at the source is not yet practiced, and removal relies on stripping of the orthophosphate from the sewage works effluent by chemical treatment. Reductions in the polyphosphate content of some detergents may also help in controlling phosphate.

Pesticide Control

Pesticides represent a particularly difficult area of pollution control, not only because the environmental effects in relation to aquatic flora and fauna are important but because human health issues have a very important bearing on the nature of the control applied. There are several thousand formulations of insecticides, herbicides, and fungicides in common use and, therefore, the potential for water pollution is very high. There are also very stringent limits on pesticides in water used for public supply and, consequently, the control of pollution from pesticides is quite crucial.

Many pesticides in water are derived from agricultural use, and it is therefore difficult to regulate their input to water bodies. Regulation can take place only by

prevention, by indirect controls on their manufacture, storage, and use. Approval for the use of pesticides is granted in the United Kingdom by the government, following expert assessment of safety and environmental risks. The active ingredients in pesticides are approved by the European Union and placed on an approved list. This Directive allows authorization provided that the pesticide is not expected to occur in groundwater at concentrations above 0.1 μg/L. Further controls are also placed on products by Directives such as that on Classification, Packaging and Labelling of Dangerous Substances.

WATERSHED MANAGEMENT PLANNING

Watershed management essentially relates to soil and water conservation by proper land use, preventing deterioration of the soil, increasing and maintaining soil fertility, reducing soil erosion, conserving water for drinking and other farm uses, increasing the availability of basic resources, and achieving the optimum productivity of land uses (66). Rai et al. (67) described the traditional conservation practices and relationship to land use in Mamlay watershed in the Sikkim Himalaya. It was observed that the agricultural land area has considerably increased during the past 40 years (66,67). The soil without tree cover on steep upland farming systems associated with more intensive agricultural practices is vulnerable to soil erosion and reduced fertility (10).

In several countries, the process of catchment or watershed planning has been introduced. Catchment management plans are designed to cover the catchment of a river and its tributaries and any associated groundwater flows. Catchment management plans are designed to be strategic in approach and to take into account regional and national policies and all activities likely to have an impact on the watercourse. As a result of the plan, the main polluting sources may be identified and solutions agreed to which can be achieved with available resources and on a timescale agreed to by all concerned.

CONCLUSION

Nonpoint source pollution is a worldwide problem and has been responsible for contamination of both surface as well as groundwater resources. The problem is a complex function of many physical, chemical, and biological interactions in relation to soil type, management practices, and climatic conditions. As progress has been made in reducing pollutant loading from point sources, the relative importance of nonpoint sources has increased. Such sources are likely to be even more critical in developing countries, where agriculture and rural habitats are still dominant. A number of special features need to be considered to tackle the problem of nonpoint source pollution. These include (1) extremely varying rainfall and stream flow pattern; (2) still largely traditional agricultural practices, average application of fertilizers and pesticides, and significant areas under farming or only marginal irrigation; (3) a very large cattle population, where agriculture is almost always linked to animal husbandry; and (4) a culture of living close to the river with dominating in-stream uses of bathing, washing, cattle wading, waste disposal, etc. and large-scale floodplain farming. There is a need to address the problems of nonpoint source pollution and to manage it as carefully as point source pollution. Catchment management plans may be designed to cover catchments of different river systems and their tributaries and associated groundwater flows. The plans should be strategic in approach and should take into account regional and national policies and all other such activities, which are likely to have an impact on the watercourse.

BIBLIOGRAPHY

1. Alexander, G.R. (1976). Best management practices for non-point source control. In: *Proc. of the Best Management Practices for Non-point Source Pollution Control Seminar*, EPA 905/76-005, U.S. Environmental Protection Agency, Chicago, IL, p. 3–5.
2. Strebel, D., Duynisveld, W.H.M., and Bottcher, J. (1989). Nitrate pollution of ground water in western Europe. *Agri. Ecosystem and Environment* **26**: 189–214.
3. Fried, J.J. (1991). Nitrates and their control in the EEC aquatic environment, Nitrate Contamination: Exposure, Consequence, and Control. *NATO ASI Ser. G.: Ecological Science 30*. I. Bogardi and R.D. Kuzelka (Eds.). Springer Verlag, New York.
4. Frink, C.R. (1991). Estimating nutrient exports to estuaries. *J. Environ. Qual.* **20**: 717–714.
5. Goodrich, J.A., Lykims, Jr., B.W., and Clark, R.M. (1991). Drinking water from agriculturally contaminated groundwater. *J. Environ. Qual.* **20**: 707–717.
6. USEPA. (1992). *1990 National Water Quality Inventory*. Report to Congress, Washington, DC, p. 305b.
7. Cooper, C.M. (1993). Biological effects of surface water pollutants on aquatic systems—a review. *J. Environ. Qual.* **22**: 402–408.
8. Spalding, R.F. and Exner, M. (1993). Occurrence of nitrate in groundwater: A review. *J. Environ. Qual.* **22**: 392–402.
9. Duda, A.M. (1993). Addressing non-point sources of water pollution must become an international priority. *Water Sci. Tech.* **28**(3–5): 1–11.
10. Rai, S.C. and Sharma, E. (1995). Land use change and resource degradation in Sikkim Himalaya: A case study from the Mamlay watershed. *Sustainable Reconstruction of Highland and Headwater Regions*. R.B. Singh and M.J. Haigh (Eds.). Oxford & IBH Publishing, New Delhi, pp. 265–278.
11. Wollast, R. (1983). Interactions in esturies and coastal waters. In: *The Major Biogeochemical Cycles and Their Interactions*. B. Bolin and R.B. Cook (Eds.). John Wiley, Chichester, UK, pp. 385–407.
12. Nielsen, N.E., Schjorring, J.K., and Jensen, H.E. (1987). Efficiency of fertilizer uptake by spring barley. In: *Nitrogen Efficiency in Agricultural Soils*. D.S. Jenkinson and K.A. Smith. (Eds.). Elsevier Applied Science.
13. Holford, I.C.R. and Doyle, A.D. (1993). The recovery of fertilizer phosphorous by wheat, its agronomic efficiency and their relationship to soil phosphorous. *Aus. J. Agric. Res.* **44**: 1745–1756.
14. World Fertilizer Consumption Statistics. (1992). International Fertilizer Industry Association, No. 24.
15. Vinten, A.J.A., Howard, R.S., and Redman, M.H. (1991). Measurement of nitrate leaching losses from arable plots

under different nitrogen input regimes. *Soil Use Magmt.* **7**: 3–14.

16. National Water Quality Inventory. (1978). Report to Congress U.S. Environmental Protection Agency, Washington, DC.
17. Duda, A.M. and Johnson, R.J. (1985). Cost effective targeting of agricultural non-point source pollution controls. *J. Soil Water Conserv.* **40**: 108.
18. Sonzogni, W.C., Monteith, T.J., Bach, W.N., and Hughes, V.G. (1978). *United States Great Lakes Tributary Loadings*. International Joint Commission, Ontario, Canada.
19. PLUARG. (1978). *Environmental Management Strategy for the Great Lakes Systems*. International Joint Commission, Ontario, Canada.
20. Wallace, S., Micheletti, B., and Sparks, C. (1997). Nonpoint source trading creates new discharge opportunities. *Industrial Wastewater* **5**: 12.
21. Hoag, D.L. and Hughes-Popp, J.S. (1997). Theory and practice of pollution credit trading in water quality management. *Rev. Agric. Econ.* **19**: 252.
22. Owens, D.W., Corsi, S.R., and Rappold, K.F. (1997). *Evaluation of nonpoint-source contamination, Wisconsin: selected topics for water year 1995*. U.S. Geol. Surv. Open-File Rep. 96-661 A, Denver, CO.
23. Jordan, T.E., Correll, D.L., and Weller, D.E. (1997). Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *J. Environ. Qual.* **26**: 836.
24. Jordan, T.E., Correll, D.L., and Weller, D.E. (1997). Nonpoint source discharges of nutrients from Piedmont watersheds of Chesapeake Bay. *J. Am. Water Resour. Assoc.* **33**: 631.
25. Sallade, Y.E. and Sims, J.T. (1997). Phosphorus transformations in the sediments of Delaware's agricultural drainageways: I. Phosphorus forms and sorption. *J. Environ. Qual.* **26**: 1571.
26. Sallade, Y.E. and Sims, J.T. (1997). Phosphorus transformations in the sediments of Delaware's agricultural drainageways: II. Effect of reducing conditions on phosphorus release. *J. Environ. Qual.* **26**: 1579.
27. Deletic, A.B. and Maksimovic, C.T. (1998). Evaluation of water quality factors in storm runoff from paved areas. *J. Environ. Eng., ASCE* **124**(9): 869–879.
28. Rai, S.C. and Sharma, E. (1998). Comparative assessment of runoff characteristics under different land use patterns within a Himalayan watershed. *Hydrol. Process.* **12**: 2235–2248.
29. Heathwaite, A.L. and Johnes, P.J. (1996). Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments. *Hydrol. Process.* **10**: 971–983.
30. Heathwaite, A.L., Johnes, P.J., and Peters, N.E. (1996). Trends in nutrients. *Hydrol. Process.* **10**: 263–293.
31. Johnes, P.J. and Heathwaite, A.L. (1997). Modelling the impact of land use change on water quality in agricultural catchments. *Hydrol. Process.* **11**: 269–286.
32. Senseman, S.A. et al. (1997). Trace level pesticide detection in Arkansas surface waters. *Environ. Sci. Technol.* **31**: 395.
33. Ma, L. and Spalding, R.F. (1997). Herbicide persistence and mobility in recharge lake watershed in York. *Nebraska, J. Environ. Qual.* **26**: 115.
34. Clark, G.M. (1997). Occurrence and flux of selected pesticides in surface water of the upper Snake River basin, Idaho and Western Wyoming. *J. Soil Water Conserv.* **52**: 381.
35. Domagalski, J.L., Dubrovsky, N.M., and Kratzer, C.R. (1997). Pesticides in the Joaquin river, california: input from dormant sprayed orchards, *J. Environ. Qual.* **26**: 454.
36. Garmouma, M., Blanchard, M., Chesterikoff, A., Ansart, P. and Chevrcuil, M. (1997). Seasonal transport of herbicides (triazines and phenylureas) in a small stream draining an agricultural basin: melarchez (France). *Klates Res.* **31**: 1489.
37. Zhang, X.C., Norton, L.D., and Hickman, M. (1997). Rain pattern and soil moisture current effects on atrazine Metolachlor losses in runoff. *J. Environ. Qual.* **26**: 1539.
38. Hong, S. and Smith, A.E. (1997). Potential movement of dithiopyr following application to golf courses. *J. Environ. Qual.* **26**: 379.
39. Lennartz, B., Louchart, X., Voltz, M., and Andrieux, P. (1997). Diuron and simazine losses to runoff water in Mediterranean vineyards. *J. Environ. Qual.* **26**: 1493.
40. Turnbull, A.B. et al. (1997). Assessment of the fate of selected adsorptive pesticides at ADAS Rosemaund. *J. Chartered Inst. Water Environ. Manage.* **11**: 24.
41. Laroche, A.M., Gallichand, J., Lagace, R., and Peasant, A. (1996). Simulating atrazine transport with HSPF in an agricultural watershed. *J. Environ. Eng., ASCE* **122**(7): 622–630.
42. Characklis, G.W. and Wiesner, M.R. (1997). Particles, metals, and water quality in runoff from large urban watershed. *J. Environ. Eng.* **123**: 753.
43. Farrell-Poe, K.L., Ranjha, A.Y., and Ramalingam, S. (1997). Bacterial contributions by rural municipalities in agricultural watersheds. *Trans. Am. Soc. Agric. Eng.* **40**: 97.
44. Line, D.E. et al. (1997). Water quality of first flush runoff from 20 industrial sites. *Water Environ. Res.* **69**: 305.
45. Jagals, P. (1997). Stormwater runoff from typical developed and developing South African urban developments: definitely not for swimming. *Water Sci. Technol. (G.B.)* **35**: 133.
46. Chui. P.C. (1997). Characteristics of stormwater quality from two urban watersheds in Singapore. *Environ. Monit. Assess.* **44**: 173.
47. Linde, D.T. and Watschke, T.L. (1997). Nutrients and sediment in runoff from creeping bentgrass and perennial ryegrass turfs. *J. Environ. Qual.* **26**: 1248.
48. Bouraoui, F. and Diallaha, T.A. (1996). Answers-2000: Runoff and sediment transport model. *J. Environ. Eng., ASCE* **122**(6): 493–502.
49. Wong, K.M., Strecker, E.W., and Stenstrom, M.K. (1997). GIS to estimate storm-water pollutant mass loading. *J. Environ. Eng., ASCE* **123**(8): 737–745.
50. Swensen, B. and Singh, B.R. (1997). Transport and transformation of urea and its derivatives through a mineral soil. *J. Environ. Qual.* **26**: 1516.
51. Nolan, B.T., Ruddy, B.C., Hitt, K.J., and Heisel, D.R. (1997). Risk of nitrate in groundwaters of the United States—a national perspective. *Environ. Sci. Technol.* **31**: 2229.
52. Department of the Environment. (1986). *Nitrates in Water—Report by the Nitrate Coordination Group*. Pollution Paper No. 26.
53. Agarwal, G.D., Lunkad, S.K., and Malkhed, T. (1999). Diffuse agricultural nitrate pollution of ground water in India. *Wat. Sci. Tech.* **39**(3): 67–75.
54. Bhatt, K. (1997). Occurrence and distribution of nitrate and pesticides in Bowdle aquifer, South Dakota. *Environ. Monit. Assess.* **47**: 223.
55. Milde, G., Pribyl, J., Kiper, M., and Friesel, P. (1982). Problems of pesticides use and the impact on groundwater. *IAH*

International Symposium on Impact of Agricultural Activities on Groundwater, Prague.

56. Kolpin, D.W. et al. (1997). Occurrence of selected herbicides and herbicide degradation products in Iowa's ground water, 1995. *Ground Water* **35**: 679.
57. Seta, A.K. and Karathanasis, A.D. (1997). Atrazine adsorption by soil colloids and co-transport through subsurface environments. *Soil Sci. Soc. Am. J.* **61**: 612.
58. Squillace, P.J., Burkart, M.R., and Simpkins, W.W. (1997). Infiltration of atrazine and metabolites from a stream to an alluvial aquifer. *J. Am. Water Resour. Assoc.* **33**: 89.
59. Guo, L., Wagenet, R.J., Hutson, J.L., and Boast, C.W. (1997). Nonequilibrium transport of reactive solutes through layered soil profiles with depth-dependent adsorption. *Environ. Sci. Technol.* **31**: 2331.
60. Kolpin, D.W. (1997). Agricultural chemicals in groundwater of the midwestern United States: Relations to land use. *J. Environ. Qual.* **26**: 1025.
61. Loague, K. and Corwin, D.L. (1998). Regional scale assessment of non-point source ground water contamination. *Hydrol. Process.*, 957–965.
62. Takarate, N., Sanchez-Perz, J.M., and Tremolieres, M. (1999). Spatial and temporal variations of nutrient concentrations in the ground water of a flood plain: effect of hydrology, vegetation and substrate. *Hydrol. Process.* **13**(10): 1511–1526.
63. Patrick, R. (1975). Some thoughts concerning correct management of water quality. In: *Urbanization and Water Quality Control*. W. Whipple, Jr. (Ed.). AWRA, Minneapolis, MN.
64. WHO. (1993). *Guidelines for Drinking Water Quality*. Vol. 1, Recommendations, 2nd Edn., World Health Organization, Geneva.
65. RCEP. (1992). *Royal Commission on Environmental Pollution, Freshwater Quality, Sixteenth Report, 1996*. Her Majesty's Stationary Office, London, pp. 65–67.
66. Sharma, E., Sundriyal, R.C., Rai, S.C., Bhatt, Y.K., Rai, L.K., Sharma, R., and Rai, Y.K. (1992). *Integrated Watershed Management*. Gyanodaya Prakashan, Nainital, p. 120.
67. Rai, S.C., Sharma, E., and Sundriyal, R.C. (1994). Conservation in the Sikkim Himalaya: Traditional knowledge and land use of the Mamlay watershed. *Env. Conserv.* **21**(1): 30–34.

ORGANIC COMPOUNDS IN GROUND WATER

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Virtually all natural waters contain at least some amounts of organic compounds. However, as human impact on the environment increases, the concentration of organic compounds, such as solvents or petroleum products, in the hydrosphere has increased in many places. Consequently, many aquifers experience a degradation of groundwater quality, and there is strong concern how to protect this valuable natural resource effectively from further contamination.

Organic compounds in groundwater can be of natural or anthropogenic origin. Naturally occurring organic compounds in terrestrial water include carbohydrates (sugars and cellulose), lipids (neutral fats), and proteins. The building blocks of proteins are amino acids, whereas functional proteins that act as biological catalysts are enzymes. Proteins are biopolymers that can form complexes with other organic compounds. Such compounds include tannins, which are phenolic compounds that occur naturally in bark, wood, leaves, or roots of many plants. The presence of elevated tannin levels in water results in a yellowish-brown discoloration. The parameter, dissolved organic carbon (DOC), is a commonly used measure for the concentration of organic compounds in aqueous solution. DOC is the fraction of total organic carbon (TOC is all carbon atoms covalently bonded in organic molecules) in water that passes through a 0.45 micron pore-diameter filter. Typical DOC concentrations for groundwater range from a few micrograms to several 10 mg per liter and more. DOC concentrations depend on various factors, such as climate, soil and vegetation coverage, and land use.

Many organic compounds, such as proteins, lignin, or cellulose, are suspended in water. These compounds are solid phase macromolecules. The size of the suspended matter is between that of individual small molecules and macroscopic objects. Particles of this size (ranging from approximately a few nanometer to millimeter are known as colloidal organic matter). The principal source of organic matter in water is from decaying plant material or kerogen, which is the organic matter deposited in the sediments of an aquifer. Organic matter in groundwater is in part made up of humic substances. The humic substances are further subdivided into humic acid and fulvic acids. Humic acid is the fraction of humic substances that is not soluble in water under acidic conditions ($pH < 2$) but is soluble at higher pH values, whereas fulvic acid is the fraction of humic substances that is soluble in water under all pH conditions. The fraction of humic substances that is not soluble in water at any pH value is referred to as humin. Humic substances are biopolymers that vary in color from light yellow-brown (fulvic acid) to dark brown (humic acid) to black (humin). The carbon based chemical structure of humic substances—especially that of humic acids and humin compounds—is very complex and is characterized by high molecular weight ($\gg$2,000 atomic mass units). The size of the macromolecules can range from 60–500 Å (1). Under the electron microscope, humic substances take the form of rings, chains, and clusters. The polarity of these compounds is intermediate between that of many (hydrophobic or nonpolar) hydrocarbons and that of polar water. For this reason, organic matter is an attractive nonpolar environment for hydrophobic compounds in aqueous solution. The partitioning of hydrophobic organic compounds to organic matter surfaces is referred to as adsorption, whereas partitioning into the organic matter is referred to as absorption. Although sorption to the solid phase of the aquifer would essentially stop or at least retard the movement of hydrophobic compounds, both adsorption and absorption to mobile organic compounds can greatly facilitate their transport in groundwater. Facilitated transport has important implications for assessing the fate and transport of organic contaminants in aqueous solution. The concentration of humic substances in groundwater increases as the DOC concentration increases and typically ranges from about

20 to 66% of the DOC mass (2). Elevated concentrations of organic matter in natural water can cause oxygen depletion, taste and odor problems, and can interfere with the water treatment process (formation of trihalomethanes as disinfection by-products during water chlorination).

Besides naturally occurring organic compounds, many waters contain compounds of anthropogenic origin. Following the definition of Schwarzenbach et al. (3), an anthropogenic compound is one that is introduced into the environment primarily or exclusively as a consequence of human activities. Thus, synthetic compounds, such as chlorinated solvents or most pesticides, as well as naturally occurring compounds, such as petroleum components, can be found in both surface and groundwater. Given the large number of synthetic chemicals and petroleum products used for domestic, industrial, and agricultural applications (including solvents, pharmaceuticals, plastics, dyes, and detergents), a discussion of individual organic compounds in the aquatic system is impractical. Hence, chemicals that share certain structural or chemical similarities are commonly grouped together. For example, those compounds that have two or more fused benzene rings are known as polynuclear aromatic hydrocarbons or polycyclic aromatic hydrocarbons (PAH), and compounds that have several chlorine atoms attached to a central biphenyl structure are called polychlorinated biphenyls (PCB) (Fig. 1). Other grouping criteria are based on (1) a common application, for example, organic compounds that are fungicides, herbicides, or insecticides; (2) a common source of origin, such as petroleum compounds that are lumped together in a group know as total petroleum hydrocarbons (TPH); or (3) similar physical properties, such as volatility. The two most often used volatility based classifications are volatile organic compounds (VOC), which include compounds such as acetone and 1,1,1-trichloroethane, and semivolatile organic compounds (SVOC), such as naphthalene and phenol. Organic compounds that typically co-occur are often discussed together. For example, benzene, toluene, ethylbenzene, and xylenes are commonly referred to as BTEX compounds. These four chemicals are aromatic petroleum hydrocarbons typically found in contaminated groundwater near leaking underground storage tanks. It is possible that a compound can fall in more than one category, for example, naphthalene (Fig. 2) is a PAH but also a common petroleum hydrocarbon and a SVOC. Table 1 provides an overview of the most common classes of anthropogenic organic compounds in the terrestrial aquatic environment.

The physical and chemical properties of many organic compounds are well known and documented. Besides some very well maintained printed data collections (5–7), a number of reputable government and commercial web sites offer information about organic compounds (e.g., www.nedi.gov/NEDI-Catalog or esc.syrres.com/efdb/Chemfate.htm). In addition, there are digital databases, such as the Environmental Fate Database (EFDB) published by United States Environmental Protection Agency (EPA), which contain data or links to data on physical/chemical properties and the environmental fate of several thousand chemicals (16).

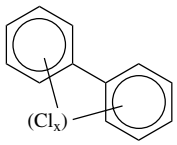


Figure 1. Polychlorinated biphenyls (PCB) are generally a complex mixture of various PCB isomers with different numbers of chlorine atoms (Cl_x) substituted onto the biphenyl rings.

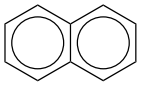


Figure 2. Naphthalene.

Many organic compounds are toxic, and even minute quantities of those chemicals make natural water unfit for human consumption. The EPA has defined threshold values for a number of organic and inorganic compounds. These so-called maximum contaminant levels (MCL) define when water is either of drinking water quality or contaminated. The MCLs and the number of entries changes with time as new scientific evidence emerges about the toxicity of listed and unlisted compounds.

New or improved analytical methods make it possible to detect compounds at lower detection limits. Better analytical resolution has also increased (and will continue to increase) the number of detectable compounds and is helping to identify possible links between the occurrence of negative health effects and the exposure to certain compounds. For example, there is evidence linking the exposure to some synthetic organic chemicals that compete with or disrupt the effects of hormones to reproductive abnormalities in wildlife, with cancer in women, and decreasing sperm counts in men. These so-called hormone or endocrine disrupters are chemicals such as some pesticides, PCBs, nonylphenols (used in surfactants), bisphenol A (a component in epoxy), phthalates (primarily used as plasticizers), and heavy metals.

Some chemicals that had been used on a large scale have been taken off the market after their detrimental biological effects and persistence in the aquatic environment became obvious. Probably the most well-known example is DDT (dichlorodiphenyltrichloroethane) (Fig. 3), which was the first chlorinated organic insecticide synthesized. DDT's effectiveness in fighting malaria and its low cost resulted in worldwide use of large quantities of that compound. In fact, DDT was credited with preventing 500 million human deaths due to malaria in little more than two decades (8). However, DDT in the environment has been linked to cancer in humans. Another organic compound that has received public attention more recently is MtBE (methyl tertiary-butyl ether) (Fig. 4). This compound has been added to gasoline and other petroleum products and has made its way into surface and groundwater. Currently, many states are trying or have already prohibited the use of MtBE as a gasoline additive after possible carcinogenic effects have been reported.

Once an organic compound has been released into the environment, bacterial activity may begin to break it down. This so-called biodegradation process works

Table 1. Important Classes of Anthropogenic Organic Compounds in Natural Waters

Class	Examples	Major uses or sources
Petroleum hydrocarbons	Benzene, toluene, ethylbenzene, xylenes, dodecane, hexane, naphthalene, pyrene	Gasoline, diesel and jet fuel, lubricating and hydraulic oils, grease, waxes
Alcohols, aldehydes, ketones, ethers	Methanol, ethanol, ethylene glycol, formaldehyde, acetone, 1,4-dioxane, tetrahydrofuran, MtBE	Solvents, chemical intermediates, antifreeze, oxygenizers (fuel additives)
Halogenated aliphatic hydrocarbons	Trichloroethene (TCE), tetrachloroethene (PCE), methylene chloride (dichloromethane), chloroform (trichloromethane), trichlorofluoromethane, methylbromide	Solvents, degreasing agents, dry cleaning fluids, refrigerants, pesticides
Polynuclear aromatic hydrocarbons (PAH)	Naphthalene, pyrene, anthracene, phenanthrene, benzo[a]pyrene, chrysene	Expect for naphthalene, there are no commercial uses. Sources: coal tar, crude oil and refined petroleum products, incomplete combustion of hydrocarbons
Polychlorinated biphenyls (PCB)	PCBs are synthetic mixtures of several congeners containing 1 to 10 chloride ions to the biphenyl. PCBs are oily liquids or waxy solids (4). Examples of commercial products containing PCB: Aroclor 1242, Clophen A30, Kenechlor 400.	Due to nonflammability, electrical insulating properties, chemical stability, and high boiling point, PCBs were used in electrical, heat transfer, and hydraulic equipment. Other uses include plasticizers in paints, plastics and rubber products; pigments, dyes, and carbonless copy paper
Substituted aromatics	Phenol, pentachlorophenol, nitrotoluene, 2,4,6-trinitrotoluene (TNT)	Pesticides, explosives, chemical intermediates
Phthalates	Di-*n*-butyl phthalate, dimethylphthlate, bis (2-ethylhexyl) phthalate. Phthalates are esters.	Plasticizers, solvents
Organosulfur and -phosphorus compounds	Malathion, Parathion, Aldicarb	Insecticides, herbicides, fungicides
Surfactants	Group of amphiphilic (partly polar, partly nonpolar) surface active compounds. Examples include alkylbenzenesulfonates (ABS), linear alkylbenzene sulfonates (LAS), fatty alcohol sulfates (FAS), quaternary ammonium chloride.	Soaps, laundry and dishwasher detergents, remediation agents

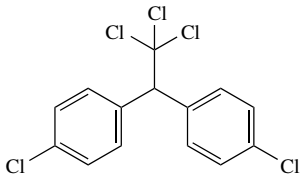


Figure 3. Dichlorodiphenyltrichloroethane (DDT).



Figure 4. Methyl tertiary-butyl ether (MtBE).

best for those compounds that are naturally occurring or similar to naturally occurring compounds (crude oil and most refined petroleum products). Unfortunately, many synthetic organic chemicals are very resistant to biodegradation and can remain in the environment for a long time. In some cases, the breakdown of a chemical can result in a compound that is even more hazardous. For example, tetrachloroethene (PCE) undergoes a complex biodegradation process during which trichloroethene (TCE), dichloroethenes (DCA), chloroethane, and vinyl chloride are formed (6,7) (Fig. 5). Vinyl chloride is a known carcinogen and even as little as 2 μg/L in water is considered unsafe for human consumption. Some synthetic organic compounds have been used as molecular markers to identify waters influenced by human activity. For example, optical brighteners are synthetic organic compounds that are being added to most laundry detergents. Because these compounds pass through sewage plants or septic tanks systems almost unchanged, they can be detected in many surface and groundwaters (9,10). Other compounds, such as caffeine or the cholesterol breakdown product coprostanol, also have been used as organic tracers (11).

Water contamination from organic compounds is a global problem and is closely related to the recalcitrant nature of many organic chemicals. For example, though the solubility of many organic compounds is very low, (less than a few milligrams per liter), they exceed by far the drinking water limits in most cases.

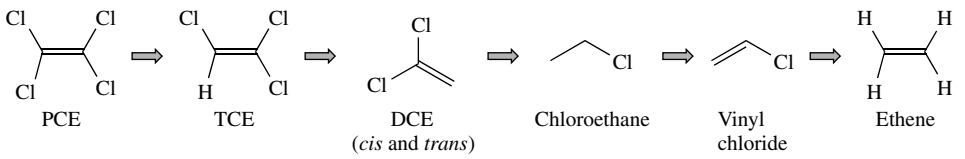


Figure 5. Simplified degradation pathway of tetrachloroethene (PCE), trichloroethene (TCE), *cis*- and *trans*-dichloroethene (DCE), chloroethane, and vinyl chloride to ethene (6).

Hence, even a relatively small spill of a toxic organic compound can contaminate a large volume of water. Many synthetic organic compounds also biodegrade very slowly, attach to organic matter or mineral surfaces, and—in the case of liquid immiscible compounds entering the subsurface—tend to have lower surface tension values than water. Thus, these compounds can enter small pore spaces or fractures from which they are hard to remove. Immiscible organic liquids are known to environmental hydrologists as nonaqueous phase liquids (NAPL). If a NAPL has a density less than that of water, it will float on the water table or the surface of a lake or a river. These compounds are called light nonaqueous phase liquids, (LNAPL). Examples of LNAPLs include gasoline, lubricating oil, and other petroleum products. Conversely, the densities of many NAPLs exceed that of water. These compounds are known as dense nonaqueous phase liquids (DNAPL). Many chlorinated solvents, such as PCE and TCE, are DNAPLs. After a NAPL, especially a DNAPL, has entered the subsurface, it is very difficult to locate and to remediate. Given the large quantities of accidentally released or illegally disposed NAPLs and other organic compounds, it will take decades or even centuries to solve the resulting environmental problems.

A number of analytical methods have been developed to analyze for organic compounds in water, but the methods approved by EPA are usually those that environmental laboratories use most (12). In many cases, the method selected depends on the desired analytical resolution and the instruments available.

Although our knowledge of organic compounds in groundwater has grown significantly during the past decades, there are still many questions to be answered. For instance, there has been a tendency to study the fate and transport of individual organic chemicals, although complex mixtures of organic compounds are much more common. Plenty of evidence now exists that interaction among multiple compounds—either synthetic or natural—results in chemical and physical behaviors distinctively different from those of simple, one-component systems. Further, physical and chemical processes in groundwater tend to be slow, and they very often exceed the length of a typical research project. Consequently, there is a slowly growing body of knowledge about the long-term (several decades) environmental fate of synthetic organic compounds in groundwater. Finally, there are a number of innovative methods under development for remediating contaminated groundwater. The expectation is that these methods will accelerate the removal of contaminants from the subsurface, therefore allowing the reuse of formerly polluted sites and, if possible, the restoration of groundwater to usable levels. Many of these methods, however, need to be tested in the field to explore their capabilities, limitations, and cost-effectiveness.

BIBLIOGRAPHY

1. Stevenson, F.J. (1985). Geochemistry of soil humic substances. In: *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*. G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy (Eds.). John Wiley & Sons, New York, pp. 13–52.
2. Thurman, E.M. (1985). Humic substances in groundwater. In: *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*. G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy (Eds.). John Wiley & Sons, New York, pp. 87–104.
3. Schwarzenbach, R.E., Gschwend, P.M., and Imoboden, D.M. (1993). *Environmental Organic Chemistry*. John Wiley & Sons, New York, p. 681.
4. United States Environmental Protection Agency. (1996). *PCBs: Cancer Dose-Response Assessment and Application to Environmental Mixtures*. EPA/600/P-96/001, September.
5. Mercer, J.W. and Cohen, R.M. (1990). A review of immiscible fluids in the subsurface. *J. Contam. Hydrol.* **17**(6): 106–163.
6. Verschueren, K. (1996). *Handbook of Environmental Data on Organic Chemicals*. 3rd Edn. John Wiley & Sons, New York, p. 2064.
7. Montgomery, J.H. (1996). *Groundwater Chemicals*. Desk Reference, 2nd Edn., Lewis Publishers, New York, p. 1345.
8. National Academy of Sciences (NAS). (1970). *The Life Sciences. Recent Progress and Application to Human Affairs, the World of Biological Research, Requirements for the Future*. National Academy of Sciences Press, Washington, DC, p. 526.
9. Stoll, J.M.A., Poiger, T.F., Lotter, A.F., Sturm, M., and Giger, W. (1997). Fluorescent whitening agents as molecular markers for domestic waste water in recent sediments of Greifensee, Switzerland. In: *Molecular Markers in Environmental Geochemistry*. R.P. Eganhouse (Ed.). ACS Symposium Series 671, American Chemical Society, Washington, DC, pp. 231–241.
10. Boving, T.B. (2002). *Fingerprinting sources of bacterial input using optical brighteners*. In preparation.
11. Sargeant, D. (1999). *Fecal Contamination Source Identification Methods in Surface Water*. Ecology Report #99–345, Dept. of Ecology, Washington State University, Pullman, WA.
12. United States Environmental Protection Agency. (1995). *Methods for the Determination of Organic Compounds in Drinking Water-Supplement III*. EPA/600/R-95-131.
13. Web-based databases: http://www.nedi.gov/NEDI-Catalog: National Environmental Data Index (NEDI) Catalog.
14. Stevenson, F.J. (1982). *Humus Chemistry; Genesis, Composition, Reactions*. John Wiley & Sons, New York, p. 443.
15. http://esc.syrres.com/efdb/Chemfate.htm: Environmental Fate Database maintained by the Syracuse Research Corporation (SRC), which is an independent, not-for-profit research and development firm chartered by the State of New York.
16. United States Environmental Protection Agency. (1995). *Environmental Fate Data Base (ENVIROFATE) Complete: XREF, CASLST, DATALOG, BIOLOG, CHEMFATE, and BIODEG (Raw Data File)*. Environmental Protection Agency, Office of Pollution, Prevention, and Toxics, Datafile-Magnetic tape, PB95-503074INC.

OVERDRAFT

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Groundwater mining (overdraft) occurs when there is a deliberate or inadvertent extraction of groundwater at a rate so in excess of replenishment that groundwater levels

decline persistently and threaten exhaustion of the supply or at least a decline of pumping levels to uneconomic depths (1).

Under natural conditions groundwater moves from areas of recharge to areas of discharge. The water is discharged to springs, lakes, streams, wetlands, and to the ocean. In most cases, equilibrium exists, and long-term recharge of groundwater is balanced by long-term discharge. Water levels in an aquifer fluctuate in response to changes in the rate of recharge and discharge. When discharge exceeds recharge, water is released from storage, and water levels decline. Declines may amount to hundreds of feet in areas where large withdrawals from wells have caused discharge to exceed recharge for long periods of time.

Groundwater in the United States is being increasingly developed for irrigation and municipal supplies. The U.S. Geological Survey has noted that groundwater availability is a significant issue in almost every state (2). The development of groundwater has led to declining water levels in a number of areas. The water table and artesian head declines have resulted in the following:

1. stream flow depletion
2. land subsidence
3. saltwater intrusion
4. increased cost to deepen wells
5. higher costs to pump water
6. decrease in well yield
7. drying up of shallow wells and springs
8. degradation of water quality

Under natural conditions, the largest fluctuations in water levels in unconfined aquifers are seasonal. Short-term fluctuations in confined aquifers commonly occur due to such factors as changes in barometric pressure. In areas where large withdrawals from wells have caused discharge to exceed recharge for long periods of time, declines may amount to tens or even hundreds of feet. These yearly declines may stop if pumpage is reduced so that discharge is equal to or less than discharge.

In a number of areas of the United States, groundwater levels have declined 300 feet or more. Five case studies were selected where groundwater mining has had a major impact: Denver, Tucson, Chicago, California, and Las Vegas. In these areas, groundwater mining has caused land subsidence, stream flow depletion, and increased costs for pumping groundwater (3).

Denver, Colorado

The Denver Basin bedrock aquifer system supplies water to rural and suburban residents of a large area along the eastern front of the Rocky Mountains in northeastern Colorado. The geologic formations that compose the aquifer system are Cretaceous and Tertiary sandstone and conglomerate shale of the Fox Hills Sandstone, Laramie Formation, Arapahoe Formation, Denver Formation, and Dawson Arkose (Fig. 1). In 1985, 12,000 wells withdrew water from these aquifers. A large part of the rapidly growing Denver metropolitan area depends on groundwater from these aquifers. For example, about 70% of the 220,000 residents in the southern metro area obtain water from bedrock aquifers. The bedrock aquifers in the Denver Basin have supplied groundwater to the Denver area for more than 100 years. Groundwater development began in the 1880s with artesian wells in downtown Denver. The artesian pressure was used for decorative fountains, powering elevators, and church organs. The water has been used for domestic, municipal, and industrial purposes. Groundwater withdrawal from the bedrock aquifers has caused water level declines, reduced well yield, and increased pumping costs. Water levels have declined as much as 12 m (40 feet) per year in some areas. In most of the area, the artesian head will be eliminated within the next 10 years. Increased use of groundwater and water level declines has alarmed water districts, government agencies, and water users because of the increased cost and depletion of the supply.

Tucson and Phoenix, Arizona

Large water level declines have caused land subsidence and earth fissures to develop in a 3000 square mile area that includes Tucson and Phoenix. The subsidence is caused by compaction of fine-grained sediments in the basin fill. The sediments deform and compact when water-level declines subject the sediments to additional compression from the weight of the overlying deposits.

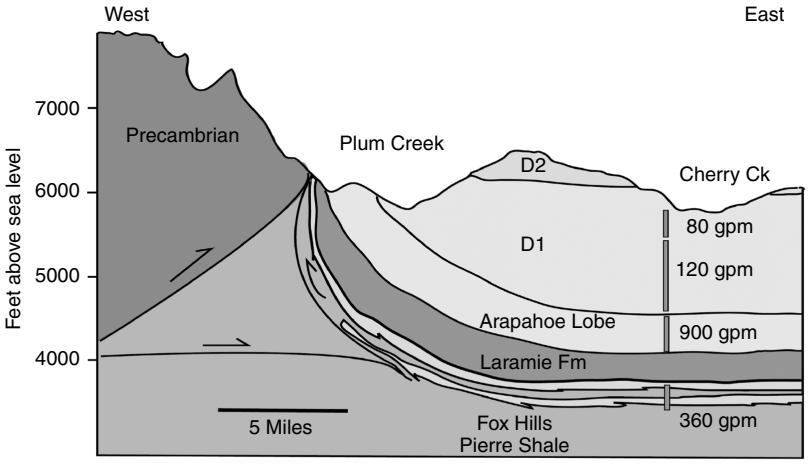


Figure 1. Denver Basin bedrock aquifers (4).



Figure 2. Pima County, Arizona. Sign warning motorists of subsidence hazard was erected after an earth fissure damaged a road in Pima County, Arizona (left photograph). Earth fissure near Picacho, Arizona (right photograph) (photographs by S.R. Anderson, U.S. Geological Survey).

Compaction increases slowly as water levels decline. Land subsidence has exceeded 15 feet since the start of groundwater development. Water levels in the Tucson area have declined 160 feet from 1945 to 1984. Compaction and land subsidence cause cracks (Fig. 2) in the land surface which can extend for hundreds to thousands of feet along the surface and can be hundreds of feet deep (5).

Central Valley, California

The Central Valley of California is one of the most intensively developed areas of irrigated agriculture. The valley is 500 miles long by 50 miles wide, and its total area is about 16,000 square miles. The valley is underlain by a large alluvial aquifer to a depth of 25,000 feet. Fresh groundwater is present to depths of as much as 4000 feet but most well water is less than 1000 feet deep. Significant development of groundwater for irrigation began in the early 1900s. As groundwater withdrawal increased to the point that groundwater withdrawal exceeded recharge, water levels started to decline. The water level declined 260 feet between 1940 and 1963. The groundwater withdrawal caused the compaction of fine-grained sediments (confining beds) which in turn resulted in subsidence of the land surface. Water level declines of 160 feet or more have resulted in land subsidence of about 30 feet in the Los Banos–Kettleman City area (Fig. 3).

Chicago, Illinois

Since 1864, large quantities of groundwater have been withdrawn from glacial drift and bedrock aquifers for municipal and industrial use. In the Chicago area, two Cambrian–Ordovician bedrock aquifers (sandstone and dolomite) supply groundwater. Water use has increased from 9.2–340 million gallons per day from 1864 to 1980. One of the first wells drilled to a depth of 711 flowed at the land surface at a rate of 400 gallons per minute. Groundwater withdrawal from the Cambrian–Ordovician bedrock aquifers (sandstone and dolomite) has caused water level (artesian head) declines of more than 800 feet (Fig. 4). No major land subsidence has been reported as a result of these large withdrawals because the rocks in the area are consolidated and resist compaction. A principal concern has been the possibility of beginning to



Figure 3. Central Valley, California: Land subsidence of 30 feet.

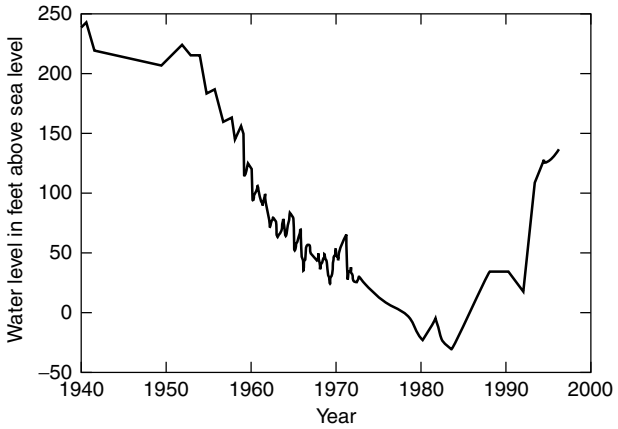


Figure 4. Chicago, hydrograph 1940–1998. (Representative trend of water levels for a deep well in Cook County, Chicago area, since 1940).

dewater the confined aquifer and thus converting it to an unconfined aquifer.

Las Vegas, Nevada

The Las Vegas Valley is the fastest growing metropolitan area in the United States. Water to support this rapid growth is being supplied by imported Colorado River water and local groundwater. Groundwater is pumped from the upper 2000 feet of unconsolidated alluvial sediments. The deeper aquifers called "principal artesian"(below 300 feet) can yield large quantities of groundwater. Overlying the principal aquifers are 100 to 300 foot thick deposits of clay. Since the 1970s, the annual groundwater withdrawal has remained between 60,000 and 90,000 acre feet. Most of the withdrawal is from the northwest area, where declines are more than 300 feet. Areas in central Las Vegas (The Strip) have experienced declines of as much as 200 feet. Since 1935, compaction of the aquifer has caused nearly 6 feet of subsidence and has led to the formation of numerous earth fissures and surface faults. Before groundwater development, the aquifer sustained the flow of many springs that discharged into Las Vegas Wash. Extensive groundwater withdrawal has caused the springs to dry up, and urban runoff has created a reservoir of poorer quality potentially contaminated water that now recharges the principal aquifer (Fig. 5).

Table 1. Subsidence and Groundwater Withdrawal

Locality	Subsidence, Feet	Subsidence, m	Area Affected, km^2
Central Valley, CA	30	9.0	13,500
Houston-Galveston, TX	9.1	2.75	12,170
Eloy, AZ	11.8	3.6	8,700
Tokyo	15.1	4.6	2,400
Po Valley, Italy	9.8	3.0	780
London	1.1	0.35	450
Venice, Italy	0.45	0.14	400
Mexico City	28.5	8.70	225

CONCLUSION

Water level declines and subsidence have been documented in Houston, Beijing, Tokyo, Bangkok, Venice, and Mexico City (Table 1).

Water conservation and regulations should be implemented in areas where groundwater is being mined (6). Some other measures that could be used to sustain the water supply are

- artificial recharge
- water reuse
- conjunctive use of groundwater and surface water
- restrictions on lawn irrigation and other water use.

BIBLIOGRAPHY

1. Wilson, W.E. and Moore, J.E. (1998). *Glossary of Hydrology*. American Geological Institute, Arlington, VA.
2. U.S. Geological Survey. (1984). *National Water Summary 1984*. U.S. Geological Survey Water Supply Paper 2275.
3. Moore, J.E. (2002). Effects of groundwater mining on aquifers-case histories Denver, Tucson, Chicago, Central Valley, Las Vegas: *IAH Congr. Mar de Plata*.
4. Johnson, K. and Raynolds, R. (2001). *Ancient Denvers*. Denver Museum at Nature and Science, p. 34.
5. U.S. Geological Survey. (1995). Colorado, New Mexico, Nevada, and Arizona. Hydrologic Atlas 730-C.
6. Alley, W.M., Riley, T.E., and Franke, O.L. (1999). *Sustainability of Ground-Water Resources*. U.S. Geological Survey Water Supply Paper 1186.

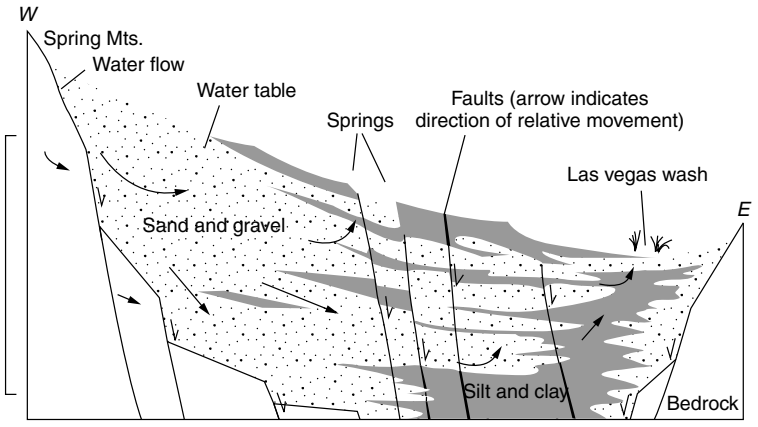


Figure 5. Las Vegas hydrogeology.

CHEMICAL OXIDATION TECHNOLOGIES FOR GROUNDWATER REMEDIATION

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INTRODUCTION

The use of chemical oxidation for the *in situ* remediation of soils and groundwater impacted with constituents of concern (COC) is a technology that has seen significant development and application in the past decade with numerous site applications in the last eight years. Three chemicals are typically utilized as oxidants:

- Hydrogen peroxide in the form of Fenton's reagent
- Potassium permanganate or sodium permanganate
- Ozone

Each has advantages and disadvantages, as does the use of chemical oxidation technology in general. There are numerous recent reviews of field application of the technology (1,2). Our purpose here is to assess the utilization of *in situ* chemical oxidation in general and the use of these three chemical oxidants in particular. In addition, these are powerful chemicals and care should be taken with their shipping, storage, and use.

Chemical oxidation has had a long history of application in the field of wastewater treatment. Hydrogen peroxide, Fenton's reagent, potassium permanganate, ozone, and combinations of ozone with other oxidants are all chemical oxidation systems that have found application for the treatment of wastewater. One of the key design issues for the application of chemical oxidation to wastewater is the total carbon load or other inorganic constituent that can be oxidized over and beyond that represented by the COC that are targeted in that waste stream. The chemical oxidants will react with and be consumed by all constituents in the wastewater stream not just the COC. In the case of the *in situ* treatment of groundwater, there are also consuming reactions associated with the geologic mineral matrix. In many instances, this adversely impacts the cost of application to the point of being impractical.

The general value of *in situ* chemical oxidation technologies resides in two areas: first, the treatment of residual free product and second, reduction of overall remediation time frames. Specifically, *in situ* oxidation is likely to be selected for difficult applications that include:

- Low permeability soils
- Highly stratified soils
- Low solubility compounds
- High concentrations of highly soluble organics (such as ketones, alcohols, or MTBE) that would be difficult to treat with conventional surface treatment technology (air stripping or activated carbon)
- Gasoline, diesel fuel, chlorinated solvents, polychlorinated biphenyls, organic pesticides, TNT, PBX, and VX
- Target compounds with low *in situ* degradation kinetic constants
- Dense, nonaqueous phase liquids (DNAPLs).

From an economic perspective, chemical oxidants are usually only practical in limited areas, typically near or in source zones. It is important to differentiate types of source zones:

- Primary source zones refer to areas that have been exposed to free phase DNAPLs. Discrete DNAPLs pools, emulsified DNAPLs, and high levels of adsorbed COC are characteristic of such zones.
- Secondary source zones refer to areas that have been exposed to high concentrations of dissolved COC. Elevated levels of adsorbed and dissolved COC are characteristics of these zones.

Chemical oxidation systems have the potential to offer rapid (from a week to a month) removal of COC. In addition, oxidation systems can be applied to dissolved plumes that are above the levels for which natural attenuation mechanisms can be expected to work within the time frames desired for site closure. Treatment of large diffuse dissolved COC plumes is possible with chemical oxidants but often not economically practical due to the effect of side reactions that consume the oxidant reagents.

The most powerful advanced oxidation systems are based on the generation of hydroxyl radicals. The hydroxyl radical is an extremely powerful oxidation agent, second only to fluorine in power. Fenton's reagent, ozone, and sonification are different means of generating those hydroxyl radicals. Each has advantages and disadvantages that can be exploited given the specific setting of a COC impacted site. A less intense, but still applicable, oxidation method involves the use of potassium or sodium permanganate. Following is a listing of common chemical oxidants, placed in the order of their oxidizing strength:

Relative Oxidation Power ($C1_2 = 1.0$)	
Fluorine	2.23
Hydroxyl radical (OH)	2.06
Activated persulfate	1.91
Atomic oxygen (singlet)	1.78
Ozone	1.50
Persulfate	1.48
Hydrogen peroxide	1.31
Perhydroxyl radical (OOH)	1.25
Potassium permanganate	1.24
Chlorine dioxide	1.15
Chlorine	1.00
Bromine	0.80
Iodine	0.54

In addition, the geology must be considered when applying a chemical oxidant *in situ*. Although the first concern is having the liquid reagents reach all of the COC in a heterogeneous situation, the soils themselves can have a significant effect on the reactions. This technology relies on water as a carrier to deliver the chemical oxidant to the COC. The macro- and microgeologic conditions do not always allow for complete contact between the chemical oxidants and the COC present in the vadose or saturated zone.

It is important to understand that COC oxidation occurs only in the aqueous phase, involving dissolved species of both the COC and the oxidant. The solubility of a targeted COC ultimately controls the rate of possible oxidation. There is interface mass transfer and then chemical oxidation. The rate of mass removal is limited by the kinetics of the COC dissolution process rather than those of the chemical oxidation reaction.

In all cases where the final product of the oxidation product is carbon dioxide, there is potential for short-term plugging of the aquifer pore space with carbon dioxide gas bubbles. In the case of Fenton's reagent, oxygen gas will also be generated and contribute to this possible problem.

Lastly, with the exception of some permanganate applications, this technology relies on the total displacement of native groundwater from the treatment zone and replacement with the reagent laden water. In the case of permanganate, the active life is sufficient that at sites with moderate to high groundwater velocities (greater than 30 ft/yr) reagent injection can take place with subsequent reliance on advection and dispersion to mix the oxidation solutions with native groundwater during transport.

CHEMICAL OXIDATION WITH FENTON'S REAGENT

Hydrogen peroxide alone has little effectiveness for the oxidation of chlorinated solvents. Fenton's reaction was first described in 1894. During the 1930s the reaction mechanisms were fully defined. Over the last 15 years commercial reactors have been available for wastewater treatment, and in the 1990s applications for *in situ* groundwater treatment have been developed. Fenton's reagent generates hydroxyl radicals through the reaction of ferrous iron and hydrogen peroxide:

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^{-}$$

The process is self-replicating because the reaction of ferric iron with hydrogen peroxide to generate the perhydroxyl radical also occurs:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^{+}$$

The perhydroxyl radical is a weaker oxidizer (between hydrogen peroxide and permanganate). But, more importantly, the process generates ferrous ions that in turn stimulate further reaction with hydrogen peroxide to produce more hydroxyl radicals. The hydroxyl radical can react with almost any hydrocarbon to produce carbon dioxide as a final product (and chlorides if a chlorinated hydrocarbon is treated). The key application issues are delivery of the reagents *in situ* and pH control. Optimum pH for the reaction, in the range of 3.0–4.5, is driven by the iron chemistry. It is possible to use iron chelates to get the desired reaction at higher pH values (3). Improper control of the reaction will only generate oxygen and water, not high-intensity oxidation. The technology is ideal for application in source zone areas where there are high concentrations of adsorbed or even interstitial free product. Cost is mostly dependent on the geochemistry of the geologic matrix and control of the iron chemistry. Soil buffering capacity may limit the ability to obtain optimal subsurface pH conditions.

Most of the original utilization of Fenton's reagent was in relatively low concentrations in wastewater applications. The main criteria for wastewater application was to have a sufficient ratio of hydrogen peroxide to the organic chemical that was to be destroyed. The chemical oxidation process is less efficient in the presence of soil. Due to the presence of competing organics and mineral surfaces (4) that are reactive to hydrogen peroxide, and the less than optimal environmental conditions, dosage requirements for *in situ* applications may increase 10–100-fold or more to accomplish the desired oxidation of COC. With regard to the rate of reaction and the degree of completion of the reaction, high concentrations of hydrogen peroxide (10–25%) are preferred. On the other hand, excess consumption of hydrogen peroxide by reactions with the geologic matrix can be controlled by using applications (possibly multiple) at concentrations of 5% or less.

Almost all soils have native iron bearing minerals as part of their geochemical makeup. When soils contain chemically available iron, supplemental iron salts may not be required with the hydrogen peroxide injection solution (5). However, problems may occur when too many iron minerals are present in the soil. If the iron is in a mineralized form not readily available for dissolution under low pH conditions, the natural catalytic activity of the mineralized iron decomposes the hydrogen peroxide to oxygen and water and does not create the hydroxyl radical. A second problem with soil mineralogy comes from soils rich in carbonate minerals or with high alkalinity. These soils produce groundwater with a high pH, which can require unacceptable amounts of acid to buffer the pH down to the required range. Carbonate minerals respond to low pH so rapidly that the geologic matrix itself will consume acid. Lastly, the carbonate ion preferentially scavenges hydroxyl radicals before they have a chance to react with the COC.

The heat generated by exothermic dissociation of hydrogen peroxide promotes contaminant volatilization. Rapid gas generation creates turbulence that further enhances the contact of the oxidant with the targeted COC impacted zones. Concentrations of hydrogen peroxide as low as 11% can cause groundwater to boil. The rate of hydrogen peroxide decomposition doubles with every 10 °C rise in temperature, so the energy release process, once initiated, rapidly accelerates. A pound of hydrogen peroxide can release 1200 BTU of heat energy and up to 6 ft^3 of oxygen gas, which creates volatilization and transport due to the created pressure gradients, which, when exploited in a controlled fashion, can have beneficial

effects regarding contact of the oxidant with the COC entrained in the geologic matrix.

For well over a decade, the cost of 50% hydrogen peroxide has been $3.50 a gallon. Hydrogen peroxide applications are frequently used with sulfuric acid (H_2SO_4) or acetic acid (CH_3CH_2OH) as a pretreatment to optimize the subsurface pH and solubilize the naturally occurring iron as a catalyst for Fenton's reagent. Sometimes ferrous sulfate is added to the hydrogen peroxide as a catalyst if naturally occurring iron is not available. Recently, sodium persulfate ($Na_2S_8O_2$) is being used with hydrogen peroxide for *in situ* oxidation processes. In this case, the heat of reaction from the hydrogen peroxide activates the much longer-lasting sulfate ($S_2O_8^{2-}$) radical.

PERMANGANATE

With the permanganate ion, the initial oxidation reactions of COC are independent of pH. For example, the oxidation rate of chlorinated alkenes by potassium permanganate is not affected by pH over a range of 3.0–11.0. However, pH does impact the type of intermediate products produced: At pH 4, formic acid is dominant; at pH 6–8, oxalic and glyoxylic acids dominate. In both cases, the organic acids are subsequently oxidized to carbon dioxide. The conversion of the intermediate oxidation products to carbon dioxide does occur more rapidly under acidic pH conditions. For the initial permanganate oxidation reactions, they can generally be characterized (7) as follows:

- Acid catalyzed reactions at pH < 5.0
- Uncatalyzed reactions at pH 5–9
- Base catalyzed reactions at pH > 10

Potassium permanganate has an affinity for organic compounds containing carbon–carbon double bonds, aldehyde groups, and hydroxyl groups. The permanganate ion borrows electron density from the pi bonds in chlorinated alkenes, which creates a bridged oxygen compound known as the cyclic hypomagnate ester (6). The intermediate ester is unstable and further reacts by a number of mechanisms including hydroxylation, hydrolysis, or cleavage. Under normal pH and temperature conditions, the primary oxidation reactions involve spontaneous cleavage of the carbon–carbon bond. Once the double bond is broken, the highly unstable carbonyl groups are immediately converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion.

Manganese dioxide (MnO_2) is the end product of the reduction of the permanganate oxyanion under neutral to basic pH conditions by the following reaction:

$$MnO_4^- + 2\ H_2O + 3\ e^- \rightarrow MnO_2 + 4\ OH^-$$

The MnO_2 is insoluble and forms colloids with a typical diameter near 1 μm (8). Plugging of the effective pore space can occur due to the precipitation of MnO_2. The manganese dioxide colloids can also cause problems with surface treatment equipment used as part of oxidation programs that rely on the creation of active circulation cells. The formation of insoluble manganese dioxide reaction products can also form a coating and seal around DNAPL mass, in effect blocking further dissolution and migration of the COC into the adjacent reaction areas (9), which can be a significant problem.

At low pH conditions, the reduction of the permanganate ion proceeds to Mn(II) by the following reaction:

$$MnO_4^- + 8\ H^+ + 5e^- \rightarrow Mn^{2+} + 4\ H_2O$$

The Mn(II) cation is soluble in water at concentrations above the regulatory limit (50 ppb) when chloride or sulfate counteranions are present.

Examples of complete reactions of permanganate with CVOCs are as follow:

$$\text{PCE } C_2Cl_4 + 2\ MnO_4^- \rightarrow 4\ Cl^- + 2\ CO_2 + 2\ MnO_{2(s)}$$

$$\text{TCE } C_2HCl_3 + 2\ MnO_4^- \rightarrow 3\ Cl^- + 2\ CO_2 + H^+ + 2\ MnO_{2(s)}$$

$$\text{DCE } C_2H_2Cl_2 + 2\ MnO_4^- \rightarrow 2\ Cl^- + 2\ CO_2 + 2\ H^+ + 2\ MnO_{2(s)}$$

The stochiometry ratios for complete oxidation reactions of permanganate as pounds of the $KMnO_4$ salt required to oxidize 1 pound of CVOC are:

PCE	1.3: 1
TCE	2.4: 1
DCE	4.4: 1
VC	8.5: 1

(The dramatic change in consumption rate is due to the fact that this analysis is on a pound per pound basis, not a molar basis. A pound of vinyl chloride has almost seven times more moles than a pound of PCE due to the loss of three heavy chlorines from the ethene backbone.)

In contrast to Fenton's reagent, the presence of carbonate minerals in the geologic matrix has generally positive effects on permanganate oxidation (10): Mn reduction stops at Mn(IV) (insoluble) rather than proceeding to potentially soluble Mn(II). Trace minerals are coprecipitated and immobilized with the manganese oxide. Consumption of permanganate by reaction with reduced mineral such a magnetite is minimized because the rates of these reactions increase with decreasing pH.

Oxidant demand from the matrix can be attributed to natural organic matter, reduced metals, carbonates, and sulfides. Permanganate demand rates can vary from a few grams of permanganate per kilogram of soil (clean sand with dissolved COC) to as much as several hundred grams of permanganate per kilogram of soil (organic clays with 6% organic carbon content and DNAPLs).

Immobile reduced metals such as chromium, uranium, vanadium, selenium, and molybdenum (all of which are soluble as oxidized oxyanionic complexes) can be oxidized and mobilized by permanganate oxidation.

When the permanganate concentration is 10 times the concentration of the CVOCs, the half-lives of TCE and

DCE range from 24 s to 18 mins; the half-life of PCE is 257 min. Typical dosage range (by weight) is 1.5–5% permanganate in the targeted treatment zone.

The potassium salt has a solubility limit of 65 g/L (6.5%); the sodium salt is significantly more soluble. However, the sodium salt is significantly more reactive. The reactivity difference between the sodium and potassium salt is not significant with regard to COC treatment. It is significant because the increased reactivity of the sodium salt presents greater safety challenges during its shipping, storage, and application.

Potassium permanganate costs $4.75 per pound.

OZONE

Ozone has been used for the treatment of drinking water since 1903. Its oxidizing power and innocuous decay products have made it ideal for that application. Ozone can generate hydroxyl radicals via catalytic decomposition of water. The oxidative power of an ozone generated hydroxyl radical is the same as those generated by Fenton's reagent. It also has specific activity toward alkenes (including chlorinated alkenes) through the attack of the double-bond carbon in a fashion similar to permanganate oxidation. Ozone bridges the carbon–carbon double bond to form unstable ozonide intermediates, which decompose into smaller oxidation species until carbon dioxide and water, or stable refractory compounds, such as acetic acid or oxalic acid, are formed. Ozone does not react well with chlorinated alkanes, particularly chlorinated methanes. Although the fate and reaction mechanisms of ozone in porous geologic media are not completely understood, it is likely that hydroxyl radical production from ozone occurs through catalytic reactions with natural inorganic (probably iron oxides) and organic material.

Ozone is fairly stable in dry air and has a half-life of several hours in low concentration. In water, ozone half-life is several minutes. As ozone is very reactive in an aqueous environment, ozone can oxidize material between 10 and 1000 times faster (11) than most oxidants used in water treatment. As ozone has such a short half-life, it cannot be compressed and stored. Instead, it must be generated on site and used immediately. Electrical generation is the only practical and safe method for large-scale applications of ozone. In practice, ozone concentrations of 1–2% using air and 3–8% using oxygen can be obtained by corona discharge generators. At a production concentration of 1% by weight in air, 650 ft^3 of air is required to produce 1 lb of ozone. As the speed of ozone destruction by decomposition is proportional to the ozone concentration, producing higher ozone concentrations with corona discharge is not feasible.

The decomposition rate of ozone has been shown to be 25 times more rapid in geologic media than in nonreactive media such as glass beads. However, the presence of carbonate ions in the groundwater can provide stabilization and double the half-life of dissolved ozone at a pH of 8.0 (12).

Other species created from ozone include superoxide anion $O_2^{\bullet -}$, which is an intermediate to the hydroxyl radical $^{\bullet}OH$; peroxide anion O_2^{2-}; oxygen atom singlet O; and the oxygen radical anion $O^{\bullet -}$.

At atmospheric pressure, the solubility of ozone is 3.4 mg/L for 1% and 7 mg/L for 2%. Note that solubility is somewhat dependent on the concentration of the ozone in the gas phase. With decreasing temperature, solubility increases. In addition, increasing hydrostatic pressure increases ozone solubility. For example, with a 1% system at 18 psi ozone solubility is 4.2 mg/L; at 25 psi it is 6.3 mg/L; and at 32 psi it is 8 mg/L.

As the TDS of the treated water increases, the solubility decreases. For example, ozone solubility is reduced 30% in seawater (13).

In most applications 1.5–3 lb of ozone is required for each pound of COC to be treated. That consumption rate is based purely on COC degradation requirements; spontaneous decay and ancillary reactions with other groundwater or mineral matrix constituents create an ozone loading requirement over and above those baseline numbers.

The cost for the generation of ozone includes the cost of the equipment: 1 lb/d unit— $7500; 10 lb/d unit— $32,500. Forty percent of the cost is for air pretreatment. The power requirements are in the range of 8–12.6 kW·h per pound of ozone produced.

PRACTICALITY OF APPLICATION

Stoichiometric Cost Comparison

The weight ratio in terms of pounds of oxidant per pound of TCE fully oxidized are 0.8 lb/lb for Fenton's reagent and 2.4 lb/lb for potassium permanganate. The cost for Fenton's regent, including hydrogen peroxide and amendments for pH control and ferrous iron addition, is typically $1.10 per pound and potassium permanganate is $4.75 per pound. So total oxidant cost per pound of TCE destroyed would be $0.88 for Fenton's reagent and $11.40 for potassium permanganate.

Calculation of a similar cost for ozone oxidation is more complicated, involving the capital costs of the equipment, the operational life of the system, electrical efficiency, and electrical costs. Following are assumptions for those key parameters.

A 10 lb/d ozone unit is purchased for $32,000 for a project life of 3 yr, which translates to a capital cost of $2.90 per pound of ozone. It requires 10 kW·h at $ 0.10 per kW·h (or $1.00) for the electrical cost to produce 1 lb of ozone. The total per pound cost for ozone is $3.90 per pound.

It requires 2.25 lb of ozone to oxidize 1 lb of COC, translating into a total cost of $8.75 for the ozone to oxidize 1 lb of COC.

Actual Application Costs

The total costs for the use of these oxidants is not accurately reflected by just the pound per pound cost required for the stochiometric oxidation of the COC. In reality, reactions with native carbon in the geologic matrix, reactions with minerals in the geologic matrix (14), and reactions with native dissolved constituents in the groundwater can increase the consumption rate of the

oxidation reagents by orders of magnitude. Fenton's reagent and ozone are particularly susceptible to these effects, potassium permanganate less so.

In practical application, these chemical oxidants are not applied based on the amount of COC present (with the exception of instances when there are significant volumes of DNAPLs present); rather, they are applied to achieve a specific reagent concentration in the treatment zone. Assuming the desired reagent concentration is 5% for Fenton's reagent and permanganate (this argument is not valid for ozone as explained below), following are the per cubic yard costs for one treatment with the respective chemical oxidant:

Fenton's reagent—$21

Potassium permanganate—$115

In practice, it is likely that two to five applications of Fenton's reagent may be required to achieve the remediation goals during a treatment campaign, raising the reagent costs to the range of $42–105. In many instances, one application of potassium permanganate will be adequate for treatment, but in cases where DNAPLs are present two or three applications may be required.

The hydrogen peroxide in Fenton's reagent can have a reaction life (under practical conditions) that ranges from 15 min to several hours. The permanganate ion can remain active in the saturated zone for months or perhaps even a year or more (10). Ozone will decompose in water within minutes, which has significant impact for *in situ* applications: Fenton's reagent can be injected directly into an aquifer, but spacing of the injection points will typically range from 1 to 7 yards. All contact with the COC occurs during advection caused by the injection process, and by mixing caused by heating and gas generation. Groundwater in the treated areas is displaced.

Permanganate salts can be injected *in situ* with the anticipation of further mixing of the reagents with the COC impacted groundwater due to natural flow conditions. Spacing of injection wells can be predicated on the impact of natural groundwater flow over a 6-month to 1-year period. Push–pull circulation systems can also be utilized to decrease the spacing of injection wells, but accommodations must be made for the removal of colloidal manganese dioxide from recovered groundwater. The reaction rate of permanganate also allows it to be applied in conditions where native groundwater flow can provide further advection for transport and dispersion for mixing. Complete displacement of native groundwater is not required.

Ozone is so reactive in water that it cannot be practically injected *in situ*. It can be used as a reactant in the bore of a circulation well or as part of a sparge system. The radius of influence of such systems is limited. As a result, the actual application of ozone as an *in situ* chemical oxidation system has been much more limited than the use of Fenton's reagent or potassium permanganate.

CONCLUSION AND CAUTIONS

A last word of caution. These are powerful chemicals. During shipment, storage, and application of chemical oxidants great care must be taken to maintain safe site conditions with regard to personnel and property.

Health and Safety Precautions for Chemical Oxidants

Hydrogen Peroxide. High strength hydrogen peroxide (greater than 5%) can cause chemical burns to the skin and eyes; lower concentrations will be irritating. In all cases, handling requires protective clothing: face shield, gloves, hard hat, rubber or PVC boots, and a rubber or PVC suit. A shower and eye wash should be available.

Decomposing hydrogen peroxide rapidly generates heat, gas, and pressure. Storage vessels and piping runs that have valve traps should have adequate ventilation and pressure relief systems.

Containers and piping should be free of all contaminants. Contaminants include copper, brass, zinc, mild steel, synthetic rubbers, polypropylene, and organic compounds (especially liquid organics). Acceptable materials for storage include aluminum, stainless steel, glass, ceramics, Teflon, polyethylene, Viton, and (for temporary storage) PVC. All metal components must be properly passivated before use.

Check valves are required to prevent backflow into hydrogen peroxide piping or tanks. Hydrogen peroxide pumps should only be constructed of stainless steel or Teflon.

Hydrogen peroxide can generate enough heat and oxygen to ignite combustible materials. Do not store hydrogen peroxide on wooden pallets or decks. Hydrogen peroxide in the presence of hydrocarbon vapors can cause vapor phase explosions. Every 10 °C increase in temperature doubles the reaction rate of hydrogen peroxide, it must be stored away from heat sources (boilers, steam lines, etc.) and should never be stored in insulated tanks.

Shipment of solutions with a concentration greater than 8% must be done as DOT hazardous.

Hydrogen peroxide is sold as a 50% solution, which is an extremely reactive material. Hydrogen peroxide vendors can readily deliver more dilute solutions. When possible, it is preferable to have the hydrogen peroxide delivered at the concentration at which it will be used for *in situ* chemical oxidization, rather than delivered at 50% and then diluted on site.

Permanganate Salts

Permanganates present a fire and explosion risk when placed in contact with organic materials. Containers of permanganate salts exposed to liquid hydrocarbons may explode. Other materials that exhibit high reactivity include metallic powders, elemental sulfur, hydrochloric acid, hydrazine, hydrogen peroxide, and metal hydrides.

Permanganate salts are irritating to the eyes, skin, respiratory system, and digestive tract from acute exposure. Chronic exposure to the skin can cause defatting and dermatitis. Chronic ingestion can cause central nervous system and kidney damage.

Employee protective equipment should include dust and mist respirator (and or area ventilation), gloves, and safety goggles.

Shipping is regulated under the Transport of Dangerous Goods Act:

TDG Classification: Class 5.1 (9.2) U.N. 1490; Packing group II

WHMIS Classification: C, E

On the DSL list

Ozone. Ozone cannot be shipped; it must be generated at the point of use. Ozone can only be generated at limited concentrations; the chief hazard is exposure to ozone inhalation.

Ozone can be detected by smell at a concentration of 0.01–0.005 ppmv. However, repeated exposure increases the detection level.

For 8 h the exposure limit is 0.1 ppmv; for 10 min the exposure limit is 0.3 ppmv. Ozone equipment and process lines should be in well ventilated areas. Exposure to aqueous ozone solutions can cause skin or eye irritation.

BIBLIOGRAPHY

1. EPA. (1998). *Field Application of In Situ Remediation Technologies: Chemical Oxidation*. EPA 542-R-98-008, September. Available: http://www.epa.gov/swertio1/download/remed/chemox.pdf.
2. ESTCP. (1999). *Technology Status Review In Situ Oxidation*. November. Available: http://www.estcp.org/documents/techdocs/ISO_Report.pdf.
3. Sun, Y. and Pignatello, J.J. (1992). *Iron (III) Chelates as Catalysts for Chemical Degradation of Pesticide Wastes by Hydrogen Peroxide*. Abstract. Division of Environmental Chemistry, AMS, San Francisco, CA, April, pp. 480–481.
4. Miller, C.M. and Valentine, R.L. (1995). Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material. *Water Res.* **29**(10): 2353–2359.
5. Teel, A.L., Wargberg, C.R., Atkinson, D.A., and Watts, R.J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Res.* **35**(4): 977–984.
6. Yan, Y.E. and Schwartz, F.W. (2000). Kinetics and mechanisms for TCE oxidation by permanganate. *Environ. Sci. Technol.* **34**(12): 2535–2541.
7. Wilberg, K.B. and Freeman, F. (1999). Kinetics of the base-catalyzed permanganate oxidation of benzaldehyde. *J. Org. Chem.* **65**: 573–576.
8. West, O.R. et al. (1997). *A Full-Scale Demonstration of in situ Chemical Oxidation Through Recirculation at the X-701B Site Field Operations and TCE Degradation*. ORNL/TM-13556.
9. Urynowicz, M.A. and Siegrist, R.L. (2000). Chemical degradation of TCE DNAPL by permanganate. In: *Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds*. The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 22–25, Vol. C2-6, pp. 75–82.
10. Nelson, M.D., Parker, B.L., Al Toma, A., Cherry, J.A., and Loomer, D. (2001). Geochemical reactions resulting from *in situ* oxidation of PCE-DNAPL by $KMnO_4$ in a sandy aquifer. *Environ. Sci. Technol.* **35**(6): 1266–1275.
11. Hongine, J. and Bader, H. (1983). Rate constants of reactions of ozone with organic and inorganic compounds in water 1: Non-dissociating organic compounds. *Water Res.* **17**: 173–183.
12. Staehelin, J. and Holgne, J. (1982). Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* **16**(10): 675–681.
13. Kosak-Channing, L.F. and Heiz, G.R. (1983). Solubility of ozone in aqueous solutions of 0–0.6 M ionic strength at 5–30 °C. *Environ. Sci. Technol.* **17**(3): 145–149.
14. Barcelona, M.J. and Holm, T.R. (1991). Oxidation–reduction capacities of aquifer solids. *Environ. Sci. Technol.* **25**(9): 1565–1572.

PARTICULATE TRANSPORT IN GROUNDWATER—BACTERIA AND COLLOIDS

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Enhanced bioremediation via bioaugmentation requires understanding of groundwater flow of both colloids and bacteria.

COLLOID TRANSPORT MECHANISM

Evaluation of mass transport of entrained material in groundwater flow systems is typically focused on two primary areas, dissolved organic or inorganic species, and flowing free phase liquids. However, although generally not as dominant overall, the movement of small particles in groundwater can cause problems at the low concentrations required by regulatory limits. In addition, the proponents of *in situ* bioaugmentation, through injection of bacteria, must rely on successful particulate mass transport through the saturated soil matrix.

Colloids are a special class of material with properties that lie between that of the dissolved state and the solid (or liquid) state. Historically, the term *colloid* is applied to particles with a size range of 0.001 to 1 micron (1 micron is 0.001 millimeter or approximately 0.00004 inches). The surface area per unit mass is very high for colloids, which has a great effect on their mass transport behavior. The sources of colloids in groundwater include the following:

- Detached soil, mineral, or contaminant particles
- Colloids formed from solutes undergoing geochemical precipitation caused by changes in redox conditions from mixing with injected or percolated surface water
- Emulsions of fine droplets from free phase hydrocarbons
- Agglomerations forming micelles seeded by macromolecules such as humic acids.

— Colloids introduced directly into the groundwater from landfills or other surface sources.

On a mass basis, colloid concentrations in groundwater range from 1 to 75 mg/L. Colloid density in natural groundwater systems can range to upper limits of 10^{10} particles per liter in igneous fractures and 10^{12} particles per liter in sandy aquifers.

Contaminants can be transported as colloids resulting in unexpected mobility of low solubility material. Colloids can also act as adsorbents for contaminants that are then transported with the colloid. If contaminants have been adsorbed to colloids, it is important to remember that the transport behavior is determined by the physical/chemical properties of the colloid, not the physical/chemical properties of the contaminant. In cases where colloids are formed *in situ*, contaminants can be incorporated (or occluded) into the colloidal particle as it forms.

MECHANICAL COLLOIDAL PROCESSES

Particles larger than 2 microns in the low-flow conditions common in groundwater systems are subject to removal by sedimentation (settling under the influence of gravity). Below 0.1 microns, the effects of adsorptive process are much more pronounced. As a result, colloids and particles in the range of 0.1 to 2.0 microns are likely to be the most mobile in groundwater. Although particles at the middle of the colloid range are overall more mobile, larger particles may travel through formations more rapidly because of size exclusion. In that process, the particle travels a reduced path length through the soil matrix because it is excluded from the smaller pore spaces. Colloids or other particles can be mechanically removed via filtration by the soil matrix. The key parameter to this process is the pore entrance size, which is a function of grain size. For fine- to coarse-grained silts, pore entrance size ranges from 0.7 to 7 microns, for fine- to coarse-grained sands from 24 to 240 microns, and for fine- to coarse-grained gravels 720 to 7200 microns.

Mechanical removal of particles occurs most often by straining, a process in which particles can enter the matrix, but are caught by the smaller pore spaces as they traverse the matrix. If within the soil matrix there is groundwater flow through heterogeneity, a surface mat may form at the interface when particles are too large to enter the finer grained matrix at all. The best example of this is along the walls of fractures through fine-grained sediments.

ADSORPTIVE COLLOIDAL PROCESSES

The primary forces that influence colloids suspended in a liquid moving through a porous solid matrix include electrostatic repulsion and attraction, London–van der Walls attraction, and brownian motion. Electrostatic charged based forces are familiar. London–van der Walls attraction is a weak (but still effective) form of chemical bonding. Brownian motion is caused by molecular collisions between a particle and the surrounding fluid matrix; it becomes apparent when particle size reaches a few microns. The effect predominates colloids 0.1 microns or smaller; the smaller the size, the higher the velocity that can be imparted because of brownian motion. Adsorptive interactions of colloids may be affected by the ionic strength of the groundwater; specific ionic composition and charge; quantity, nature, and size of the suspended colloids; geologic composition of the soil matrix; and flow velocity of the groundwater.

In most instances, however, the mobility of a colloid is dependent on groundwater chemistry rather than on forces caused by advective flow. Higher mobility occurs at lower overall concentrations of total dissolved solids (TDS). Higher levels of TDS encourage deposition of colloids.

The reasons for this behavior deserves some explanation. Surfaces in an aquifer matrix at normal, near-neutral pH in general have a net negative electrostatic charge because of the predominance of silica in the minerals of the matrix. This charge on the matrix surfaces and the colloids in the groundwater system has a configuration that is described as an electric double layer. The first layer forms because of the collection of positive ions on the exposed negatively charged interfacing surfaces. Anions in solution then form the second diffuse layer around the first to counter the resulting positive surface charge.

As the ionic strength of the groundwater increases, the thickness of the double layer decreases. When a negatively charged colloid approaches a negatively charged grain within the groundwater matrix (both with double electrical layers), mutually repulsive forces increase. Conversely, if the two surfaces can approach past the repulsive maximum, attractive London–van der Waals forces will take over, overcome the repulsive forces, and the colloid is attached to the matrix surface. The high velocities imparted to colloids smaller than 0.1 microns because of brownian motion provides the mechanism for overcoming the electrostatic repulsion of the double layers. The process is delicately balanced such that the reduction of the electrical double layer thickness through increased ionic strength is also required.

The result of this colloidal behavior is beneficial with regard to typical surface contaminant sources such as landfills. The high ionic strength of leachate will serve to provide optimum conditions for the immobilization of entrained colloids. Conversely, the injection of low ionic strength water has the potential to enhance colloid mobility and even mobilize previously adsorbed material.

PARTICULATE TRANSPORT IN GROUNDWATER—BACTERIA

The transport of bacteria in groundwater systems is of concern from both ends of the mobility spectrum. Mobility is essential for the injection of bacteria using the bioaugmentation approach to saturated zone *in situ* bioremediation. Conversely, there is high concern with mobility, and a desire for immobility, with regard to pathogens from septic systems or other sources. Bacteria range in size from 0.2 to 5 microns and viruses from 0.005 to 0.1 microns, which is within the size range considered

colloidal. Therefore, bacteria transport is effected by many of the same processes as those for colloids.

As with colloids in groundwater, factors affecting bacteria transport include mechanical and adsorptive processes. However, bacteria are live organisms capable of responding to environmental conditions and have other unique qualities that impact their transport properties. These qualities include surface hydrophobicity, reactive groups on the surface of the bacterial cell wall, and coatings that can be "sticky."

Mechanical Processes

Removal of bacteria can occur solely by straining within the aquifer matrix. The size of the pore space in relation to bacteria size is important enough to repeat: In fine- to coarse-grained silts, pore entrance size ranges from 0.7 to 7 microns; for fine- to coarse-grained sands from 24 to 240 microns; and for fine- to coarse-grained gravels 720 to 7200 microns. As a general rule, bacteria should be half the size of the pore entrance for adequate success in passage, and if the average bacteria size is greater than 5% of the grains (not the pore size) within the porous matrix, straining becomes an important removal mechanism.

In addition to reduction of hydraulic conductivity through the accumulation of bacterial cells, as described above, other processes unique to bacteria can mechanically reduce transport efficiency. Bacteria may excrete extracellular polymers, low solubility metabolic precipitates, or gaseous products (such as nitrogen, methane or carbon dioxide) that can potentially block pore passages.

Adsorption Processes

Increasing ionic strength of groundwater increases the capability of bacteria to adhere to soil surfaces by increasing the availability of ions to act as bridges between the surfaces of the cell and soil particles, and by decreasing the thickness of the electric double layer (a phenomena described above). Increased ionic strength also enhances the ability of bacteria to aggregate, which forms a larger overall particle more likely to be captured in pore spaces. For example, transport efficiency of bacteria through clean sands has been shown to be 2% to 3% in water with 750 ppm of total dissolved solids (TDS) versus 70% to 100% in deionized water.

Bacteria have an overall negative charge on the surface of their cell wall, primarily because of the presence of peptidoglycan, the structural backbone of the bacterial cell wall, which is rich in carboxyl and amino groups. Teichoic acids are a phosphate-rich component of bacterial cell walls, which also help contribute to the presence of a negative charge. So that conversely to the above, bacterial adsorption to positively charged surfaces (such as those presented by iron and other metal oxyhydroxides) is at its maximum under conditions of low ionic strength. In a manner similar to that for inorganic anions, the sorption of bacteria to oxyhydroxides is also pH-dependent. As a consequence, to evaluate bacteria mobility, it is important to know the specific chemical and mineralogical character of the soil matrix. In some circumstances, because of soil chemistry, high levels of bacterial adsorption will occur irrespective of the manipulation of ionic strength in the surrounding groundwater. This news is good for those concerned with septic systems, but bad for those wishing to inject bioaugmentation bacteria.

The bacterial cell wall also contains varying amounts of lipids that are responsible for hydrophobic behavior. Hydrophobic bacteria have the tendency to adsorb to surfaces in the groundwater system because of repulsion from the polar water molecule. The effect of electrostatic repulsive force decreases with increasing hydrophobicity of a bacterial species.

Biological Processes

Attachment of bacteria to a surface is a two-stage process. First, the initial adsorption caused by electrostatic or hydrophobic forces takes place. This adhesion is reversible, given adequate shearing from groundwater flow. The second stage is the irreversible binding through cellular production of exopolymers that anchor the cell to the surface. The production of these exopolymers is stimulated by the initial adsorption and has been observed to increase five-fold once a cell has attached itself to a surface.

Bacterial motility may be important under conditions of static flow or chemotaxis. Motility is the ability of bacteria to move through the use of appendages such as flagella or pili. Chemotaxis is the movement or orientation of bacteria cells along a chemical concentration gradient. By this mechanism, porous media can be penetrated by bacteria that literally grow through the pore space. Growth rates have been observed in cores at ranges up to 0.01 to 0.05 cm/hr. However, pore space is occupied by bacterial biomass, the blockage from which ultimately prevents the transport of required nutrients to the growth area.

Starvation of cells will reduce their size to less than 0.3 microns, therefore reducing overall filtration effects and allowing for penetration of a finer grained matrix. However, in response to the starvation stress, many bacteria will increase the stickiness of their cell walls to improve the chance of adhesion to a surface. In general, bacterial adsorption in uncontaminated water is driven by electrostatic forces. Bacteria adsorption rates are high in groundwater at a pH of 6 or lower. Bacteria transport mobility increases above pH 6.0, significantly so above pH 7.5. In contaminated groundwater, the situation is much more complex and is specific to the site, contaminant properties, and the bacterial species present. In the presence of contamination, bacteria metabolic processes play a much more dominant role in transport properties, overwhelming physical/chemical effects.

Coarse-grained groundwater flow systems or large aperture fracture flow systems (such as karst) have the capacity to support substantial bacterial transport. Bacteria injection is possible, and pathogen transport from septic systems is probable under such conditions. However, bacteria transport in finer grained groundwater systems is more problematic. The high TDS associated with septic systems (or other potential sources of pathogens) will enhance the tendency for immobilization. Bacterial injection for bioaugmentation may be mechanically impossible because of straining and will require careful assessment under marginal porosity conditions.

Bioaugmentation

Bioaugmentation is a technology to enhance bioremediation. One type of bioaugmentation includes culturing indigenous bacteria and reintroducing that population back into the aquifer. A second type of bioaugmentation includes culturing a specific laboratory selected strain of bacteria that has had proven success degrading a specific contaminant and injecting that bacteria into the aquifer. Based on experience, the former is more likely to be successful because the indigenous bacteria are acclimated to the site-specific conditions and food source. Injection pressures for bioaugmentation tend to be 40 psi or less. Pressures approaching 100 psi will get the bacteria further into the aquifer; however, cell walls may start to burst at higher pressures. In addition, injection pressures sufficient to fracture the sediments in an injection zone will induce flow by hydrofracturing, possibly short-circuiting the bulk of a targeted treatment zone. As a rough rule of thumb, injection pressures can increase by 1 psi for each foot of depth. Injections pressures higher than that are likely to stimulate hydrofracturing.

Groundwater flow studies must take into account both colloids and bacteria for successful enhanced bioremediation projects.

PERCHED GROUNDWATER

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Perched ground water is subsurface water that forms a saturated horizon within porous media at an elevation higher than the local or regional groundwater table. This condition may result from various field conditions, but the requisite condition is a soil or rock horizon of significantly lower vertical hydraulic conductivity (K_v) (perching unit) amid contrastingly higher K_v strata. Downward movement of infiltrating water through the higher K_v materials is retarded and accumulates above and/or within the perching unit, which typically "mounds" saturated water above the perching unit, leaving an unsaturated (vadose) horizon below the perching unit. The upper limit of saturation in a perched zone is referred to as a perched water table, whereas the lower limit has been defined as an inverted water table.

HYDRAULIC PROPERTIES

K_v contrasts typically of the order of 10 to 20% of the K_v of the overlying materials, are believed to have the potential to produce perched groundwater (Fig. 1) (1,2). Stratigraphically, such contrasts are often conceptualized as fine silty or clayey lenses layered between coarser sediments such as sands or sandy gravels. Equivalent K_v contrasts can result within other stratigraphic analogues such as saprolite or ash horizons between adjacent lava flows, anisotropic fractures patterns in homogeneous crystalline rocks, or intraflow structures within flood basalts. Perching units can vary considerably in areal extent, ranging from extensive, essentially continuous strata to localized, discontinuous lenses.

Porosity within perching and overlying stratigraphic units is typical of the types of materials that comprise these strata. Notably, the porosity of clayey materials is typically higher than that of other granular materials, thereby providing high capacity for storing water but a lesser or slower rate of yield. Secondary porosity of clays, such as fractures, may facilitate downward movement, particularly as water is mounded above the perching unit.

Elastic properties are another potentially important factor in regard to perched groundwater involving clayey units. Specifically, shrinking of the clay lattice may occur upon desiccation, and swelling may occur upon

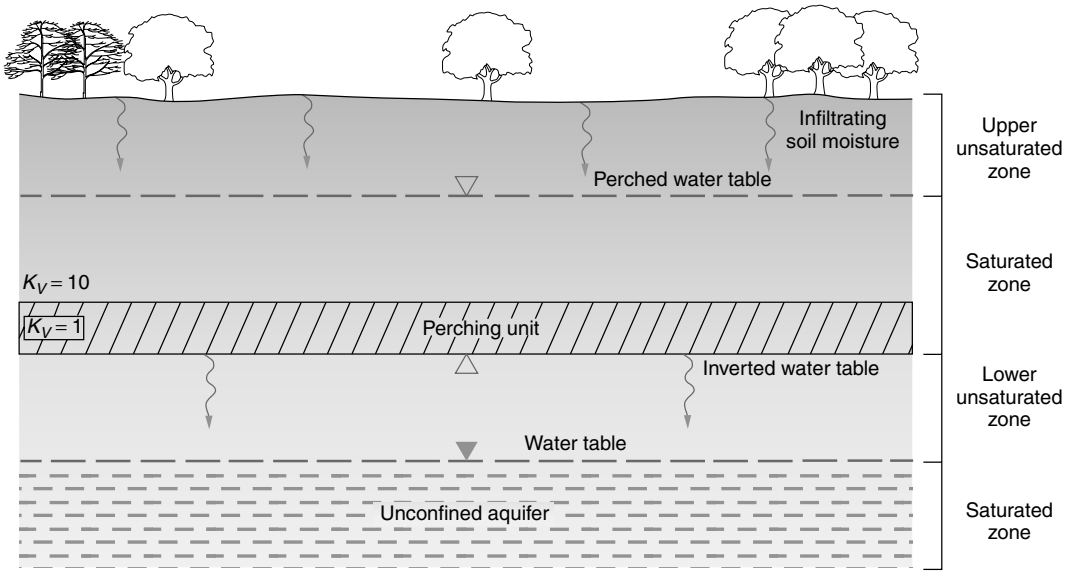


Figure 1. Perched groundwater resulting from hydraulic conductivity contrast and surface infiltration.

wetting, thereby, respectively, enabling greater or lesser rates of water movement through the perching unit. Other rarer forms of secondary porosity may result from certain geochemical interactions, such as dissolution or precipitation of minerals upon wetting.

HYDROLOGIC CONDITIONS

Hydrologic conditions that give rise to perched ground water are variable. Perched groundwater tables have resulted from various high volume natural recharge events, such as flooding or intense and long-term precipitation; artificial recharge resulting from infiltration basins, water line leaks, irrigation, disposal pits, or artificial impoundments; and transient conditions such as falling water tables. In general, all of these mechanisms involve downward movement or drainage of subsurface water. For this reason, perched groundwater is often characterized as transient or ephemeral. However, longer term recharge and discharge may give rise to near steady-state perched groundwater. Wells tapping perched groundwater can have highly variable yields, depending on the specific hydrologic conditions. Generally, however, perched groundwater is not exploited.

Mathematical equations describing the rise and fall of groundwater mounds were developed by Hantush (3) and generally relate to conditions underlying recharge basins. These equations are also applicable to perched groundwater.

Except for perched groundwater resulting from falling water tables, development of a perched groundwater zone can be conceptualized as having three phases: growth, accumulation, and drainage. The perched zone growth phase involves the initial downward movement of subsurface water and its encounter with the perching unit. The downward flux of water must be sufficient to overcome soil moisture tension and is subject to the classical principles of unsaturated flow.

Once a sufficient volume of water encounters the perching unit, accumulation or "mounding" of groundwater begins. Initially, this mounding may be limited to the overlying coarser grained units (or equivalent units in other terrains). As downward flux continues, the mound will accrete both vertically and laterally. As accumulation continues, the added hydraulic head can advance the inverted water table downward into the perching unit. Likewise, lateral movement may continue, potentially extending to the edges of the perching unit, where "spillage" into the underlying unsaturated zone can occur.

The drainage phase represents waning of the perched zone. If the rate of recharge is insufficient to maintain the areal and vertical extent of the perched zone, then it will slowly drain through or off the ends of the perching unit. Another source of discharge may result from evapotranspiration, if the perched groundwater is shallow and within reach of phreatophytes.

Examples of Perched Groundwater

Tucson Basin. The municipality of Tucson, Arizona, relied solely on its underlying aquifer for water supply until the recent delivery of Colorado River water via the Central Arizona Project. As a result of the region's population growth and associated increases in water demand since the early 1950s, the water table declined more than 200 feet within some areas of the basin. The rapid lowering of the water table that averaged 3 to 4 feet per year from 1950 to 2000 left saturated remnants in several parts of the basin (4). The basin sediments comprise a heterogeneous sequence of unconsolidated to semiconsolidated strata ranging in textures from laterally discontinuous facies of sandy gravels to silty clays. Perched groundwater has reportedly been encountered at depths ranging from 30–85 feet below land surface and ranges in saturated thickness from less than 1 foot to more than 85 feet (5–7). In some places within the basin, the elevation of the perched water table is within the perching unit as opposed to the overlying sediments. In other areas, the perched groundwater is sustained as a result of natural recharge from runoff or artificially from irrigation.

High Volcanic Islands. Perched groundwater is common in high volcanic islands, such as Hawaii and Tahiti, owing to high precipitation upon highland areas and extreme K_v contrasts in layered shield volcanics (8–11). Perched groundwater is often classified as "high level" compared with basal groundwater, which occurs as near or below sea level lenses, "floating" on intruded seawater (Fig. 2). As also seen in the figure, high level water can also result from intrusive dikes, which act as "subsurface dams." Perching units are generally sedimentary strata, often saprolites, dense lavas, or ash beds interbedded among lava flows. Yields from such perched sources are highly variable; however, exploitation by horizontal wells and tunnels has provided adequate local supplies. As a result of high relief, perched groundwater can often intercept the surface topography and discharge as a spring. Equivalent examples are also found in high-relief fractured crystalline terrains.

Flood Basalts. The hydrogeology of extensive flood basalts such as occur in the Columbia Plateau in parts of Washington, Oregon, and Idaho is controlled largely by the characteristics of intraflow structures. Interflow structures such as those sedimentary interbeds and saprolites described for shield volcanics are also important. In such volcanic terrains, individual lava flows are much thicker than those in shield volcanics, ranging up to 10s to 100s of meters. Intraflow structures from the base to top of an individual flow generally comprise a contact or pillow palagonite, representing a chill zone; a colonnade, consisting of prismatic, hexagonal columns with vertical cooling joints; an entablature, comprising slender, hackly, often-intersecting columns; and a flow top of vesicles and rubbly materials (Fig. 3). From flow to flow, the proportional thicknesses of these structures may vary extensively.

Interflow contacts generally represent zones of higher porosity and permeability than the dense flow interiors. Such zones of comparatively higher porosity preferentially store and transmit higher volumes of water, thereby potentially creating multiple perched horizons. Being

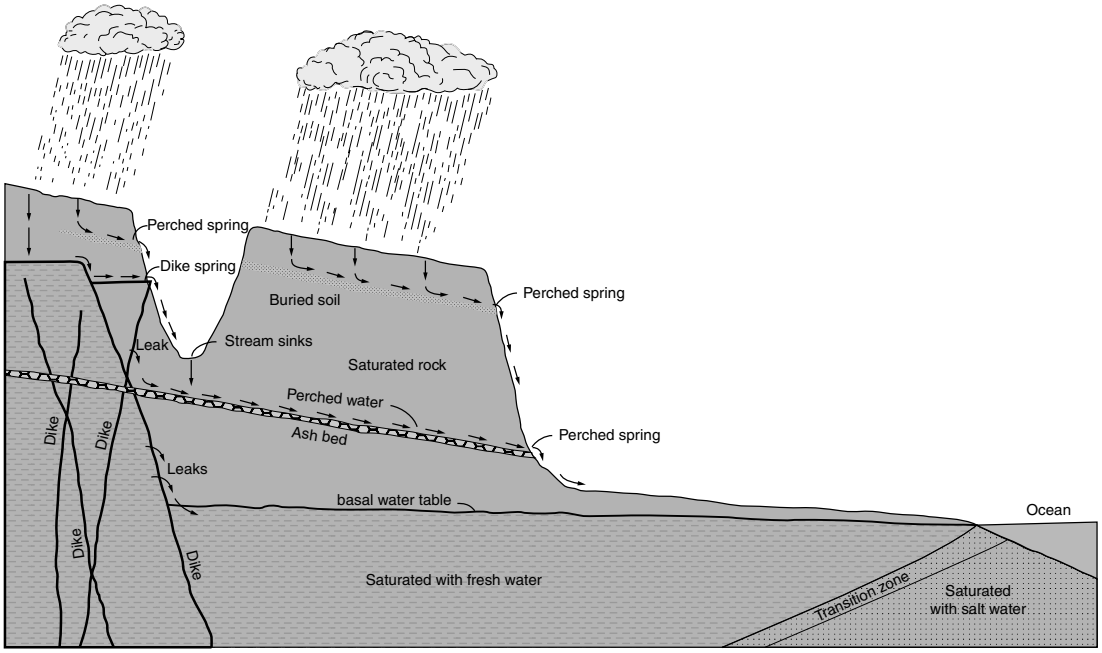


Figure 2. Conceptualization of perching on high volcanic islands (8).

a relatively competent rock, wells completed in basalt are often uncased. This construction often results in the borehole penetrating into several variably saturated horizons. As a result, cascading water from shallower perched zones is common and can be observed in borehole video logs and even heard by listening at the wellhead.

ROLE OF PERCHED GROUNDWATER IN CONTAMINANT MOVEMENT

Considering the position of perched groundwater bodies in relation to the surface, where much contaminant generation occurs, and the groundwater table, it is easy to conceptualize how perched groundwater can play a role in controlling the movement of contaminants in the subsurface. First, perched groundwater may result from artificial recharge due to the handling and disposal of liquids and liquid wastes. Leaky impoundments, such as disposal pits and sumps, underground storage tanks (USTs), pipelines, drywells, landfills, channels and ditches, sewers, and poorly constructed wells can produce reservoirs of contaminated perched groundwater. Similarly, nonpoint sources such as agricultural areas that receive fertilizer and pesticide applications, construction sites, industrial sites, and municipal areas can also constitute sources of liquid contamination.

Such reservoirs of contaminated perched groundwater can act to control the movement and fate of these contaminants within the subsurface. Perched horizons may act as continuing sources, "filters," vapor reservoirs, or nonaqueous phase liquid (NAPL) reservoirs, depending on both the nature of the contaminant source and the site hydrogeology. At some sites, perching of contaminants may locally prevent contamination of underlying groundwater by intercepting the downward migration of contaminants. On the other hand, this condition may only postpone the inevitable contamination and may prevent earlier detection of sources and incipient problems.

Related Terms & Concepts

Semiperched Groundwater. Semiperched groundwater may be described as a zone of saturation that overlies a semiconfined aquifer. Thus, the perching unit is leaky, and a hydraulic relationship exists between the semiperched aquifer and the underlying semiconfined aquifer and often allows upward migration of water into the semiperched zone. In this case, the saturated zone effectively extends to the top of the semiperched zone, in contrast to the traditional perched zone, which is positioned over an unsaturated zone. Failure to recognize and account for such zones has been identified as a potential issue in interpreting regional groundwater level trends (13).

In another context, semiperched groundwater that occurs among cyclothems in coal regions of Pennsylvania is discussed. Again, the permeability contrasts created in a stratigraphic sequence of alternating lithologies detains or retards the vertical movement of water through the unsaturated zone creating both perched and semiperched groundwater. Depending on topography, these zones may also discharge as springs. Such terrains have been termed "hydrologic islands" and have been related to a hierarchical classification of local, intermediate, and regional groundwater flow (14).

Tension-Saturated Zone. Tension-saturated zone is another term for the capillary fringe overlying the saturated zone wherein pores of the medium are saturated, but the pressure heads are less than atmospheric (15).

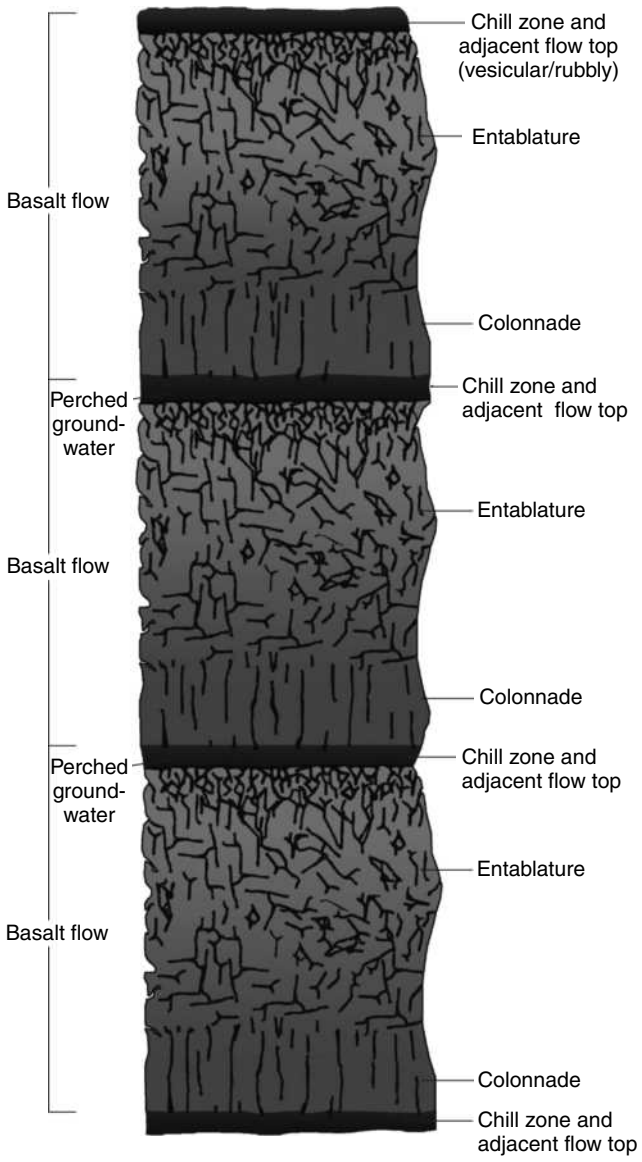


Figure 3. Conceptualized intraflow structures in flood basalts (12).

Temporary Saturated Zones. Perched groundwater may result locally from various ephemeral events as well as in response to surface disturbances. Conditions that lead to sudden recharge are favored by high antecedent moisture conditions; high-intensity rainfall; and various conditions related to storm duration, infiltration, slope, and subsurface strata. Anthropogenic activities such as timber clearing, grading, road construction, and extreme natural events such as flooding and snowmelt may create perched groundwater. In some instances, perched groundwater has been cited as a cause for slope failure (16).

BIBLIOGRAPHY

1. Bouwer, H. (1978). *Groundwater Hydrology*. McGraw-Hill, New York.
2. Freeze, R.A. (1971). Three-dimensional, transient, saturated-unsaturated flow in a groundwater basin. *Water Resour. Res.* **8**: 347–366.
3. Hantush, M.S. (1967). Growth and decay of groundwater-mounds in response to uniform percolation. *Water Resour. Res.* **3**: 227–234.
4. Anderson, S.R. (1988). *Potential for Aquifer Compaction, Land Subsidence, and Earth Fissures in the Tucson Basin, Pima County, Arizona*. U.S. Geological Survey Hydrologic Investigations Atlas HA-713.
5. Parsons. (1986). *Aviation Corridor Highway (State Route 210), Junction I-120 to Junction SR-210: Subsurface Investigations, Phase I, Geotechnical Report*. Prepared by Parsons, Brinkerhoff, Quade, Douglas, Inc. for Arizona Department of Transportation, Highways Division.
6. Leake, S.A. and Hanson, R.T. (1987). *Distribution and Movement of Trichloroethylene in Ground Water in the Tucson Area, Arizona*. U.S. Geological Survey Water-Resources Investigation Report 86–4313.
7. Nelson, D.F. and Dulaney, A.R. (1996). *A Resource Effective Management Tool for Multi-Agency Projects Through GIS: As Implemented in the Downtown Tucson Groundwater Study*. Arizona Department of Environmental Quality. ESRI Symposium Paper.
8. Stearns, H.T. and Macdonald, G.A. (1946). *Geology and Ground-Water Resources of the Island of Hawaii*. Hawaii Division of Hydrography, Bull. 9.
9. Peterson, F.L. (1972). Water development of tropic volcanic islands—types example: Hawaii. *Ground Water* **10**(5): 18–23.
10. Stearns, H.T. (1966). *Geology of the State of Hawaii*. Pacific Books, Palo Alto, CA.
11. Macdonald, G.A., Abbott, A.T., and Peterson, F.L. (1983). *Volcanoes in the Sea: The Geology of Hawaii*, 2nd Edn. University of Hawaii Press, Honolulu, HI.
12. USFS. Columbia River Basalt. Website constructed by Portland State University on behalf of U.S. Forest Service. Available: http://www.fs.fed.us/r6/columbia/basalt.htm.
13. Pederson, D.T. (2001). Effect of semi-perched ground water on monitoring of ground water levels in a developed aquifer. *Irrigation Drainage Abstr.* **27**(4): 292.
14. Poth, C.W. (1963). *Geology and Hydrology of the Mercer Quadrangle, Mercer, Lawrence, and Butler Counties, Pennsylvania*. PA Topographic and Geological Survey, Water Resource Report No. 15.
15. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
16. Chatwin, S.C., Howes, D.E., Schwab, J.W., and Swanston, D.N. (1994). A guide for management of landslide-prone terrain in the Pacific Northwest. *Land Management Handbook* No. 18. 2nd Edn. British Columbia Ministry of Forests.

PERMEABILITY

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Permeability is a measure of the ease with which fluids pass through a porous medium. It was established

experimentally by Darcy in 1856 that

$$k = (Q/A)n(dp/ds)^{-1}$$

in which k is the permeability, Q is the volume of fluid which passes in unit time through area A in the direction s of the pressure gradient dp/ds, and n is the viscosity of the fluid. The unit of permeability in most common use by geologists and members of the oil industry is the darcy (D), which corresponds to a flow of 1 $cm^3\,s^{-1}\,cm^{-2}$ at a pressure gradient of 1bar cm^{-1}. If the fluid is water, material with a permeability of 1D will pass 10^{-3} $cm^3\,s^{-1}\,cm^{-1}$ at a pressure gradient of 1 $g\,cm^2\,cm^{-1}$.

A few typical values of permeability for specific rock types are listed in Table 1. The permeability values quoted in Table1 have been determined in experiments in which the rock specimens have usually been subjected to moderate and constant confining pressure.

Permeability is measured in darcys. One darcy is equal to the passage of 1 cm^3 of a fluid with a viscosity of 1 cP (centipoise) in 1 s under a pressure difference of 1 atm through a porous medium having a cross section of 1 cm^2 and length of 1 cm (1). The centipoise is 1/100 of a poise, which is the cgs unit of dynamic viscosity. The poise is equal to 1 $dyn\,s\,cm^{-2} = 0.1$ Pa s (because dynes/square centimeter = pressure). Permeability ranges from 1 to 5 darcy in loose sediments and from 0.05 to 1 darcy in rocks. The lowest value (0.05 darcy) applies to cherts, which are practically impermeable masses of microcrystalline quartz. A rock may have high porosity but no permeability because the holes are not interconnected (e.g., a vesicular lava) or because they are too small (e.g., clay).

Permeability is high where pore spaces are large and numerous and where they are freely intercommunicating. If the pores are large but are not intercommunicating, the rock may have low permeability even though its porosity is high. A rock with pore spaces of given size, abundance, and continuity is more permeable to fluids of low than of high viscosity. Permeability is sometimes called tightness. An oil-bearing rock is tight if it yields its oil with difficulty, and it is open if it yields its oil freely.

In the study of groundwater, the permeability of rocks is of fundamental importance. Generally speaking, highly permeable rocks form good aquifers. Sand and gravel are more permeable than silt and clay. Therefore, gravel and sand constitute a very large proportion of well-developed aquifers. Sandstones generally make good aquifers. Rocks of volcanic origin, such as basalts, make good aquifer materials only if they are fractured, vesicular, and porous. Granite, gneiss, and other crystalline and metamorphic rocks are generally impermeable and hence, do not form good aquifers (3). A geologic formation that is completely impermeable and is devoid of water is called an aquifuge.

Table 1. Typical Values of the Permeability of Some Rock Types[a]

Rock Type	Permeability, k, (D)
Sandstones and limestones	10^0–10^{-2}
	10^{-2}–10^{-5}
Argillaceous	10^{-5}
	10^{-6}–10^{-8}
Halite	$< 10^{-6}$
Marble	$< 10^{-7}$

[a]Reference 2.

When aquifers are confined by an impermeable layer or stratum, the aquifers are called confined aquifers. If the confining unit is relatively impermeable, such as clay, it is called an aquiclude. If, however, the stratum is not completely impermeable, such as sandy clay, then it is called an aquitard. Such poorly permeable strata leak water to adjacent aquifers.

The permeability of rocks depends on

1. The size and shape of the constituent grains. A uniformly coarse-grained gravel forms a highly permeable aquifer, but when the same rock consists of fractions of various sizes, there is a tendency for smaller sediments to get into and fill or block the interstices rendering it less permeable. Rounded fractions result in higher porosity and hence better permeability than angular fractions in the same grain size range (3).
2. Sorting of grains. Well-sorted materials (i.e., where grains of a particular size are in one layer followed by grains of the next size) have higher permeability than ill-sorted or unsorted grains in a rock.
3. Continuity and nature of interstices, especially when they are secondary. The mere presence of cracks or cavities or joints does not make a rock permeable; all openings must also be interconnected or mutually communicating; only then is the flow of water through the rock mass possible.

Permeability Investigation for a Reservoir Site

Many types of rocks may be traversed by a proposed reservoir. For ideal conditions, they should be impervious and impermeable. The main object of permeability investigations is, therefore, to determine the character of the rocks of the reservoir region and locate the "highly permeable" formations that can be treated as most unsuitable for the reservoir or dam site.

For reservoir sites, rocks may be divided into three groups: highly permeable, occasionally permeable, and least permeable. Highly permeable rocks include well-sorted gravel, sand, and coarse sandstone and deposits of glacial origin such as moraines and till. Occasionally permeable includes those rocks that acquire permeability due to secondary features such as cracks, fissures, solution cavities, and gas cavities. Limestone, vesicular basalt, jointed granite, and gneiss are examples of such rocks, which are otherwise impervious but are often rendered unsuitable because of prolific development of the secondary features described. Least permeable are igneous rocks, which are unjointed and thoroughly crystalline; massive limestones and sandstones can generally be considered impermeable.

Relation of Porosity and Permeability

Good correlation if pores are clean (if pore tortuosity is low); poor to no correlation if pore tortuosity is high because of clay cements, etc.

BIBLIOGRAPHY

1. Emiliani, C. (1997). *Planet Earth Cosmology, Geology and the Evolution of Life and Environment*. Cambridge University Press, New York, p. 322.
2. Fyfe, W.S., Price, N.J., and Thompson, A.B. (1978). *Fluids in the Earth's Crust*. Elsevier Scientific, New York, p. 255.
3. Singh, P. (1978). *Engineering and General Geology*. Katson, Ludhiana, p. 369.

GROUNDWATER VULNERABILITY TO PESTICIDES: AN OVERVIEW OF APPROACHES AND METHODS OF EVALUATION

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INTRODUCTION

Groundwater contamination is one of the most important environmental quality concerns. The subsurface migration of hazardous wastes from point sources firmly caught the public's attention in 1977 with the well-publicized Love Canal story. Characteristically, point sources are relatively easy to identify and control. Groundwater contamination from nonpoint sources (NPSs) is a greater environmental problem (1). Nonpoint sources, as a result of contaminants entering the environment over an extensive area, are difficult (at best) or impossible to trace to a specific location and have the potential for maintaining a relatively long active presence in entire ecosystems. Historically, point sources have received the greatest attention because of the conspicuous severity of their impacts. In recent years, public, political, and scientific attention have shifted toward NPSs. This shift reflects an awareness of the scope and potential impact of NPS pollution (2,3). Regulation, monitoring, litigation, and remediation have each helped to control or reduce both point and NPSs of groundwater contamination.

The word *pesticide* is a general term used to refer to the chemicals that are employed to control, destroy, mitigate, prevent, or repel pests (plant or animal). There are several classes of pesticides (e.g., algaecides, fungicides, germicides, herbicides, insecticides, miticides, molluskicides, rodenticides, and termiticides). In the United States, the Environmental Protection Agency (EPA) regulates pesticides under the authority of the 1996 amendments to the *Federal Insecticide, Fungicide, and Rodenticide Act* (FIFRA) of 1947. All pesticides must be registered and carry a *label* (providing the rules for application rates and frequencies) approved by the EPA. The distribution and trends of pesticides in the atmosphere (4), groundwater (5), surface water (6), and fluvial sediments and aquatic biota (7) have been carefully assessed. For example, there have been well over 100 monitoring studies in recent years, which quantitatively document the occurrence of pesticides in groundwater (5). The impact of widespread pesticide use, in what Freeze (8) calls *the age of awakening* (i.e., environmental perspective) or *the age of social upheaval* (i.e., new right perspective), was lucidly bought to the public's attention by Rachel Carson in her 1962 book *Silent Spring* (9), which in large part forced the banning of DDT. Barbash and Resek (5) provide a glossary of 600 pesticides that are of interest relative to groundwater impacts. Table 1 identifies 31 pesticides that have received considerable attention.

In many areas of the world, successful agriculture depends on both pesticides and irrigation. The combination of repeated pesticide applications and irrigation over a large NPS area often leads to leaching through the vadose zone and, subsequently, to groundwater contamination. For example, in the semiarid San Joaquin Valley in California, where groundwater contamination concentrations have been among the highest reported, the amount of active pesticide ingredient applied annually is on the order of 50 million kilograms. A spill of concentrated pesticide at a mixing or distribution site is an example of point source pollution. For example, in April 1977, there was an accidental spill of approximately 1900 liters of the pesticide EDB (see Table 1) within approximately 20 meters of a well that provided drinking water to the village of Kunia on the Hawaiian island of Oahu. The area around the spill eventually became a *Superfund* site.

VULNERABILITY ASSESSMENT

Assessment involves determination of the change in some constituent over time. This change can be measured in either real time or simulated by a model. Real-time measurements reflect the activities of the past, whereas simulations can provide useful glimpses into the future. Both means of assessment are valuable. The distinct advantage of simulation is that it can be used to alter the occurrence of detrimental conditions before they occur. It should be pointed out that simulation cannot replace *real* data.

By definition, a model integrates existing knowledge into a framework of rules, equations, and relationships to quantify the way a system behaves. As long as a model is applied over the range of conditions from which they it was initially developed, it serves as a useful tool for prognostication. Models can range in complexity from the simplest empirical equation to complex sets of partial differential equations that are solvable only by numerical approximation techniques.

Table 1. Thirty-One Important Pesticides[a]

Common Name	Chemical Name	Use
1,2-Dichloropropane[b,c]	1,2-Dichloropropane	Nematicide
2,4-D[b]	2,4-Dichlorophenoxy acetic acid	Herbicide
2,4-DP[c]	Butoxyethyl ester of (±) 2-(2,4-dichlorophenoxy)propanoic acid	Herbicide
Alachlor[b]	2-Chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide	Herbicide
Aldicarb[b]	2-Methyl-2-(methylthio)-propionaldehyde *O*-(methylcarbamoyl)oxime	Insecticide
Atrazine[b,c]	2-Chloro-4-ethylamino-6-isopropylamino-*S*-triazine	Herbicide
Bromacil[b]	5-Bromo-3-(*sec*-butyl)-6-methyluracil	Herbicide
Carbaryl[b]	1-Naphthyl-*N*-methylcarbamate	Insecticide
Carbofuran[b]	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-*n*-methylcarbamate	Insecticide
Carboxin[b]	5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxanilide	Fungicide
Chlorothalonil[b]	Tetrachloroisophthalonitrile	Fungicide
Cyanazine[b]	2[[4-Chloro-6(ethylamino)-*S*-triazin-2-yl]amino]-2-methylpropionitrile	Herbicide
Dalapon[b,d]	2,2 Dichloropropionic acid (sodium salt)	Herbicide
DBCP[c,d]	1,2-Dibromo-3-chloropropane	Nematicide
DCPA[b]	Dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate	Herbicide
Diazinon[b,c]	*O*, *O*-Diethyl-*O*-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothiote	Insecticide
Dicamba[b,c]	2-Methoxy-3,6-dichlorobenzoic acid	Herbicide
Dinoseb[b,d]	2-*sec*-Butyl-4,6-dinitrophenol	Herbicide
Diphenamid[b,d]	*N*,*N*-Dimethyl-α -phenylbenzeneacetamide	Herbicide
Disulfoton[b]	*O*,*O*-Diethyl *S*-[2-(ethylthio)ethyl]phosphorodithioate	Insecticide
Diuron[b,c]	3-(3,4-Dichlorophenyl)-1,1-dimethylurea	Herbicide
EDB[c,d]	1,2-Dibromoethane	Insecticide
Methomyl[b]	*S*-Methyl-*N*-(methylcarbamoyl)oxy)-thioacetamidate	Insecticide
Metolachlor[b]	2-Chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide	Insecticide
Oxamyl[b]	Methyl 2-(dimethylamino)-*N*-[[(methylamino)carbonyl]oxy]-2-oxoethanimimdothioate	Insecticide
Prometon[c]	6-Methoxy-*N*,*N*′-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine	Herbicide
Prometryn [c]	*N*,*N*′-Bis(1-Methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine	Herbicide
Propazine[c,d]	6-Chloro-*N*,*N*′-*bis*(1-methylethyl)-1,3,5-triazine-2,4-diamine	Herbicide
Simazine[b,c]	2-Chloro-4,6-bis(ethylamino)-s-triazine	Herbicide
Tebuthiuron[b]	*N*-[5-(1,1-Dimethyl)-1,3,4-thiadizol-2-yl]-*N*,*N*′-dimethylurea	Herbicide
Trifluralin[b]	2,6-Dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenemamine	Herbicide

[a] abstracted from the 341 pesticides in Hornsby et al. (10)
[b] Identified by EPA (11) as high risk for groundwater contamination.
[c] Detected in groundwater in California (12).
[d] Cancelled or severely restricted in the United States.

The use of models to aid in the assessment of groundwater vulnerability is now a well-established tool, employed both in industry and by regulatory agencies. The various mechanisms that facilitate the migration of pesticides from the surface/near surface to the water table and the methods used to simulate these processes have been the subject of considerable review (13–27). In general, subsurface flow and pesticide transport are, respectively, estimated by Richards' equation and the advection–dispersion equation, or simplifications. The processes that are important to consider in assessing groundwater vulnerability to pesticide contamination are advection, diffusion, dispersion, sorption, transformation, and volatilization (28). The increasing availability of geographic information system (GIS) software to those assessing the potential for NPS groundwater contamination from pesticides has resulted in the generation of regional-scale multicolored vulnerability maps for use in decision management (29).

Three categories of models for assessing groundwater vulnerability from pesticides are (1) regression models, (2) index models, and (3) transient-state solute transport models. Regression models generally use multiple linear regressions to relate various causative factors. Index models, which can be property or process based, compute an index of pesticide mobility. Transient-state, process-based models are capable of simulating the concentration/movement of a pesticide in a dynamic flow system.

One of the first and most promoted regional-scale groundwater vulnerability methods for assessing the impact of pesticides was the DRASTIC index (30). The early process-based simulations by Petach et al. (31) were both elegant and ambitious considering the large scale of the pesticide leaching assessments. During the last two decades, a number of process-based models have been developed for assessing the behavior of pesticides in the near surface (e.g., PRZM (32), LEACHM (33), GLEAMS (34), HYDRUS-1D (35), LEACHP (36), RZWQM (37), PRZM-2 (38), PELMO (39), MACRO (40), HYDRUS-2D (41), and PESTLA (42)). Table 2 lists selected pesticide leaching assessments for California, Hawaii, and Tenerife.

UNCERTAINTY

There can be considerable uncertainty in assessments of point and NPS pollution to groundwater from pesticides. Three sources of error inherent in modeling are (1) model error, (2) input error, and (3) parameter error. Model

Table 2. Summary of Selected Pesticide Leaching Assessments in California, Hawaii, and Tenerife

Location	Model Name	Model Category[f]	Reference
San Joaquin Valley, California	PSCLR	R	(43)
	AF[a]	I	(44,45)
	PRZM-2[b]	TSST	(46)
	TTF[c]	TSST	(47)
Oahu, Hawaii	AF	I	(48–56)
	PRZM[d]	TSST	(57–60)
Tenerife, Canary Islands, Spain	AF	I	(61,62)
	Li[e]	I	(63)
	AF, PRZM-2	I, TSST	(64)

[a] Attenuation factor (65).
[b] Pesticide root zone model - Version 2 (37).
[c] Type transfer function model (66).
[d] Pesticide root zone model (31).
[e] Leaching index (67).
[f] R: regression model; I: index model; and TSST: transient-state solute transport model.

error results in the inability of a model to simulate the given process, even with the correct input and parameter estimates. Input error is the result of errors in the source terms. Input error can arise from measurement, juxtaposition, and/or synchronization errors. Parameter error has two possible connotations. For models requiring calibration, parameter error usually is the result of model parameters that are highly interdependent and not unique. For models with physically based parameters, parameter error results from an inability to represent aerial distributions on the basis of a limited number of point measurements. The aggregation of model error, input error, and parameter error is the total (or simulation) error. For multiple-process and comprehensive models, simulation error is complicated further by the propagation of error between model components.

The methods for characterizing uncertainty can, in general, be grouped into three categories (68): (1) first-order analysis, (2) sensitivity analysis, and (3) Monte Carlo analysis. First-order analysis is a simple technique for quantifying the propagation of uncertainty from input parameter to model output. Sensitivity analysis is used to measure the impact that changing one factor has on another. Monte Carlo analysis is a stochastic technique for characterizing the uncertainty in complex hydrologic response model simulations. Loague and Corwin (68) provide examples of first-order uncertainty analysis, sensitivity analysis, and Monte Carlo simulation. Note that most of the groundwater vulnerability assessments listed in Table 2 were designed to identify the uncertainty in the estimates relative to the uncertainty in the chemical, climate, and soil databases.

FRESNO CASE STUDY, AN EXAMPLE

Between the late 1950s and the time of its statewide cancellation in August of 1977, there was widespread use of DBCP (see Table 1) throughout the San Joaquin Valley in California. More than two decades after its cancellation, DBCP-contaminated groundwater persisted as a problem in the San Joaquin Valley. The objective of the Fresno case study (46,69) was to address, from a simulation perspective, if *label recommended* NPS applications were likely to be the principal source of the DBCP groundwater contamination in Fresno County (note that DBCP was a legacy when the study was conducted). The relatively unique characteristic of the Fresno case study is that both the unsaturated near surface and the saturated subsurface were considered for a 2184 km^2 area.

The numerical model used for 1-D simulations (46) of dissolved phase DBCP concentration profiles in the unsaturated zone was PRZM-2 (37). The potential fate and transport of DBCP between the surface and the water table for multiple NPS applications were quantitatively estimated from 1172 separate 35-year simulations. The aggregate of the DBCP concentrations loaded to the water table made up the annual loading files for the 3-D saturated transient transport simulations. The numerical models used for the 3-D simulations (69) of saturated subsurface fluid flow and DBCP transport, for the same 35-year period, are MODFLOW (70) and MT3D (71), respectively. A 76,440-element mesh was used for the saturated simulations.

The simulation results from the Fresno case study lead to several conclusions (46,69): (1) the areas most likely to facilitate DBCP leaching through the entire unsaturated soil profile were targeted; (2) the first appearance of DBCP above the detectable limit at the water table was simulated as most likely to have occurred between 1961 and 1965; (3) the estimated DBCP concentrations reaching the saturated subsurface exceed the maximum contaminant level (MCL) at several locations at different times; (4) the first appearance above the MCL was between 1965 and 1970 (note that by 1990, the concentrations are below the MCL); (5) relative to the size of the study area, the extent and duration of the estimated DBCP contamination was small; (6) DBCP concentrations are a function of spatial and temporal variations in the application rates, the application frequency, the unsaturated profile thickness, the soil-hydraulic properties, and the near-surface sorption; and (7) the DBCP plume evolves (grows and retracts) with time due to the loading rates at the water table. Figure 1 shows 1971 snapshots of the simulated DBCP loading to the water table and the 3-D DBCP plume in the saturated subsurface. Note that the Fresno case study assessments were critically evaluated and extended (72,73).

EPILOGUE

The ethics, efficacy, and economics of widespread pesticide applications have all received considerable attention in recent years. Without question, it is important to assess the vulnerability of groundwater to contamination from widespread applications of pesticides. For more than 10 years, the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program has played a key role in this assessment; more than 50 major river basins and aquifers were studied (74). The overall picture emerging from the NAWQA program is that pesticides

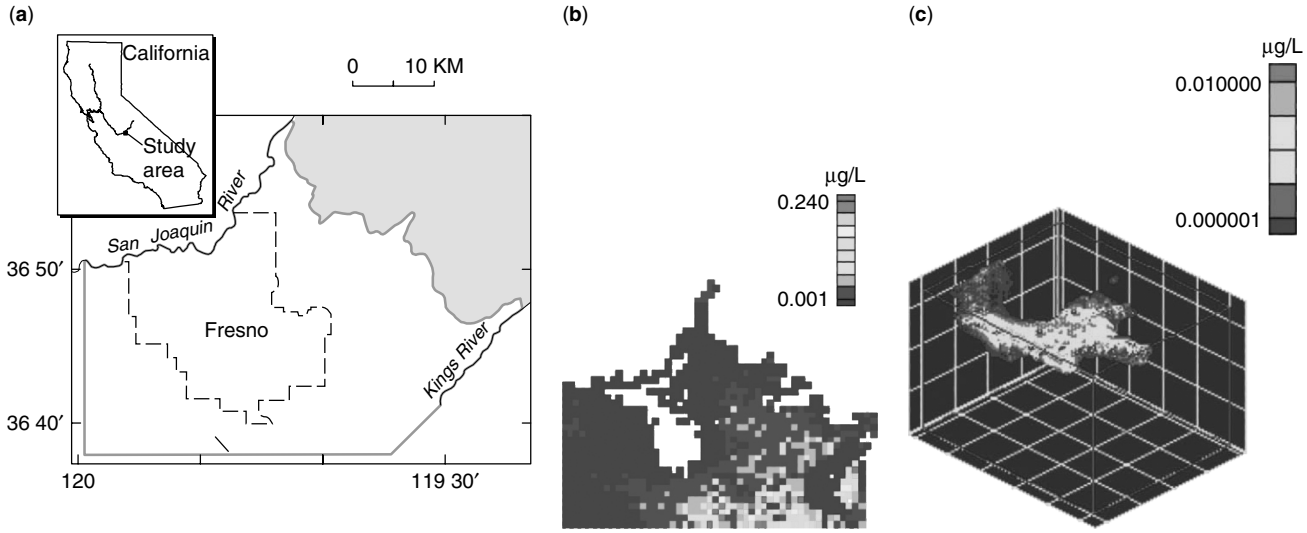


Figure 1. Results from the Fresno case study. (**a**) Location of study area. (**b**) Plan view snapshot of the simulated DBCP concentration loading at the water table for 1971 (46). (**c**) 3-D snapshot of the simulated DBCP concentration plume for 1971 (69).

typically occur at low levels, punctuated by seasonal pulses in concentration (75). Specific to groundwater, pesticides were most frequently found in shallow systems in urban and agricultural areas (74). The patterns of pesticide detection (over space and in time) identify problem areas and chemicals, warn of potential problems, and provide valuable feedback on to improve conditions (75). The use of mathematical models for assessing groundwater vulnerability from pesticides, especially after ground truth comparisons, fills in information gaps, identifies critical areas and chemicals for future monitoring, and provides the "what if" capability needed for both regulation and remediation.

BIBLIOGRAPHY

1. National Research Council. (1993). *Ground Water Vulnerability Assessment: Predicting Relative Contamination Potential under Conditions of Uncertainty*. National Academy Press, Washington, DC.
2. Corwin, D.L. and Loague, K. (Eds.). (1996). *Applications of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone*. Special Publication 48, Soil Science Society of America, Madison, WI.
3. Corwin, D.L., Loague, K., and Ellsworth, T.R. (Eds.). (1999). *Assessment of Non-Point Source Pollution in the Vadose Zone*. Geophysical Monograph 108, AGU Press, Washington, DC.
4. Majewski, M.S. and Capel, P.D. (1995). *Pesticides in the Atmosphere: Distributions, Trends, and Governing Factors*. Ann Arbor Press, Chelsea, MI.
5. Barbash, J.E. and Resek, E.A. (1996). *Pesticides in Ground Water: Distributions, Trends, and Governing Factors*. Ann Arbor Press, Chelsea, MI.
6. Larson, S.J., Capel, P.D., and Majewski, M.S. (1997). *Pesticides in Surface Water: Distributions, Trends, and Governing Factors*. Ann Arbor Press, Chelsea, MI.
7. Nowell, L.H., Capel, P.D., and Dileanis, P.D. (1999). *Pesticides in Stream Sediments and Aquatic Biota: Distributions, Trends, and Governing Factors*. CRC Press, Boca Raton, FL.
8. Freeze, R.A. (2000). *The Environmental Pendulum: A Quest for the Truth About Toxic Chemical, Human Health and Environmental Protection*. University of California Press, Berkeley, CA.
9. Carson, R. (1962). *Silent Spring*. Houghton Mifflin, Boston, MA.
10. Hornsby, A.G., Wauchope, R.D., and Herner, A.E. (1996). *Pesticides Properties in the Environment*. Springer-Verlag, New York.
11. Environmental Protection Agency. (1988). *Pesticides in Groundwater Database 1988 Interim Report*. Environmental Fate and Groundwater Branch, Office of the Pesticide and Toxic Substances, Environmental Protection Agency, Washington, DC.
12. Domagalski, J.L. and Dubrovsky, N.M. (1992). Pesticides residues in groundwater of the San Joaquin Valley, California. *J. Hydrol.* **130**: 299–338.
13. Guenzi, W.D. (Ed.). (1974). *Pesticides in Soil and Water*. Soil Science Society of America, Madison, WI.
14. Garner, W.Y., Honeycutt, R.C., and Nigg, H.N. (1986). *Evaluation of Pesticides in Ground Water*. American Chemical Society, Washington, DC.
15. Giorgini, A. and Zingales, F. (Eds.). (1986). *Agricultural Non-Point Source Pollution: Model Selection and Applications*. Elsevier, New York.
16. Saltzman, S. and Yaron, B. (Eds.). (1986). *Pesticides in Soil*. Van Nostrand Reinhold, New York.
17. Sawhney, B.L. and Brown, K. (Eds.). (1989). *Reactions and Movement of Organic Chemicals in Soils*. SSSA Special Publication No. 22, Soil Science Society of America, Madison, WI.
18. Cheng, H.H. (Ed.). (1990). *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*. Soil Science Society of America, Madison, WI.
19. Hutson, D.H. and Roberts, T.R. (Eds.). (1990). *Environmental Fate of Pesticides*. John Wiley & Sons, New York.
20. Jury, W.A. and Roth, K. (1990). *Transfer Functions and Solute Movement Through Soil: Theory and Applications*. Birkhauser Verlag, Boston, MA.

21. Schnoor, J.L. (Ed.). (1992). *Fate of Pesticides and Chemical in the Environment*. John Wiley & Sons, New York.
22. Gustafson, D.I. (1993). *Pesticides in Drinking Water*. Van Nostrand Reinhold, New York.
23. Honeycutt, R.C. and Schabacker, D.J. (1994). *Mechanisms of Pesticide Movement into Ground Water*. Lewis, Boca Raton, FL.
24. Leng, M.L., Leovery, E.M.K., and Zubkoff, P.L. (Eds.). (1995). *Agrochemical Environmental Fate: State of the Art*. Lewis, Boca Raton, FL.
25. Vighi, M. and Funari, E. (Eds.). (1995). *Pesticide Risk in Groundwater*. Lewis, Boca Raton, FL.
26. Flury, M. (1996). Experimental evidence of transport of pesticides through field soils—a review. *J. Environ. Qual.* **25**: 25–45.
27. Thorsen, M., Feyen, J., and Styczen, M. (1996). Agrochemical modeling. In: *Distributed Hydrological Modelling*. Dondredit, M.B. Abbott and J.C. Refsgaard (Eds.). Kluwer Academic, The Netherlands, pp. 121–141.
28. Jury, W.A. and Horton, R. (2004). *Soil Physics*. 6th Edn. John Wiley & Sons, Hoboken, NJ.
29. Corwin, D.L., Vaughan, P.J., and Loague, K. (1997). Modeling nonpoint source pollutants in the vadose zone with GIS. *Environ. Sci. Technol.* **31**: 2157–2175.
30. Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., and Hackett, G. (1987). DRASTIC: A standardized system for evaluating ground water pollution potential using hydrogeologic settings, EPA-600/2-87-035. U.S. Environmental Protection Agency, Ada, OK.
31. Petach, M.C., Wagenet, R.J., and DeGloria, S.D. (1991). Regional water flow and pesticide leaching using simulations with spatially distributed data. *Geoderma* **48**: 245–269.
32. Carsel, R.F., Smith, C.N., Mulkey, L.A., Dean, J.D., and Howise, P. (1984). User's manual for the pesticide root zone model (PRZM), Release 1. US/EPA-600/3-84-109. U.S. Environmental Protection Agency, Washington, DC.
33. Wagenet, R.J. and Huston, J.L. (1987). LEACHM: A finite-difference model for simulating water, salt, and pesticide movement in the plant root zone. Continuum 2. New York State Water Resources Institute, Cornell University, Ithaca, NY.
34. Davis, F.M. Leonard, R.A., and Knisel, W.G. (1990). Groundwater loading effects of agricultural management systems (GLEAMS). User Manual. USDA-ARS, Southeast Watershed Research Laboratory and University of Georgia, Rifton, GA.
35. Kool, J.B. and van Genuchten, M.Th. (1991). HYDRUS one-dimensional variability saturated flow and transport model, including hysteresis and root uptake. U.S. Salinity Laboratory, USDA-ARS, Riverside, CA.
36. Huston, J.L. and Wagenet, J.R. (1992). LEACHP: A process-based model of water and solute movement, transformations, plant uptake, and chemical reactions in the unsaturated zone (Version 3). Research Series 92-3, Department of Soil, Crop, and Atmospheric Sciences, New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, NY.
37. DeCoursey, D.G., Ahuja, L.R., Hanson, J., Shaffer, M., Nash, R., Rojas, K.W., Hebson, C., Hodges, T., Ma, Q., Johnsen, K.E., and Ghidey, F. (1992). Root zone water quality model, Version 1.0. Technical Documentation. USDA-ARS, Great Plains Systems Research Unit, Fort Collins, CO.
38. Mullins, J.A., Carsel, R.F., Scarbough, J.E., and Ivery, A.M. (1993). PRZM-2, A model for predicting pesticide fate in the crop root and unsaturated soil zones: Users manual for release 2. EPA-600/R-93/046. USEPA Environmental Research Laboratory, Athens, GA.
39. Klein, M. (1993). PELMO—Pesticide leaching model, Version 1.5, User's Manual. Frauenhofer-Institut fur Umweltchemie and Okotoxikolgie, Schmallenberg.
40. Jarvis, N. (1994). The MACRO model (Version 3.1)—Technical description and sample simulations. Monograph, Reports, and Dissertations, 19, Department of Soil Science, Swedish University of Agricultural Science, Uppsala, Sweden.
41. Simunek, J.M, Sejna, M., and Van Genuchten, M.Th. (1996). HYDRUS-2D. Simulating water flow and solute transport in two-dimensional variability saturated media. U.S. Salinity Laboratory, USDA-ARS, Riverside, CA.
42. van den Berg, F. and Boesten, J.J.T.I. (1998). Pesticide leaching and accumulation model (PESTLA). Version 3.3. Description and user's guide, Technical Document 43, DLO-Starting Centrum, Wageningen, The Netherlands.
43. Teso, R.R., Poe, M.P., Younglove, T., and McCool, P.M. (1996). Use of logistic regression and GIS modeling to predict groundwater vulnerability to pesticides. *J. Environ. Qual.* **25**: 425–432.
44. Blanke, J.S. (1999). *Vulnerability to groundwater contamination due to agrochemical use in the San Joaquin Valley, California*. Masters Thesis, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA.
45. Mills, M.B. (2004). *Groundwater vulnerability due to pesticide use in the San Joaquin Valley, California*. Masters Thesis, Earth Systems Program, Stanford University, Stanford, CA.
46. Loague, K., Lloyd, D., Nguyen, A., Davis, S.N., and Abrams, R.H. (1998). A case study simulation of DBCP groundwater contamination in Fresno County, California: 1. Leaching through the unsaturated subsurface. *J. Contam. Hydrol.* **29**: 109–136.
47. Stewart, I.T. and Loague, K. (2003). Development of type transfer functions for regional-scale non-point source groundwater vulnerability assessments. *Water Resour. Res.* **39**(12): 1359, doi:10.1029/2003WR002269.
48. Khan, M.A. and Liang, T. (1989). Mapping pesticide contamination potential. *Environ. Manage.* **13**: 233–242.
49. Loague, K.M., Yost, R.S., Green, R.E., and Liang, T.C. (1989). Uncertainty in a pesticide leaching assessment for Hawaii. *J. Contam. Hydrol.* **4**: 139–161.
50. Loague, K. et al. (1990). Impact of uncertainty in soil, climatic, and chemical information in a pesticide leaching assessment. *J. Contam. Hydrol.* **5**: 171–194; 405.
51. Loague, K. (1991). The impact of land use on estimates of pesticide leaching potential: Assessments and uncertainties. *J. Contam. Hydrol.* **8**: 157–175.
52. Loague, K. (1994). Regional scale ground water vulnerability estimates: Impact of reducing data uncertainties for assessments in Hawaii. *Ground Water* **32**: 605–616.
53. Kleveno, J.J., Loague, K., and Green, R.E. (1992). An evaluation of a pesticide mobility index: Impact of recharge variation and soil profile heterogeneity. *J. Contam. Hydrol.* **11**: 83–99.
54. Yost, R.S., Loague, K., and Green, R.E. (1993). Reducing variance in soil organic carbon estimates: Soil classification and geostatistical approaches. *Geoderma* **57**: 247–262.
55. Giambelluca, T.W., Loague, K., Green, R.E., and Nullet, M.A. (1996). Uncertainty in recharge estimation: Impact on groundwater vulnerability assessments for the Pearl Harbor Basin, Oahu, Hawaii. *J. Contam. Hydrol.* **23**: 85–112.

56. Li, Z.C., Yost, R.S., and Green, R.E. (1998). Incorporating uncertainty in a chemical leaching assessment. *J. Contam. Hydrol.* **29**: 285–299.
57. Loague, K.M., Green, R.E., Liu, C.C.K., and Liang, T.C. (1989). Simulation of organic chemical movement in Hawaii soils with PRZM: 1. Preliminary results for EDB. *Pac. Sci.* **43**: 67–95.
58. Loague, K. et al. (1989). Simulation of organic chemical movement in Hawaii soils with PRZM: 2. Predicting deep penetration of DBCP, EDB, and TCP. *Pac. Sci.* **43**: 362–383.
59. Loague, K. (1992). Simulation of organic chemical movement in Hawaii soils with PRZM: 3. Calibration. *Pac. Sci.* **46**: 353–373.
60. Loague, K. et al. (1995). Chemical leaching near the Waiawa Shaft, Oahu, Hawaii: 2. Modeling results. *Ground Water* **33**: 124–138.
61. Diaz-Diaz, R., Garcia-Hernandez, J.E., and Loague, K. (1998). Leaching potentials of four pesticides used for bananas in the Canary Islands. *J. Environ. Qual.* **27**: 562–572.
62. Diaz-Diaz, R. and Loague, K. (2000). Regional-scale leaching assessments for Tenerife: Impact of data uncertainties. *J. Environ. Qual.* **29**: 835–847.
63. Diaz-Diaz, R., Loague, K., and Notario, J.S. (1999). An assessment of agrochemical leaching potentials for Tenerife. *J. Contam. Hydrol.* **36**: 1–30.
64. Diaz- Diaz, R. and Loague, K. (2001). Assessing the potential for pesticide leaching for the pine forest areas of Tenerife. *Environ. Toxicol. Chem.* **20**: 1958–1967.
65. Rao, P.S.C., Hornsby, A.G., and Jessup, R.E. (1985). Indices for ranking the potential for pesticide contamination of groundwater. *Soil Crop Sci. Soc. Fl. Proc.* **44**: 1–8.
66. Stewart, I.T. and Loague, K. (2004). Assessing San Joaquin Valley, California, groundwater vulnerability with the type transfer function model. *J. Environ. Qual.* **33**: 1487–1498.
67. Bacci, E. (1994). *Ecotoxicology of Organic Contaminants*. Lewis, New York.
68. Loague, K. and Corwin, D.L. (1996). Uncertainty in regional-scale assessments of non-point source pollutants. In: *Applications of GIS to the Modeling of Non-Point Source Pollutants in the Vadose Zone*. D.L. Corwin and K. Loague (Eds.). Special Publication 48, Soil Science Society of America, Madison, WI, pp. 131–152.
69. Loague, K. et al. (1998). A case study simulation of DBCP groundwater contamination in Fresno County, California: 2. Transport in the saturated subsurface. *J. Contam. Hydrol.* **29**: 137–163.
70. McDonald, M.G. and Harbaugh, A.W. (1988). A modular three-dimensional finite-difference groundwater flow model. Scientific Software Group, Washington, DC.
71. Zheng, C. (1992). MT3D: A modular three-dimensional model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems (Version 1.5). S.S. Papadopulos and Associates, Bethesda, MD.
72. Soutter, L.A. and Loague, K. (2000). Revisiting the Fresno DBCP case study simulations: The impact of upscaling. *J. Environ. Qual.* **29**: 1794–1805.
73. Loague, K. and Abrams, R.H. (1999). DBCP contaminated groundwater: Hot spots and non-point sources. *J. Environ. Qual.* **28**: 429–445.
74. Gilliom, R.J. (2001). Pesticides in the hydrologic system—what do we know and what's next? *Hydrological Processes* **15**: 3197–3201.
75. Graffy, E.A. (1998). Low-level detection of pesticides... so what? *J. Soil Water Conserv.* **53**: 11–12.

HIGH pH GROUNDWATER—THE EFFECT OF THE DISSOLUTION OF HARDENED CEMENT PASTES

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INTRODUCTION

Concrete is the most widely used construction material manufactured by mixing together cement, aggregates, water, air, and various admixtures. Conventional hardened concrete comprises approximately 30% by volume of cement paste phase and 18% pore voids. Many concrete structures are built above and below ground, some in contact with surface and/or groundwater. In these cases, pore voids within concrete are filled with water. Groundwater chemistry is affected when brought into contact with or close proximity to such structures since the hydration products of cement can be dissolved and leached into the groundwater.

In fact, groundwater chemistry close to aboveground structures is affected by the rainwater falling on these structures prior to soaking into the ground and becoming groundwater. The composition of groundwater varies widely, depending on the soil or rock with which the water is in equilibrium. Rainwater can be acidic ("acid rain"), which may be quickly consumed. The local soil, rocks, and minerals result in dissolution of some ions into the resulting runoff. For example, acid rain leached aluminum into lakes in the northern United States, killing the local aquatic life in those lakes. Acidic mine runoff is another source for acid groundwater. On the other hand, limestone strata result in hard water with higher pH and seawater results in higher ionic concentrations from dissolved salts. It is well known that some ions in groundwater can migrate into concrete and even deteriorate the integrity of the concrete structures.

The focus here is on how the hydration products of cements affect the pH of groundwater since they have very high equilibrium pH values. To fully evaluate this effect requires knowledge of cement chemistry, the characteristics of hydration products, and the transport of ions in hardened concrete. We first summarize cement chemistry, the effect of supplementary cementing materials on this chemistry, and the dissolution and leaching of hydration products of cement. The last section discusses the interaction with cement and its leached ions. For a given case, the known cement chemistry can be used to project what to expect for the local groundwater in question.

CHARACTERIZATION AND HYDRATION CHEMISTRY OF PORTLAND CEMENT

Portland cement is the most used cementing material in construction. It is a hydraulic cement produced by

pulverizing clinker and calcium sulfate (usually gypsum—$CaSO_4 \cdot 2H_2O$) as an interground addition. Cement clinker consists mainly of tricalcium silicate ($3CaO \cdot SiO_2$—C_3S), dicalcium silicate ($2CaO \cdot SiO_2$—C_2S), tricalcium aluminate ($3CaO \cdot Al_2O_3$—C_3A), and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$—$C_4AF$). Different types of Portland cement are manufactured to meet various normal physical and chemical requirements for specific purposes. ASTM C150 specifies five types of common Portland cement produced by adjusting the proportions of their minerals and finenesses.

In the presence of water, C_3S and C_2S in cement hydrate to form calcium silicate hydrate gel (C-S-H gel) and $Ca(OH)_2$. In the presence of calcium sulfate, C_3A hydrates to form calcium trisulfoaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$—AFt or ettringite), or calcium monosulfoaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$—AFm or monosulfate). In the absence of calcium sulfate, C_3A reacts with water and calcium hydroxide to form tetracalcium aluminate hydrate [$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$]. C_4AF reacts with water to form calcium aluminoferrite hydrates ($6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O$). These hydration reactions can be expressed as follows:

$$3(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

$$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 2(3CaO \cdot Al_2O_3) + 4H_2O \rightarrow 3(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O) \quad (4)$$

$$3CaO \cdot Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O \quad (5)$$

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O \quad (6)$$

A hardened cement paste is a heterogeneous multiphase system. At room temperature, a fully hydrated Portland cement paste consists of 50–60% C-S-H gel, 20–25% $Ca(OH)_2$, 15–20% ettringite (or AFt) and AFm by volume. The minor hydration products, such as $Ca(OH)_2$, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, and AFt, form in small quantities depending on the composition of the cementing material and hydration conditions.

Portland cement also contains a small amount of alkalis; but the amount is dependent on the raw materials and production process used. The presence of a small amount of alkalis does not have a significant effect on the hydration process of the cement but may have a significant effect on the pH of the pore solution. Usually, the pH value of the pore solution of a hardened Portland cement is over 12.5 to values as high as 13.5, due to the presence of alkalis.

USE OF SUPPLEMENTARY CEMENTING MATERIALS AS CEMENT REPLACEMENTS

For construction use, supplementary cementing materials, such as granulated/pelletized blast furnace slag, coal fly ash, volcanic ashes, condensed silica fume, rice husk ash, and natural pozzolans, are often used to replace Portland cement to reduce the cost or to improve the performance of concrete.

When Portland pozzolan cement contacts water, Portland cement hydrates first; the lime released from the hydration of Portland cement reacts with pozzolan to form new products depending on the composition of the pozzolan and hydration conditions. The main hydration product in lime–pozzolan mixtures is C-S-H with a C/S ratio less than 1.5, depending on the local concentration of reactants. The aluminate in the pozzolan may yield a variety of hydrates: calcium aluminate hydrate (C_4AH_{19}), gehlenite hydrate (C_2ASH_8), AFt ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$), and AFm ($C_3A \cdot CaSO_4 \cdot 12H_2O$). The pozzolanic reactions can be generally expressed as follows:

$$Ca(OH)_2 + SiO_2 + (n-1)H_2O \rightarrow xCaO \cdot SiO_2 \cdot nH_2O \quad (7)$$

$$Ca(OH)_2 + Al_2O_3 + (n-1)H_2O \rightarrow xCaO \cdot Al_2O_3 \cdot nH_2O \quad (8)$$

$$Ca(OH)_2 + Al_2O_3 + SiO_2 + (n-1)H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O \quad (9)$$

$$(1.5–2.0)CaO \cdot SiO_2 \cdot aq + SiO_2 \rightarrow (0.8–1.5)CaO \cdot SiO_2 \cdot aq \quad (10)$$

The relationship between the C/S ratio of C-S-H and equilibrium pH is shown in Fig. 1. There are two plateaus for the equilibrium pH. One corresponds to around pH 12, where the C/S ratio is greater than 1.0. The other plateau corresponds to pH 10, where the C/S ratio of C-S-H varies from 0.05 to 0.6. Typically, the C/S ratio of C-S-H from the hydration of Portland cement ranges from 1.4 to 1.7.

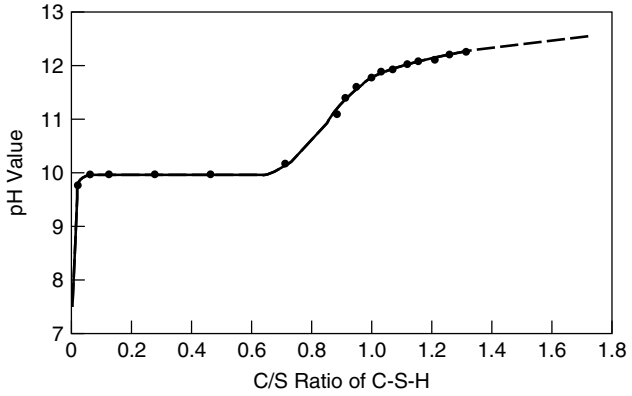


Figure 1. Relationship between C/S ratio of C-S-H and equilibrium pH. (Based on Reference 1).

DISSOLUTION AND LEACHING OF HYDRATION PRODUCTS OF CEMENTS

Table 1 lists the solubility products of common hydration products of hydraulic cements. It can be seen that $Ca(OH)_2$ has the highest solubility among all hydration products. The solubility of C-S-H decreases as its C/S ratio decreases, which means that the use of supplementary cementing materials converts the more soluble $Ca(OH)_2$ into the less soluble C-S-H.

The dissolution of $Ca(OH)_2$ and the decalcification of the C-S-H phase occur so as to maintain the chemical equilibrium of Ca^{2+} between the solid hydrates and the pore solution. Once the concentration of Ca^{2+} in the pore solution of a cement-based material is decreased by diffusion, the dissolution of $Ca(OH)_2$ starts, depleting the $Ca(OH)_2$, followed by the decalcification of the C-S-H phase. The dissolution of $Ca(OH)_2$ and the partial decalcification of C-S-H are given by the following chemical equilibrium equations:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (11)$$

$$xCaO \cdot SiO_2 \cdot yH_2O \rightarrow (x-m)CaO \cdot (1-n)SiO_2 \cdot (y-m)H_2O + mCa(OH)_2 + nSiO_2 \quad (12)$$

Chemical equilibrium of the solid cement hydrates and the pore solution with regard to Ca^{2+} is applied according to the model shown in Fig. 2. The initial concentration of Ca^{2+} in the pore solution is approximately 0.02 mol/L of solution and must be maintained as long as the $Ca(OH)_2$ remains in the solid. Subsequently, after all the $Ca(OH)_2$ is dissolved, the decalcification of C-S-H will ensue depending on the concentration of Ca^{2+} with the chemical equilibrium shown in the curved portion of Fig. 2.

Table 1. Solubility Product of Common Hydration Products of Cements

Compound	Solubility Product	Reference
$Ca(OH)_2$	5.5×10^{-6}	2
C-S-H[a]	$1.0 \times 10^{-24 \text{ to } -14}$	3
C_4AH_{13}	3.2×10^{-28}	2
C_2ASH_8	8.1×10^{-52}	4
AFt	1.0×10^{-40}	5
AFm	1.7×10^{-28}	5

[a]The solubility product increases as the C/S ratio of C-S-H decreases.

Table 2. pH Value and Concentrations of Ions in Immersion Water at 12 Weeks

		Ion Concentration (mmol/L)				
W/C	pH	Ca^{2+}	K^+	Na^+	SO_4^{2-}	Al^{3+}
0.4	12.8	400	110	38	1.9	2.4
0.55	13.0	710	89	33	2.4	2.5
0.7	13.0	760	38	19	2.6	2.6
0.85	13.0	840	32	12	2.7	2.8

Source: Reference 7.

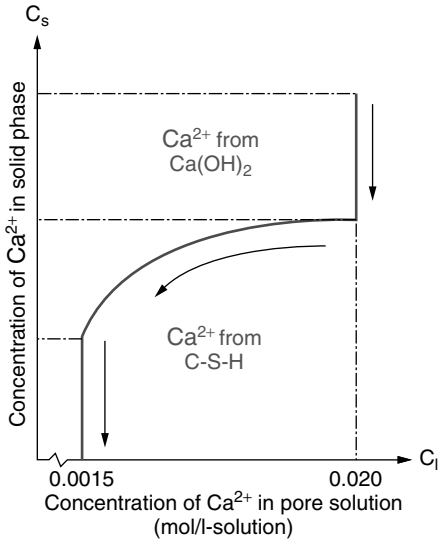


Figure 2. Relationship between Ca^{2+} concentrations in solid and liquid phases (6).

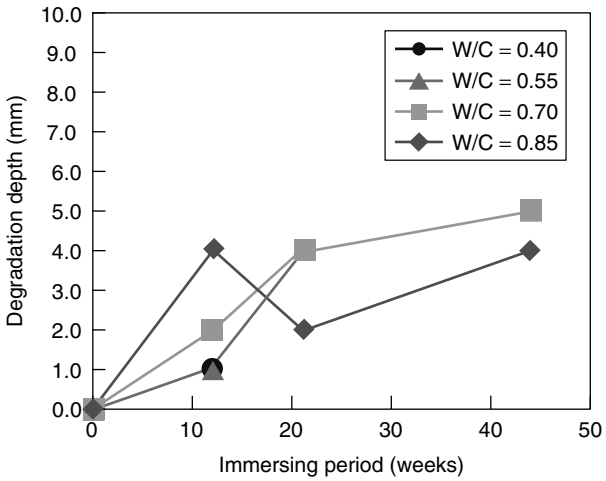


Figure 3. Degraded depths of cement pastes after immersion in water. (Based on Reference 7).

Kosuke Yokozeki et al. (7) investigated the leaching out of ingredients from hardened cement pastes made with different water to cement ratios. They immersed $20 \times 20 \times 20$ mm hardened cement cubes in water with a water to cube (by volume) ratio of 20, then measured the degraded depths of cement paste, as shown in Fig. 3, and pH values and ion concentrations of the immersed water after 12 weeks of immersion, as shown in Table 2.

The results in Fig. 3 indicate that the degradation depth increases with immersion time, but the water to cement ratio does not show an obvious effect. The pH value of immersed water is almost 13 regardless of the water to cement ratio. The Ca^{2+}, K^+, and Na^+ concentrations are high, and the rest are low.

Several researchers (6,8–10) Sugiyama et al. confirmed that hardened cement pastes dissolve and degrade in the following five steps: (1) leaching of calcium hydroxide; (2) decalcification of C-S-H; (3) formation of C-S-H with

C/S ratio or calcium aluminate hydrates; (4) leaching of C-S-H; and (5) leaching of silica gel. As shown in Eq. 11, the initial dissolution and leaching of Ca^{2+} are always associated with hydroxyl ion. Laboratory results clearly indicate a gradual pH drop on the surface of concrete after immersion in water or a solution (11). Once it is controlled by the leaching of C-S-H, the pH of hardened concrete is around 10, as indicated in Fig. 1.

EFFECT OF LEACHING OF HYDRATION PRODUCTS OF CEMENTS ON pH OF GROUNDWATER

In general, the water chemistry is controlled by two large bulk systems: concrete and soil-rock. Both bulk systems are porous with an interfacial transitional zone. Cement chemistry dominates within the bulk of concrete structure and local groundwater chemistry dominates within the bulk of the soil-rock.

As discussed above, the pH of pore solution within concrete is over 12.5 to values as high as 13.5, due to the presence of alkalis, which is significantly higher than groundwater. Hydroxyl ions always transport from concrete to groundwater. Increased pH of groundwater can be expected around the surface of concrete but is not expected to penetrate far into the groundwater matrix, because the transport rate from the concrete is low. A transition zone in the aqueous chemistry exists at the interface between these two bulk systems, as illustrated in Fig. 4.

The width of this transitional zone is controlled mainly by the rate of flow of the groundwater around the surface of the concrete, with higher flows resulting in a narrower zone. For example, a fast-flowing river around a concrete structure makes this zone very thin, or even negligible, sweeping the surface of the concrete clean of ions leached from the concrete and turbulently mixing these ions with the river water. The width of the transitional zone can be significant for concrete sitting in quiescent perched water. Diffusion is very slow, so much so that leaching from a monolithic concrete structure can be dominated by the permeation of water through the porous concrete matrix.

BIBLIOGRAPHY

1. Buil, M., Revertegat, E., and Oliver, J. (1992). A model of the attack of pure water or undersaturated lime solutions on cement. In: *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, Vol. 2, STP 1123. T.M. Gilliam and C.C. Wiles (Eds.). ASTM, Philadelphia, PH, pp. 227–241.
2. Reardon, E.J. (1990). An ion interaction model for the determination of chemical equilibria in cement/water system. *Cement Concrete Res.* **20**(2): 175–192.
3. Glasser, F.P., Lachowski, E.E., and Macphee, D.E. (1987). Compositional model for calcium silicate hydrate (C-S-H) gels, their solubilities, and free energies of formation. *J. Am. Ceramic Soc.* **70**(7): 481–485.
4. Atkins, M., Glasser, F.P., and Kindness, A. (1991). *A Thermodynamic Model for Blended Cements*. Research Report for Department of Environment, DoE/HMIP/RR/92/005.
5. Day, R.L. (1992). *The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Review*. Department of Civil Engineering, Research Rep. No. CE 92-2, University of Calgary.
6. Sugiyama, T., Ritthichauy, W., and Tsuji, Y. (2003). Simultaneous transport of chloride and calcium ions in hydrated cement systems. *Adv. Concrete Technol.* **1**(2): 127–138.
7. Yokozeki, K., Watanabe, K., Sakata, N., and Otsuki, N. (2003). Prediction of changes in physical properties due to leaching of hydration products from concrete. *J. Adv. Concrete Technol.* **1**(2): 161–171.
8. Furusawa, Y. (1997). Research trends on degradation of concrete caused by calcium leaching and modeling. *Concrete J. JCI* **35**(12): 29–32 (in Japanese).
9. Watanabe, K., Yokozeki, K., Furusawa, Y., Otsuki, N., and Daimon, M. (2000). Mechanisms of deterioration of cement composites due to leaching of calcium. In: *CANMET/ACI Durability of Concrete*. SP-192-70, Vol.2, pp. 1155–1172.
10. Yokozeki, K. et al. (2002). Analysis of old structures and numerical model for degradation of concrete by calcium ion leaching. *Concrete Lib. JSCE* **40**: 209–226.
11. Sergi, G., Yu, S.W., and Page, C.L. (1992). Diffusion of chloride and hydroxyl ions in cementitious materials exposed to a saline environment. *Mag. Concrete Res.* **44**(158): 63–69.

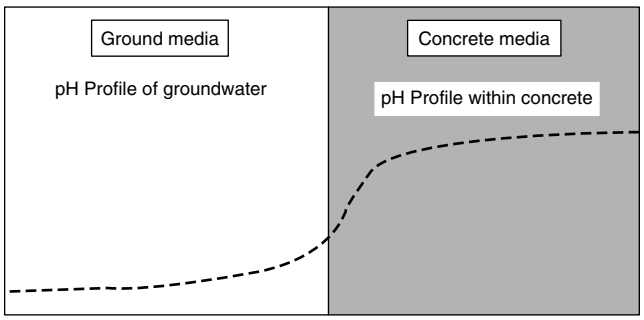


Figure 4. Schematic illustration of pH profiles between groundwater and concrete.

PHYTOEXTRACTION AND PHYTOSTABILIZATION: TECHNICAL, ECONOMIC AND REGULATORY CONSIDERATIONS OF THE SOIL-LEAD ISSUE

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Lead is a common environmental contaminant, produced from multiple anthropogenic sources. The cost of traditional remediation techniques for lead-contaminated soils is prohibitive. As a result, new technologies such as phytoextraction, the removal of contaminants from soil and water sources by plants, and phytostabilization, the immobilization of contaminants in the soil, are being examined as remediation alternatives for lead-contaminated soils. Only a few plant species have been identified so far that

can tolerate and accumulate lead partly because lead is relatively immobile in soils and has low phytoavailability. However, lowering the pH or the use of soil amendments or chelating agents such as EDTA can enhance the uptake of lead by plants. Lead is already relatively immobile in most soils, so phytostabilization is a promising remediation strategy. However, phytostabilization leaves the contaminant in the soil (albeit in an insoluble form), so long-term monitoring is required to verify that the contaminant does not become soluble again. Although only limited studies on the economic viability of phytoextraction and phytostabilization have been done, the estimated costs are significantly lower than those of traditional methods.

INTRODUCTION

Lead is a bluish-gray heavy metal, which is usually found naturally in soils in levels ranging from 15 to 40 mg/kg. Galena (PbS) is the major mineral source of naturally occurring lead in soils. More than 85% of the lead mined in the United States comes from southeastern Missouri (1). It is common to find lead in soils at levels between 100 and 3000 mg/kg due to the use of lead-based paints, storage batteries, plumbing fixtures, gasoline, explosives, ammunition, and mining and smelting (2,3). According to the Toxic Release Inventory, almost 144 million pounds of lead were released to land and water in the United States between 1987 and 1993, most of which were from lead and copper smelting (1). Lead contamination in soils can lead to many environmental problems, such as lead toxicity in humans, animals, and plants; loss of vegetative cover; and ground water contamination (4). In humans, short-term exposure to lead can interfere with red blood cell activity, cause mental and physical developmental delays in babies and young children, and increase the blood pressure of adults. Long-term exposure to lead has the potential to cause cancer, kidney disease, and stroke in adults (1). Current remediation techniques for lead-contaminated soils include excavation, stabilization, and/or removal to a landfill (3). These techniques are expensive and can result in secondary problems such as human exposure and habitat destruction (3).

PHYTOREMEDIATION

Phytoremediation is the use of plants to remediate contaminated soils, sediments, sludge, ground/surface water, or wastewater (5). Phytoremediation uses a variety of plant biological processes to degrade, remove, or immobilize contaminants (3). Phytoremediation can be an attractive alternative to traditional remediation techniques because it is driven by photosynthesis and is performed on site, reducing costs and human exposure (1). Two specific methods of phytoremediation, phytoextraction and phytostabilization have been used to treat lead-contaminated soils (5,6).

Phytoextraction

Phytoextraction is the uptake of contaminants by a plant, and the toxic substance is then sequestered in the tissues (5). The plants that take up contaminants at the highest rates are called hyperaccumulators (0.1 to 3% of dry biomass) (7). *Brassica juncea* (Indian Mustard), *Helianthus annuus* (common sunflower), *Nicotiana tabacum* (tobacco), and *Zea mays* (corn) have been identified in the literature as hyperaccumulators of lead (2,8). For lead to be taken up by a plant, it must be in an aqueous phase, either in soil solution or in groundwater (9,10). The solubility of lead (in the form of Pb^{2+}) is low at neutral or alkaline pH, so only about 0.1% of the lead in lead-contaminated soils is available for uptake by plants (3). Kumar et al. (2) reported that the ratio of lead in the dry weight of plant to that in soil (called the phytoextraction coefficient) in *B. juncea* was 1.7; in comparison, Cr^{6+} and Cd^{2+} have coefficients over 50. Decreasing the pH of the soil can increase the phytoavailability of lead; however, most plants have an ideal pH range of 5–8 (3,11). Chelating agents, such as EDTA (ethylenediaminetetraacetic acid), increase lead phytoavailability and also increase the amount of lead accumulated in the aboveground biomass (12). However, by making lead more soluble, the danger exists of allowing more lead to enter the food chain or leach into groundwater (13).

Phytostabilization

In phytostabilization, vegetation is used to modify the biological, physical, and chemical properties of soil to reduce the movement of contaminants. *Brassica juncea, Festuca rubra* cv Merlin (red fescue), and *Agrostis tenuis* cv Goginan (colonial bentgrass) have been used to stabilize lead mine wastes (14). One phytostabilization study showed that lead-contaminated soil had 740 mg/kg of lead in the leachate without plant cover, compared with 22 mg/kg with *B. juncea* cover (5). Phytostabilization can be achieved through root absorption, accumulation, and adsorption. Plants may also release exudates in the root zone that could result in precipitation, complexation, or a change in the valence state of a metal contaminant (15). Roots can help precipitate lead in the form of lead phosphate (5). Some grasses, such as ryegrass, have been investigated as possible phytostabilizers due to their extensive roots and widespread growth patterns (14). In addition, plants can prevent wind and water erosion from spreading contaminants to surrounding areas. However, because contaminants are left in the soil in an insoluble form in phytostabilization, the area has to be monitored continuously to verify that they do not become soluble with time (16).

TECHNICAL CONSIDERATIONS

Vegetation

Several plants reportedly accumulate small amounts of lead, but hyperaccumulators are those plants that can take up the metal to tissue concentrations greater than 1000 mg/g (17). For effective phytoextraction, the plant should also be able to translocate lead to aboveground tissues, which allows easier harvesting and helps the next crop of plants to grow quickly due to an already

existing root system (16). Depth of roots is an important characteristic of candidate plants for phytoremediation. Most hyperaccumulator plants have shallow root systems; the effective depth is about 12 inches and hence can only take up contaminants from shallow soils (6). Hyperaccumulating plants that have faster growth rates, higher biomass, and an extensive root system would be more effective for phytoremediation (18). Plants used in phytostabilization have to grow and survive long term in contaminated soils. A large root mass would also be advantageous for greater soil–root contact surface area, which would also result in the secretion of larger amounts of enzymes or exudates to immobilize lead. Prospective plants should also be hearty and tolerate the environmental stresses in a given contaminated area (16).

Soil and Lead Chemistry

Soil pH is very important in the solubility of metals such as lead. The solubility of lead is relatively low at neutral or alkaline pH (3). Decreasing the pH of the soil by using soil amendments or acidifiers can increase the solubility and hence the phytoavailability of lead. However, as the pH decreases, aluminum (Al^{3+}), which is ubiquitous in soils and toxic to plants, also becomes more phytoavailable. The optimum pH range for most plants is 5–8, so this would make the optimum pH range for lead uptake between 5 and 6.5 (11). Chelating agents, such as EDTA, have been used to increase solubility and thereby increase plant uptake (13,19). Chelating agents can also increase the translocation of lead into the aboveground biomass (19). On the other hand, by increasing the solubility of lead, there exists the danger of lead entering the food chain or leaching into underground water sources. Strategies for properly using chelating agents include using plants that rapidly take up lead and harvesting them immediately to reduce environmental risks (12).

Soil amendments can also be used to decrease solubility. Increasing the pH of soil via alkalizing agents or mineral oxides increases lead precipitation potential. Organic matter and biosolids have also been used to immobilize lead in soil (20). Phosphates can bind with lead and precipitate it from solution, usually in the form of lead carbonates, hydroxides, and phosphates (21). Therefore, when adding fertilizers to plants involved in phytoextraction, phosphate should be added typically to leaves and not to the soil itself (12). The type of soil and the amount of organic matter present can complicate the uptake of lead. Contaminated areas generally also have multiple contaminants, and there are substantial variations in the concentrations of contaminants at a single site. These scenarios can reduce the effectiveness of any phytoremediation project (16).

Other Considerations

Phytoextraction and phytostabilization use natural plant processes, so it takes longer to remediate contaminated areas using these techniques, compared with traditional methods (5,15). The length of the growing season and rainfall patterns in a contaminated area will also substantially impact the amount of time required for any phytoremediation project. Using plants that have faster growth and high biomass may reduce the time necessary for phytoextraction compared to hyperaccumulators, the majority of which are slow growing and low biomass plants (16). In phytostabilization, selecting plants that produce more exudates or enzymes can speed up the remediation process. Any phytoremediation project requires continuous monitoring of the site. However, a phytostabilization project needs long-term monitoring because of the lead that stays on site. On-site plant tissue sampling to ensure little or no lead uptake and soil and local source water sampling, to ensure that lead remains immobilized may be required for many years (16). Although some herbivorous animals avoid plants with high levels of accumulated metals, it may be necessary to restrict access to hyperaccumulating plants during phytoextraction through fencing, netting, or harvesting before the plants reach the flowering stage to avoid transfer of metals to the food chain (22).

ECONOMIC CONSIDERATIONS

To date, economic viability data for phytoextraction and phytostabilization projects are rather limited. Moreover, the available data are typically gathered from small, pilot-scale studies, which may not accurately reflect the costs and efficiency of large-scale operations (16). The costs of any potential phytoremediation project must consider the initial feasibility studies, which includes site characterization, selecting the most appropriate plants, and determining if soil amendments are necessary (16). Before remediation can begin, site start-up costs may include debris removal, fencing, irrigation systems, and drainage control measures (23). Besides the costs of planting, watering, fertilizing, and pesticide use, project costs must also include periodic monitoring for pH, nutrient levels, and contaminant levels in soils and possibly nearby surface and groundwater sources and disposal of contaminated vegetation (16). Still, estimated costs for most phytoremediation applications are usually 50–80% lower than those of traditional techniques (24). A small-scale study of lead phytoextraction in 1997 predicted that the costs of the phytoextraction project at the Magic Marker site in New Jersey would range from 50–65% of the remediation costs of traditional methods (19). In 1997, another study estimated that the costs for phytoremediating a lead-contaminated area of soil 60 cm deep would be $\$6/m^2$ compared to $\$15–\$730/m^2$ for more traditional remediation techniques (20). One of the disadvantages of using phytoremedation as a cleanup technique is that it can easily take several growing seasons to reduce the lead concentrations to acceptable levels. The cost incurred by not using the land during the period of the phytoremediation project may be a deterrent for a business expecting to make a profit from that land immediately (25). The estimated costs of a typical phytostabilization project may range from $200 to $10,000 per hectare (1 meter

root depth) (7). However, the contaminants essentially stay in place in this method, so the costs of long-term monitoring (to verify that the lead has not become soluble again) should be included in any project (7). The number of cost estimates for actual phytoextraction and phytostabilization projects is limited, but there is general agreement that the costs are much lower than those of currently practiced traditional *ex situ* remediation techniques. For phytoextraction, the future recovery and eventual resale of extracted metals has been proposed; however, it is unclear if the technology and markets exist to make such an idea feasible and profitable on a large scale (16).

REGULATORY CONSIDERATIONS

Specific federal regulations for phytoremediation have not yet been developed, but several existing federal acts, statutes, and programs have implications for phytoremediation technologies (26) The Resource and Recovery Act (RCRA) of 1976, an amendment to the Solid Waste Disposal Act, deals with waste management. Two of the sections (Subtitles C - Hazardous Waste Management and D - Solid Waste Management) are most likely to impact phytoremediation projects. Remediation of treatment, storage, or disposal units will fall under the RCRA requirements. These requirements, however, are performance-based and are delegated to the states. It is up to the state authorities to assess the individual site requirements to determine if phytoremediation can be part of a site cleanup. Disposal of plants used in phytoextraction may also be governed by RCRA. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) was enacted in 1980 to cleanup hazardous waste contaminated sites. The trust fund created by CERCLA provides money for the cleanup of designated hazardous waste sites. Under CERCLA, a feasibility study must be completed to determine if phytoremediation is appropriate for a specific site. Any remediation plan must meet the nine criteria set forth in the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) (27). States may have stricter guidelines for cleanup requirements and remaining material limitations. Any state or federal regulation concerning how much material may be left on site may have important implications for phytostabilization. In addition, the Maximum Contamination Levels (MCLs) put forth by the Safe Drinking Water Act (SDWA) may also apply. Executive Order 13112 signed in 1999 prohibits the use of invasive species unless it can be shown that the benefits of using such species outweigh the potential harm (28). Other regulations and acts that may apply to phytoremediation include the Clean Air Act, Department of Agriculture statutes, and the Toxic Substances Control Act (26).

FUTURE PROSPECTS FOR LEAD PHYTOREMEDIATION

Lead phytoextraction seems to be limited to low to medium lead soil contamination levels and to the root zone of the plants being used, so phytoextraction may emerge as a common polishing step in a multiple step process aimed at total site remediation. For some cleanup projects, traditional remediation techniques could be used to reduce the contamination to plant-tolerant levels followed by phytoextraction to reduce the contamination even further (23). Similarly, appropriate plants can be used to stabilize the remaining pollutants to reduce their bioavailability and potential for leaching as the final remediation step (20). Lead is relatively insoluble in a soil solution, so phytostabilization might be a more promising technique for lead-contaminated soils (2,23). The search for fast-growing and high biomass phytoextracting and phytostabilizing accumulator plants is ongoing (29). Selective breeding and genetic engineering of more suitable plants is a possibility. However, more information on the ecological impact of using genetically modified plants would be needed. The current regulations and the societal view of using genetically modified organisms could also hinder the use of these technologies (23).

BIBLIOGRAPHY

1. U.S. EPA. (2002). *Lead in Drinking Water Regulation: Public Education Guidance*. EPA/816/R-02/010. Office of Water, Washington, DC.
2. Kumar, N.P.B.A., Dushenkov, V., Motto, H., and Raskin, I. (1995). Phytoextraction: The use of heavy metals to remove heavy metals from soils. *Environ. Sci. Technol.* **29**: 1232–1238.
3. Huang, J.W. and Cunningham, S.D. (1996). Lead phytoextraction: Species variation in lead uptake and translocation. *New Phytol.* **134**: 75–84.
4. Todd, A.C. et al. (1996). Unraveling the toxicity of lead: An essential priority for environmental health. *Environ. Health Perspect*: 104–146.
5. Salt, D.E. et al. (1995). Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology* **13**: 468–474.
6. Blaylock, M.J., Elless, M.P., Huang, J.W., and Dushenkov, S.M. (1999). Phytoremediation of lead-contaminated soil at a New Jersey brownfield site. *Remediation* **9**: 93–101.
7. Cunningham, S.D., Berti, W.R., and Huang, J.W. (1995). Phytoremediation of contaminated soils. *TIBTECH* **13**: 393–397.
8. Brooks, R.R. (Ed.). (1998). Geobotany and hyperaccumulators. In: *Plants That Hyperaccumulate Heavy Metals*. CAB International, New York.
9. Paterson, S., Mackay, D., Tam, D., and Shiu, W.Y. (1990). Uptake of organic chemicals by plants: A review of processes, correlations and models. *Chemosphere* **21**: 297–331.
10. Shimp, J.F. et al. (1993). Beneficial effects of plants in the remediation of soil and groundwater contaminated with organic materials. *Crit. Rev. Environ. Sci. Technol.* **23**: 41–77.
11. Chlopecka, A., Bacon, J.R., Wilson, M.J., and Kay, J. (1996). Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland. *J. Environ. Qual.* **25**: 69–79.
12. Huang, J.W., Chen, J., Berti, W.R., and Cunningham, S.D. (1997). Phytoremediation of lead contaminated soils: Role

of synthetic chelates in lead phytoextraction. *Environ. Sci. Technol.* **31**: 800–805.

13. Wu, J., Hsu, F.C., and Cunningham, S.D. (1999). Chelate-assisted Pb phytoextraction: Pb availability, uptake, and translocation constraints. *Environ. Sci. Technol.* **33**(11): 1898–1904.
14. Smith, R.A.H., and Bradshaw, A.D. (1979). The use of metal tolerant plant populations for the reclamation of metalliferous wastes. *J. Appl. Ecol.* **16**: 595–612.
15. Ernst, W.H.O. (1996). Availability of heavy metals and decontamination of soils by plants. *Appl. Geochem. - J. Int.* **11**: 163.
16. Pivetz, B.E., and U.S. EPA. (2001). *Ground water issue: Phytoremediation of contaminated soil and ground water at hazardous waste sites*. EPA/540/S-01/500. Office of Research and Development, Washington, DC, February 2001.
17. Brooks, R.R. (Ed.). (1998). General introduction. In: *Plants That Hyperaccumulate Heavy Metals*. CAB International, New York, pp. 1–14.
18. McGrath, S.P. (1998). Phytoextraction for soil remediation. In: *Plants That Hyperaccumulate Heavy Metals*. R.R. Brooks (Ed.). CAB International, New York, pp. 261–287.
19. Blaylock, M.J. et al. (1997). Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environ. Sci. Technol.* **31**: 860–865.
20. Berti, W.R. and Cunningham, S.D. (1997). In-place inactivation of Pb in Pb-contaminated soils. *Environ. Sci. Technol.* **31**: 1359–1364.
21. McBride, M.B. (1994). *Environmental Chemistry of Soils*. Oxford University Press, New York.
22. Pollard, A.J. (1996). *Ecology and evolution of hyperaccumulation in natural populations: Implications for phytoremediation of metals*. *Int. Phytoremediation Conf.*, May 8–10, 1996, Arlington, VA. International Business Communications, Southborough, MA.
23. U.S. EPA. (2000). *Introduction to phytoremediation*. EPA/600/R-99/107. Office of Research and Development, Washington, DC.
24. Glass, D.J. (1998). *The 1998 United States Market for Phytoremediation*. D. Glass Associates, Inc., Needham, MA.
25. Gulledge, C.S. (2004). *Personal correspondence*. Professional Performance Development Group, Inc.
26. U.S. EPA. (2000). Land Remediation & Pollution Control Remediation & Containment Phytoremediation of Hazardous Wastes: Potential Regulatory Acceptability. EPA's Office of Research and Development, Office of Solid Waste and Emergency Response, and the Office of Pollution Prevention and Toxics. Available: http://www.epa.gov/ORD/NRMRL/lrpcd/rcb/phytohaz.htm.
27. U.S. EPA. (2001). National Oil and Hazardous Substances Pollution Contingency Plan; National Priorities List, 40 CFR Part 300 [FRL-6963-3]. Available: http://www.epa.gov/fedrgstr/EPA-WASTE/2001/June/Day-12/f14470.htm.
28. U.S. EPA. (2001). Oceans, Coasts and Estuaries, Draft Report for Public Comment, U.S. Environmental Protection Agency Office of Water, Office of Wetlands, Oceans and Watersheds, Office of Wastewater Management, Washington, DC. Available: http://www.epa.gov/owow/invasive_species/ballast_report/current.html.
29. Datta, R. and Sarkar, D. (2004). Effective integrations of soil chemistry and plant molecule biology in phytoremediation of metals: An overview. *Environ. Geoscience* **11**(2): 53–63.

PHYTOEXTRACTION OF ZINC AND CADMIUM FROM SOILS USING HYPERACCUMULATOR PLANTS

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INTRODUCTION

Mining, manufacturing and various other human activities have contributed to extensive soil contamination during the past century; heavy metals being the main group of inorganic contaminants (1). Accelerated release of metals into ecosystems has resulted in serious environmental problems and poses a threat to human health because most heavy metals are toxic at higher concentrations (2). Heavy metals can cause toxicity for several reasons: (1) by causing oxidative stress; (2) by replacing other essential metals in biomolecules, thereby disrupting their function; and (3) by reacting with thiol groups, thereby interfering with protein structure and function (3).

Zinc and Cd are ubiquitous pollutants that tend to occur together at many contaminated sites (4). Cadmium occurs in natural environments typically in association with Zn ores. Cadmium is emitted into the atmosphere from natural as well as anthropogenic sources. Metal production (drying of Zn concentrates, roasting, smelting and refining of ores) is the largest source of anthropogenic atmospheric Cd emissions, followed by waste incineration, production and disposal of nickel-cadmium batteries, fossil fuel combustion, and generation of dust by industrial processes, such as cement manufacturing (5). In the air, Cd vapor is rapidly oxidized and transferred to the soil by wet or dry deposition.

Most of the commercial production with Zn involves galvanizing iron and manufacturing of brass. Zinc oxide is also used in large quantities as an accelerant in tire vulcanizing. Worn tires are a major contributor to environmental Zn contamination (6). Zinc is also a major effluent from industries, such as soft drink flavoring, fur dressing and dyeing, fish processing, and laundry (7).

Cadmium derives its toxicological properties from its chemical similarity to Zn, which is an essential micronutrient for plants, animals, and humans. In humans, long-term exposure to Cd is associated with renal dysfunction, obstructive lung disease, and bone defects. In Japan, a bone disease called 'itai-itai' has been associated with prolonged exposure to Cd in rice and water (8). Cadmium and Zn are chemical antagonists; Zn deficiency can cause accelerated absorption of Cd (9). Zinc is an essential cofactor in a variety of cellular processes, including DNA synthesis, behavioral responses, reproduction, bone formation, growth, and wound healing. Although humans can handle relatively large quantities of Zn, very high levels of Zn can cause irritation and corrosion of the gastrointestinal tract, renal tubular necrosis, and interstitial nephritis (9).

Conventional soil cleanup methods for heavy-metal-contaminated soils include soil washing, excavation and reburial of soil, and pump and treat systems (10), which are rather expensive techniques. The use of plants for remediating metal-contaminated sites offers an attractive alternative because it is solar-driven and can be carried out *in situ*, minimizing the cost and human exposure (11). It offers a cheaper, safer, and environmentally friendly solution for the cleanup of metal-contaminated soils. The technique of phytoextraction depends on the extent to which plants can take up metals from soils and concentrate them in aboveground tissues (12). Plants that can accumulate metals to exceptionally high concentrations in their shoots are called hyperaccumulators (13).

Hyperaccumulators are an invaluable resource for successful phytoextraction of heavy metals, such as, Zn and Cd, either as phtoremediation crops themselves or as sources of genes for improving other phytoremediation crops (12). In this article, we focus on factors affecting Zn and Cd bioavailability in soils, the mechanism of Zn and Cd hyperaccumulation in plants, and future directions in improving phytoextraction through biotechnology and improved agronomic practices.

FACTORS AFFECTING ZINC AND CADMIUM BIOAVAILABILITY IN SOILS

Zinc

The amount of different Zn forms in soils varies considerably depending on the type and nature of soil constituents. Alkaline soils that are calcareous are generally high in the carbonate form of Zn, whereas soils rich in organic matter are high in organic forms (14). Water-soluble and exchangeable forms of Zn are readily bioavailable to plants; other forms of Zn are either unavailable or not as readily available to plants for uptake. In agriculture agronomic management practices can affect the distribution of metals among soil constituents. In Norwegian soils treated with farmyard manure, rock phosphate, or mixed fertilizers, the majority of the Zn (~78%) was reportedly associated with the oxides and residual matrices (15). In polluted soils from Poland, the majority of the Zn (~65%) was found in the oxide and residual fractions (16). The predicted dominant Zn species in soil solution below pH 7.7 is the divalent metal ion, Zn^{2+} (17). Above this pH, $ZnOH^{+}$ is more dominant (14).

Cadmium

In unpolluted soils, most of the Cd is associated with the residual fraction, which is generally not available for plant uptake (14). In contrast, the greatest amount of Cd (~37%) in heavily polluted soil in Norway was found in the exchangeable fraction; the oxide and residual fractions accounted for relatively lower concentrations, 23% and 15% of the Cd, respectively (18). Based on several studies, it has become apparent that Cd from mining and smelting activities is likely to be more bioavailable than Cd from unpolluted soil because increasing contamination results in increased amounts of Cd in the labile fractions of the soil (14). Most of the Cd in soil solutions is generally present as Cd^{2+} ions (14).

Cadmium–Zinc Interactions

The close association of Cd and Zn in geologic deposits and the chemical similarity of the two elements carry over into biological systems (14). Cadmium has no known biological function, whereas Zn is an essential nutrient. Cadmium competes with Zn in forming protein complexes, so a negative association between the two can be expected. The interaction between Zn and Cd is either antagonistic or synergistic (14). The addition of Cd-treated sewage sludge to calcareous soil decreased the concentrations of Zn in the shoots of the many plants studied (19). However, at higher levels of Cd, increasing concentrations of Zn increased Cd uptake (20). The variable results are related to the plant species, soil type, Zn/Cd status, source and level of applied Zn or Cd, and the Zn/Cd ratio (14).

PHYTOEXTRACTION OF ZINC AND CADMIUM

Phytoextraction is a term for the process by which plants remove significant quantities of substances from their substrate (21). Generally, the metal phytoextraction protocol consists of the following steps: (1) plant cultivation on a contaminated site, (2) removal of harvested metal-rich biomass, (3) postharvest treatments and subsequent disposal of the biomass as hazardous waste, and (4) eventual recovery of metals from the harvested biomass (22). Metal hyperaccumulation is a relatively rare phenomenon that occurs only in a few terrestrial plants. Only about 400 species have so far been identified as natural metal hyperaccumulators, representing <0.2% of all angiosperms (13). Threshold values of metal concentrations are used to define metal hyperaccumulation, which varies from element to element, for example, 10,000 mg/kg dry shoot weight for Zn and Mn; 100 mg/kg for Cu, Co, Ni, As, and Se; and 100 mg/kg for Cd (21). These concentrations are two to three orders of magnitude higher than in normal plant species growing on uncontaminated soils. The common traits shared by all hyperaccumulators include (1) a bioconcentration factor greater than 1, in some cases as high as 50–100; (2) a shoot-to-root ratio of metal concentration greater than 1, indicating efficient root to shoot transport; and (3) enhanced tolerance to metals in the medium and inside the plant cells, indicating strong internal detoxification (21).

Several species of plants that hyperaccumulate Zn have been investigated, but only one Cd hyperaccumulator, *Thlaspi caerulescens,* has been extensively studied. Many Zn hyperaccumulators are in the family Brassicaceae and in the genus *Thlaspi.* In addition, *Cardaminopsis halleri* and *Viola calaminaria* also hyperaccumulate Zn. The first indication of the possibility of phytoextraction of Zn was obtained from pot experiments in background and sludge-treated soils using *Thlaspi caerulescens* (23). It was estimated that a crop of *T. caerulescens* could take up 34 kg/ha of Zn and 0.16 kg/ha Cd. McGrath et al. (24) performed a field study on metal-contaminated soil from 20 years of sewage sludge application and reported that

hyperaccumulator plants accumulated 10,625 mg/kg of Zn from a soil concentration of 406 mg/kg. McGrath and Dunham (25) reported that *T. caerulescens* and *C. halleri* plants, at field removal rates of 150 and 34 g/ha, could remove 10 years worth of Cd accumulation from agricultural land where P fertilizers added Cd at a rate of 3 g/ha/y. Only the bioavailable fraction of the total metal is of major ecological and human health concern, so it is acknowledged that all the metal need not be removed from the soil, a concept described as 'bioavailable element stripping' (BES). From the study of McGrath and Dunham (25), it is evident that in terms of BES, the bioavailable fraction of Cd can be removed from the soil by *T. caerulescens* in about four harvests.

Brown et al. (26) showed that *T. caerulescens* contained 18,000 mg/kg of Zn and 1,020 mg/kg of Cd in their shoots when grown on contaminated soils, there was no effect on yields, and the result was a in significant reduction in bioavailable metal concentration in the soils. McGrath and Dunham (25) used data from their field experiment to show that *T. caerulescens* and *C. halleri* could remove a maximum of 41 and 0.15 kg/ha/y of Zn and Cd, respectively. It is, however, not known if these extraction rates would decline with time and soil metal concentration.

Although Zn and Cd are chemically similar, as the above case studies illustrate, there are marked differences in their accumulation by hyperaccumulator plants. Cadmium and Zn also differ due to the difference in accumulation and also in relation to their response to concentrations in the soil. McGrath et al. (24) showed that *T. caerulescens* responded to increasing soil Zn concentrations by maintaining consistent hyperaccumulation of the metal. However, Cd accumulation depends much more on soil conditions, especially pH and extractable Cd concentrations (21), which indicates that there are differences in the mechanisms for accumulating the two metals in hyperaccumulators.

MOLECULAR BASIS OF ZINC AND CADMIUM HYPERACCUMULATION

Considerable progress has been made in understanding the molecular basis of metal hyperaccumulation, but the entire picture is far from complete (21). A genetic study using crosses between Zn hyperaccumulator *Arabidopsis halleri* and the nonaccumulator *Arabidopsis petraea* showed that Zn tolerance and hyperaccumulation are independent traits and that tolerance is controlled by a single major gene (27). Several studies have shown that metal hyperaccumulation of Zn and Cd by *T. caerulescens* involves enhanced metal uptake by the roots (4,28). Several Zn transporter genes cloned recently from *T. caerulescens* belong to the ZIP (Zn-regulated transporter/Fe-regulated transporter-like proteins) family (29). These genes, named *ZNT1* and *ZNT2*, are highly expressed in the roots of *T. caerulescens,* but their expression is not responsive to the Zn status of the plant. Through functional complementation in yeast, it was shown that *ZNT1* mediates high-affinity uptake of Zn^{2+} and low-affinity uptake of Cd^{2+} (30). Specific alterations in Zn-responsive elements, such as transcriptional activators, may play an important role in Zn hyperaccumulation in *T. caerulescens* (30). However, increased uptake of Cd by *T. caerulescens* cannot be explained by the Zn transport pathway but may be related to an enhanced expression of the *IRT1* gene, which is essential for Fe uptake (31). The *IRT1* gene, it was shown, can mediate high-affinity uptake of Cd^{2+} in *A. thaliana* (32,33).

Enhanced root-to-shoot transport is another important element of metal hyperaccumulation. Lasat et al. (34) reported that most of the Zn in the nonaccumulator species *T. arvense* was localized in the root cell vacuoles, whereas in the hyperaccumulator *T. caerulescens,* more Zn was transported to the shoot and accumulated in the vacuoles of shoot cells. This pattern of sequestration could be due to tissue-specific expression of transporters responsible for vacuolar Zn sequestration or enhanced xylem loading (12). Very little progress has been made in understanding how hyperaccumulators differ from nonaccumulators in this area (12). Increased metal tolerance is essential for the hyperaccumulation phenotype to occur in majority of natural hyperaccumulator plants (21). Hypertolerance is achieved by internal detoxification and possibly involves compartmentation and complexation. Several studies have reported that metals are sequestered in leaf vacuoles in Zn, Cd, Ni, and As hyperaccumulators (31,35,36). Metal transporter genes encoding putative vacuolar ion transport proteins have been cloned from *T. caerulescens* (*ZPT1*) (37). The *ZTP1* gene belongs to the cation diffusion facilitator (CDF) family and, it was found, is highly expressed, predominantly in *T. caerulescens* leaves. Enhanced tonoplast transport of Zn probably plays an important role in metal tolerance in hyperaccumulator plants. With regard to complexation, Zn was found coordinated with histidine in roots and with organic acids or uncomplexed in shoots of *T. caerulescens* (38).

Phytochelatins (PCs) are small metal-binding peptides whose synthesis from glutathione (39), homo-glutathione, hydroxymethyl-glutathione (40), or γ-glutamylcysteine (41) is catalyzed by a transpeptidase, named phytochelatin synthase (PCS), which is a constitutive enzyme that requires posttranslational activation by heavy metals (39,42). There is strong evidence that phytochelatins are essential for constitutive tolerance to Cd in nonhyperaccumulator plants, but recent reports indicate that in *T. caerulescens,* PCs are not involved in the tolerance of Cd (43). Phytochelatin synthase, it has been shown, is activated by a broad range of metals and metalloids, in particular Cd, Ag, Pb, Cu, Hg, Zn, Sn, Au, and As, both *in vivo* and *in vitro* (42,44). Naturally selected heavy metal hypertolerance, which is commonly found in plant populations from strongly metal-enriched soils, does not seem to be associated with enhanced PC synthesis. De Knecht et al. (45) obtained equal capacities and activation constants for Cd-induced PC synthesis in crude protein extracts prepared from the roots of Cd/Zn-hypertolerant and nonmetallicolous *Silene vulgaris* plants. The root PC concentrations measured *in vivo*, however, were much lower in the hypertolerant plants, even when compared at equal rates of Cd uptake. In the same species, Zn-induced accumulation of PCs in roots were also much higher in

nonmetallicolous plants than in Zn-hypertolerant plants when compared at equal metal exposure levels and at equal rates of metal accumulation in the roots (46). Artificial overexpression of enzymes and transporters involved in the PC-based metal sequestration machinery, it has been shown, increases metal tolerance, in general, and Cd tolerance in particular (47–49). Several examples of enhanced PC synthesis in cell lines artificially selected for Cd hypertolerance have also been reported (50). However, there is no evidence of naturally selected enhanced PC synthesis in hypertolerant plant populations from Cd- and Zn-toxic environments (43).

OPTIMIZATION OF PHYTOEXTRACTION WITH AGRONOMIC PRACTICES AND GENETIC ENGINEERING

Successful phytoextraction of heavy metals such as Zn and Cd depends on a number of factors; the most important is the selection of appropriate plant species. The rate of metal removal depends on the biomass of the plant as well as the concentration of metals in the harvested parts. Hyperaccumulator plant species have the capacity to bioconcentrate metals, but their use is limited by their small size and slow growth rate. On the other hand, in nonaccumulator species, low potential for metal bioconcentration could be compensated for by production of a large biomass (51). The benefits of using fast-growing, high biomass nonaccumulators versus slow-growing, low biomass hyperaccumulators for phytoextraction have been debated extensively. Chaney et al. (52) analyzed the rate of Zn and Cd phytoextraction and concluded that nonaccumulator crops do not remove enough metal to support phytoextraction, despite their higher biomass. Moreover, metal phytotoxicity would further reduce their biomass in highly contaminated soils.

Lasat (53) argues that the success of phytoextraction would ultimately depend on agronomic practices applied at the site. Chaney et al. (52) proposed the use of ammonium sulfate as a soil additive to provide nutrients necessary for high plant yield and to acidify soil for greater metal bioavailability. Another important factor that affects biomass production is plant density (53). Other agronomic considerations include the use of crop rotation, weed and pest control and proper irrigation methods (53).

Conventional breeding approaches have also been proposed to overcome the two major disadvantages of using hyperaccumulators for phytoextraction; low biomass and slow growth rates. The success of this approach is limited by sexual incompatibility caused by anatomical differences between parent plants. Biotechnology has the potential to overcome this limitation by allowing direct gene transfer (53). No reports involving the expression of metal hyperaccumulator genes in nonaccumulator species are so far available, but an alternative approach has been used to transfer hyperaccumulation capacity to a nonaccumulating, high biomass plant species. Brewer et al. (54) used somatic hybridization to create a hybrid between *T. caerulescens* and *Brassica napus*. Some of the hybrids had high biomass combined with high metal tolerance and accumulation that make them attractive for metal phytoextraction.

SUMMARY AND FUTURE DIRECTIONS

Phytoextraction is an environmentally friendly approach for remediating metal-contaminated soils that has been widely accepted in recent years. If applied successfully, this technology has the capability to extract metals from large surface areas in a cost-effective manner. The cost of soil cleanup can be less than a quarter of the cost of excavation or *in situ* contaminant fixation (55). On the other hand, phytoextraction technology has the distinct disadvantage of taking much longer to accomplish cleanup goals compared with other conventional treatments. There have also been very few successful demonstrations of phytoextraction under field conditions, which require further optimization of the technique. Successful implementation of this technology is likely to be achieved in the near future as research progresses in the following fields: (1) improved agronomic practices to increase productivity of hyperaccumulators, (2) use of appropriate soil amendments to increase metal availability to plants, (3) development of conventional breeding or tissue culture techniques to improve metal uptake and accumulation capabilities of high biomass nonaccumulators, and (4) use of biotechnology to develop transgenic plants capable of efficient phytoextraction.

BIBLIOGRAPHY

1. Adriano, D.C. (1992). Bioengineering of trace metals. In: *Advances in Trace Substances Research*. Lewis, Boca Raton, FL.
2. Marschner, H. (1995). *Mineral Nutrition of Higher Plants*. 2nd Edn. Academic Press, London.
3. Pilon-Smits, E. and Pilon, M. (2002). Phytoremediation of metals using transgenic plants. *Crit. Rev. Plant Sci.* **21**(5): 439–456.
4. Zhao, F.J., Hamon, R.E., Lombi, E., McLaughlin, M.J., and McGrath, S.P. (2002). Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator, *Thlaspi caerulescence*. *J. Exp. Bot.* **53**: 535–543.
5. Kazantzis, G. (1987). Cadmium. In: *Genotoxic and Carcinogenic Metals: Environmental and Occupational Occurrence and Exposure*. L. Fishbein et al. (Eds.). Advances in Modern Environmental Toxicology, Vol. 11, Princeton Scientific, Princeton, NJ.
6. Callender, E. and Rice, K.C. (2000). The urban environmental gradient: Anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. *Environ. Sci. Technol.* **34**: 232–238.
7. Dinesan, K.C. and George, K.C. (1993). *Histopathological Studies on Zinc Toxicity in Milkfish Chanos Frsskal*. K. Rengarajan et al. (Eds.). CMFRI Special Publication: Mariculture Research Part 3, Cochin, India, pp. 25–27.
8. Nogawa, K., Honda, R., Kido, T., Tsuritani, I., and Yamada, Y. (1987). Limits to protect people eating cadmium in rice, based on epidemiological studies. *Trace Substances Environ. Health* **21**: 431–439.
9. Barceloux, D.G. (1999). Zinc. *J. Toxicol.: Clin. Toxicol.* **37**: 279–292.
10. Glass, D.J. (1999). *U. S. and International Markets for Phytoremediation, 1999–2000*. Report, D. Glass Assoc. Inc., Needham, MA.

11. Salt, D.E., Smith, R.D., and Raskin, I. (1998). Phytoremediation. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **49**: 643–668.
12. Pollard, J.A., Powell, K.D., Harper, F.A., and Smith, J.A.C. (2002). The genetic basis of metal hyperaccumulation in plants. *Crit. Rev. Plant Sci.* **21**: 539–566.
13. Baker, A.J.M., McGrath, S.P., Reeves, R.D., and Smith, J.A.C. (2000). Metal hyperaccumulator plants: A review of the ecology and physiology of a biochemical resource for phytoremediation of metal polluted soils. In: *Phytoremediation of Contaminated Soil and Water*. N. Terry and G. Banuelos (Eds.). Lewis, Boca Raton, FL, pp. 85–107.
14. Adriano, D.C. (2001). *Trace Elements in Terrestrial Environments*. 2nd Edn. Springer-Verlag, New York.
15. Jeng, A.S. and Singh, B.R. (1995). Cadmium status of soils and plants from a long-term fertility experiment in southeast Norway. *Plant Soil* **175**: 67–74.
16. Chlopecka, A., Bacon, J.R., Wilson, M.J., and Kay, J. (1996). Forms of cadmium, lead, and zinc in contaminated soils from Southwest Poland. *J. Environ. Qual.* **25**: 69–79.
17. Lindsay, W.L. (1979). *Chemical Equilibria in Soils*. John Wiley & Sons, New York.
18. Hickey, M.G. and Kittrick, J.A. (1984). Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.* **13**: 372–376.
19. Bingham, F.T. and Page, A.L. (1975). *Proc. Int. Conf. Heavy Metals Environ*. University of Toronto, Ontario, Canada.
20. Gerritse, R.G., Van Driel, W., Smilde, W.W., and Van Luit, B. (1983). Uptake of heavy metals by crops in relation to their concentration in the soil solution. *Plant Soil* **75**: 393–404.
21. McGrath, S.P. and Zhao, F.J. (2003). Phytoextraction of metals and metalloids from contaminated soils. *Curr. Opin. Biotechnol.* **14**: 1–6.
22. Blaylock, M. and Huang, J. (2000). Phytoextraction of metals. In: *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment*. I. Raskin and B. Ensley (Eds.). John Wiley & Sons, New York, pp. 53–69.
23. Baker, A.J.M., Reeves, R.D., and McGrath, S.P. (1991). *In situ* decontamination of heavy metal polluted soils using crops of metal-accumulating plants—a feasibility study. In: *In situ Bioreclamation*. R.E. Hinchee and R.F. Olfenbuttel (Eds.). Butterworth-Heinemann, Stoneham, MA, pp. 539–544.
24. McGrath, S.P., Sidoli, C.M.D., Barker, A.J.M., and Reeves, R.D. (1993). The potential for the use of metal-accumulating plants for the *in situ* decontamination of metal-polluted soils. In: *Integrated Soil and Sediment Research: A Basis for Proper Protection*. H.J.P. Eijsackers and T. Hamers (Eds.). Kluwer Academic, Dordrecht, The Netherlands, pp. 673–676.
25. McGrath, S.P. and Dunham, S.J. (1997). Potential Phytoextraction of Zinc and Cadmium from Soils using Hyperaccumulator Plants. *Proc. 4th Int. Conf. Biogeochemistry Trace Elements*. Berkeley, Ann Arbor Press, Chelsea, MI.
26. Brown, S.L., Chaney, R.L., Angle, J.S., and Barker, A.J.M. (1994). Phytoremediation potential of *Thlaspi caerulescence* and bladder campion for zinc- and cadmium-contaminated soil. *J. Environ. Qual.* **23**: 1151–1157.
27. Mcnair, M.R., Bert, C., Huitson, S.B., SaumitouLaprade, P., and Petit, D. (1999). Zinc tolerance and hyperaccumulation are genetically independent characters. *Proc. R. Soc. London Ser B* **266**: 2175–2179.
28. Lasat, M.M., Baker, A.J.M., and Kochian, L.V. (1996). Physiological characterization of root Zn^{2+} absorption and translocation to shoots in Zn hyperaccumulator and nonaccumulator species of *Thlaspi*. *Plant Physiol.* **112**: 1715–1722.
29. Maser, P. et al. (2001). Phylogenetic relationships within cation transporter families of *Arabidopsis*. *Plant Physiol.* **126**: 1646–1667.
30. Pence, N.S. et al. (2000). The molecular physiology of heavy metal transport in the Zn/Cd hyperaccumulator, *Thlaspi caerulescence*. *Proc. Natl. Acad. Sci. USA* **97**: 4956–4960.
31. Lombi, E. et al. (2002). Influence of iron status on calcium and zinc uptake by different ecotypes of the hyperaccumulator *Thlaspi caerulescens*. *Plant Physiol.* **128**: 1359–1367.
32. Vert, G. et al. (2002). *IRT1*, an *Arabidopsis* transporter essential for iron uptake from the soil and for plant growth. *Plant Cell* **14**: 1223–1233.
33. Connolly, E.L., Fett, J.P., and Guerinot, M.L. (2002). Expression of the *IRT1* metal transporter is controlled by metals at the levels of transcript and protein accumulation. *Plant Cell* **14**: 1347–1357.
34. Lasat, M.M., Baker, A.J.M., and Kochian, L.V. (1998). Altered Zn compartmentation in the root symplasm and simulated Zn absorption into the leaf as mechanisms involved in Zn hyperaccumulation in *Thlaspi caerulescens*. *Plant Physiol.* **118**: 875–883.
35. Kupper, H., Zhao, F.J., and McGrath, S.P. (1999). Cellular compartmentation of zinc in leaves of the hyperaccumulator *Thlaspi caerulescense*. *Plant Physiol.* **199**: 305–312.
36. Kramer, U., Pickering, I.J., Prince, R.C., Raskin, I., and Salt, D.E. (2000). Subcellular localization and speciation of nickel in hyperaccumulator and nonaccumulator *Thlaspi* species. *Plant Physiol.* **122**: 1343–1353.
37. Assuncao, A.G.L. et al. (2001). Elevated expression of metal transporter genes in three accessions of the metal hyperaccumulator *Thlaspi caerulescence*. *Plant Cell Environ.* **24**: 217–226.
38. Salt, D.E., Prince, R.C., Baker, A.J.M., Raskin, I., and Pickering, I.J. (1999). Zinc ligands in the hyperaccumulator, *Thlaspi caerulescence* as determined using X-ray absorption spectroscopy. *Environ. Sci. Technol.* **33**: 713–717.
39. Grill, E., Loffler, S., Winnacker, E.L., and Zenk, M.H. (1989). Phytochelatins, the heavy-metal-binding peptides of plants, are synthesized from glutathione by a specific γ-glutamylcysteine dipeptidyl transpeptidase (phytochelatin synthase). *Proc. Natl. Acad. Sci. USA* **86**: 6838–6842.
40. Klapheck, S., Schlunz, S., and Bergman, L. (1995). Synthesis of phytochelatins and homo-phytochelatins in *Pisum sativum* L. *Plant Physiol.* **107**: 515–521.
41. Hayashi, Y., Nakagawa, C.W., and Mutoh, N. (1991). Two pathways in the biosynthesis of cadystins (γ-EC)nG in the cell-free system of the fission yeast. *Biochem. Cell Biol.* **69**: 115–121.
42. Chen, J., Huang, J.W., Caster, T., and Cunningham, S.D. (1997). *Arabidopsis* as a model system for studying lead accumulation and tolerance in plants. In: *Phytoremediation of Soil and Water Contaminants*. K.L. Kruger et al. (Eds.). American Chemical Society, Washington, DC, pp. 264–273.
43. Schat, H., Llugany, M., Vooijs, R., Hartley-Whitaker, J., and Bleeker, P.M. (2002). The role of phytochelatins in constitutive and adaptive metal tolerances in hyperaccumulator and non-hyperaccumulator metallophytes. *J. Exp. Bot.* **53**: 2381–2392.
44. Grill, E., Winnacker, E.L., and Zenk, M.H. (1987). Phytochelatins, a class of heavy-metal-binding peptides from

plants, are functionally analogous to metallothioneins. *Proc. Natl. Acad. Sci. USA* **84**: 439–443.

45. De Knecht, J.A. et al. (1995). Synthesis and degradation of phytochelatins in cadmium-sensitive and cadmium-tolerant *Silene vulgaris*. *Plant Sci.* **106**: 9–18.
46. Harmens, H., Cornelisse, E., Den Hartog, P.R., Ten Bookum, W.M., and Verkleij, J.A.C. (1993). Phytochelatins do not play a key role in naturally selected zinc tolerance in *Silene vulgaris* (Moench) Garcke. *Plant Physiol.* **103**: 1305–1309.
47. Ortiz, D.F., Ruscitti, T., McCue, K.F., and Ow, D.V. (1995). Transport of metal-binding peptides by HMT1, a fission yeast ABC-type B vacuolar membrane protein. *J. Biol. Chem.* **270**: 4721–4728.
48. Clemens, S., Kim, E.J., Neuman, D., and Schroeder, J.I. (1999). Tolerance to toxic metals by a gene family of phytochelatin synthases from plants and yeast. *EMBO J.* **18**: 3325–3333.
49. Zhu, Y.L., Pilon-Smits, E.A.H., Jouanin, L., and Terry, N. (1999). Overexpression of glutathione synthase in Indian mustard enhances cadmium accumulation and tolerance. *Plant Physiol.* **119**: 73–79.
50. Chen, J. and Goldsbrough, P.B. (1994). Increased activity of γ-glutamyl cystein synthetase in tomato cells selected for cadmium tolerance. *Plant Physiol.* **106**: 233–239.
51. Ebbs, D.S., Lasat, M.M., Brady, D.J., Cornish, J., Gordon, R., and Kochian, L.V. (1997). Phytoextraction of cadmium and zinc from a contaminated site. *J. Environ. Qual.* **26**: 1424–1430.
52. Chaney, R.L., Li, Y.L., Angle, J.S., Baker, A.J.M., Reeves, R.D., Brown, S.L., Homer, F.A., Malik, M., and Chin, M. (1999). Improving metal hyperaccumulator wild plants to develop commercial phytoextraction systems: Approaches and progress. In: *Phytoremediation of Contaminated Soils and Water*. N. Terry and G.S. Banuelos (Eds.). CRC Press, Boca Raton, FL.
53. Lasat, M.M. (2000). Phytoextraction of metals from contaminated soil: A review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *J. Hazard Substance Res.* **2**: 1–25.
54. Brewer, E.P., Saunders, J.A., Angle, J.S., Chaney, R.L., and McIntosh, M.S. (1999). Somatic hybridization between the zinc accumulator *Thlaspi caerulescence* and *Brassica napus*. *Theor. Appl. Genet.* **99**: 761–771.
55. Black, H. (1995). Absorbing possibilities: Phytoremediation. *Environ. Health Perspect.* **103**: 1106–1108.

PHYTOREMEDIATION ENHANCEMENT OF NATURAL ATTENUATION PROCESSES

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Phytoremediation is a remediation method that uses what is in essence enhanced natural attenuation for cleanup. There are a variety of phytoremediation methods, some having multiple names: phytostabilization, rhizodegradation (phytostimulation, rhizosphere bioremediation, or plant-assisted bioremediation), rhizofiltration (contaminant uptake), phytodegradation (phytotransformation), phytovolatilization, and Phytoaccumulation (phytoextraction or hyperaccumulation). Various types of plants can be used in phytoremediation, including poplar trees, alfalfa, black locust, Indian mustard, fescue grass, crested wheatgrass, and Canada wild rye.

Figure 1 and Tables 1 and 2 summarize the overall concepts of phytoremediation and the types of processes and chemicals that can be treated.

A form of natural attenuation for indigenous plants at a site and enhanced bioremediation for cultivated plants, phytoremediation acts through two fundamental remediation processes: enhancement of saturated zone *in situ* biodegradation and phytoextraction.

The rhizosphere is the zone in the subsurface occupied by the plants' root systems. Root depths of 6–30 ft are common, with some trees and shrubs capable of root penetration to 60 ft. Phreatophytes are deep-rooted plants that draw water from beneath the water table; xerophytes are shallow-rooted and depend more directly on infiltrating rainwater. Depending on site conditions and contaminant distribution, either type of plant can be of value for phytoremediation.

Within the rhizosphere, plants contribute to enhanced *in situ* biodegradation through the supply of carbonaceous substrate and oxygen transfer. Rhizodeposition is partially

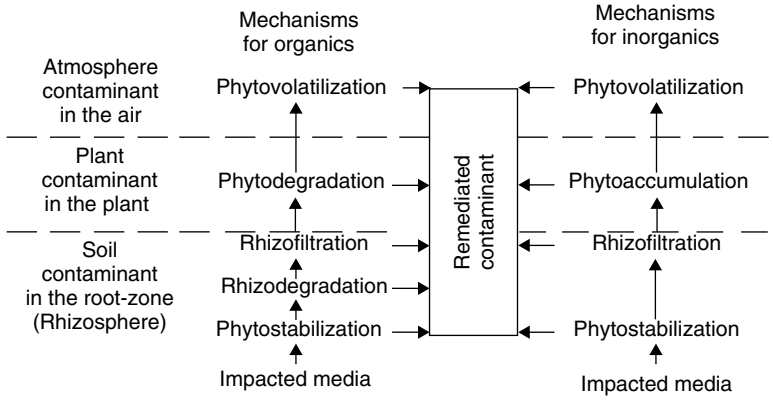


Figure 1. Overview of phytoremediation. (After Ref. 1).

Table 1. Types of Phytoremediation for Organic Constituents

Type of Phytoremediation	Process Involved	Contaminant Treated
Phytostabilization	Plants control pH, soil gases, and redox conditions in soil to immobilize contaminants. Humification of some organic compounds is expected.	Expected for phenols, chlorinated solvents (tetrachloromethane and trichloromethane), and hydrophobic organic compounds
Rhizodegradation (phytostimulation, rhizosphere bioremediation, or plant-assisted bioremediation)	Plant exudates, root necrosis, and other processes provide organic carbon and nutrients to spur soil bacteria growth by two or more orders of magnitude. Exudates stimulate degradation by mycorrhizal fungi and microbes. Live roots can pump oxygen to aerobes and dead roots may support anaerobes.	Polyaromatic hydrocarbons, BTEX, and other petroleum hydrocarbons, perchlorate, atrazine, alachlor, polychlorinated biphenyl (PCB), and other organic compounds
Rhizofiltration (contaminant uptake)	Compounds are taken up or sorbed by roots (or sorbed to algae and bacteria).	Hydrophobic organic chemicals
Phytodegradation (phytotransformation)	Aquatic and terrestrial plants take up, store, and biochemically degrade selected organic compounds to harmless by-products, products used to create new plant biomass, or by-products that are further broken down by microbes and other processes to less harmful products. Reductive and oxidative enzymes may be used in series in different parts of the plant.	Munitions (TNT, DNT, HMX, nitrobenzene, picric acid, nitrotoluene), atrazine, halogenated compounds (tetrachloromethane, trichloromethane, hexachloroethane, carbon tetrachloride, TCE, tetrachlorethane, dichloroethant), DDT and other chlorine and phosphorus based pesticides, phenols, and nitrites
Phytovolatilization	Volatile organic compounds are taken up and transpired. Some recalcitrant organic compounds are more easily degraded in the atmosphere (photodegradation).	Chlorinated solvents (trichloroethane), organic VOCs, BTEX, MTBE

Source: Adapted from Reference 1.

Table 2. Types of Phytoremediation for Inorganic Constituents

Type of Phytoremediation	Process Involved	Contaminant Treated
Phytostabilization	Plants control pH, soil gases, and redox conditions in soil to immobilize contaminants. Humification of some organic compounds is expected.	Proved for heavy metals in mine tailing ponds
Rhizofiltration (contaminant uptake)	Compounds are taken up or biosorbed by roots (or sorbed to algae and bacteria).	Heavy metals and radionuclides
Phytoaccumulation (phytoextraction or hyperaccumulation)	Metals and organic chemicals are taken up by the plant with water, or by cation pumps, sorption, and other mechanisms.	Nickel, zinc, lead, chromium, cadmium, selenium, other heavy metal radionuclides
Phytovolatilization	Volatile metals are taken up, changed in species, and transpired.	Mercury and selenium

Source: Adapted from Reference 1.

the result of the decay of dead roots and root hairs. Also important are carbonaceous root exudations, such as leakage from epidermal cells, secretions resulting from metabolic activity, mucilages from root tips (which act as lubricants for root penetration), and lysates from sloughed cells. Exudates are composed of a wide range of chemicals that include sugars, amino acids, organic acids, fatty acids, and numerous other compounds. It is estimated that 7–27% of the total plant mass is annually deposited as carbonaceous material in the rhizoshpere, amounting to 85–155 tons/acre. This carbonaceous material stimulates overall bacterial activity as well as providing substrate to support cometabolic degradation of xenobiotic hydrocarbons.

The capability to support oxygen transfer can be divided into three categories of plants: nonwetland herbaceous and woody plants with poor oxygen transfer capacity; wetland woody plants with moderate capacity; and wetland herbaceous plants with high oxygen transport capacity. Plants of the first variety will ultimately die with their roots under saturated conditions. Wetland plants adsorb oxygen through their leaves, twigs, stems, bark, and unflooded roots. This oxygen is in turn transported to the roots, where it diffuses out into the rhizosphere. Consequently, wetland plants are able to support aerobic biooxidation in the rhizosphere at rates that are significantly greater than that seen through saturated zone diffusion alone. Due to the processes described above, it is not uncommon to find bacterial population levels in the rhizoshpere elevated a magnitude or more above surrounding undeveloped soils.

The primary *in situ* remediation potential of plants for hydrocarbons lies in their capacity to enhance oxidation rates in the subsurface and provide cometabolic

substrate. However, plants also have the ability to remove compounds, a process termed phytoextraction, which can be applied to organic or metal contaminants. In the case of hydrocarbons, the compound must be water soluble and have a moderate degree of lipid solubility. Lipid solubility is a function of the octanol–water partition coefficient (K_{ow}) for the compound. Compounds most readily mobilized by plants have log K_{ow} values in the range of 1–3. Compounds with values of K_{ow} in this range include BTEX hydrocarbons, chlorinated solvents, and other short-chain aliphatic hydrocarbons.

Once in the interior of the plant, the adsorbed hydrocarbons may be stored via lignification, volatilized, partially degraded through metabolization, or completely mineralized.

Compounds with values of log K_{ow} higher than 3 such as PNAs are incapable of entering the root; those with log K_{ow} values lower than 1 are rejected by the root membrane. In addition, the desorption and mass transfer of contaminant hydrocarbons from the geologic matrix may be the rate limiting step in the remediation process.

In phytoremediation of metals, the dominant active mechanism is phytoextraction and accumulation in the tissues of the plant, which is a process that has long been familiar to exploration geologists in the mining industry. Geobotany is concerned with the identification of plants or plant conditions common to metal-rich soils and biogeochemistry is concerned with actual metal concentrations in parts of plants.

The mechanisms for metal accumulation include:

- Chelation
- Precipitation
- Compartmentalization
- Translocation

These same mechanisms often contribute to the metal tolerance of the plant. To date, accumulators of lead, cadmium, chromium, nickel, cobalt, zinc, and selenium have been identified. To successfully apply this technology to a metal contaminated site, it is important that pH, organic complexes, and interfering elements be assessed and that plant species with the appropriate metal selectivity be utilized. In some instances, it may be necessary to apply soil amendments to enhance the process.

A key part of the metal extraction process is played by phytochelatins, which are low molecular weight peptides that have the capability to bind metals. Their presence in plants has likely evolved because toxicity to the plant is reduced by having the metals bound by the phytochelatins. Currently, there are several hyperaccumulating plants that have been discovered such as Indian mustard and pennycress. However, these plants are small and slow growing and thus lack enough biomass to remove significant amounts of metals. For example, there are 26 known plants that are hyperaccumulators of cobalt and exhibit desirable properties of common crops such as high growth rates and easy harvesting.

Lastly, plants have other properties with potential remediation applications. In semiarid climates, sufficient numbers of trees are capable of depressing the water table through transpiration, up to the equivalent of 3 ft of rainfall per year. Phytoremediation can be used as a form of hydraulic control. In tight soils, root penetration can improve the overall mass transport properties.

Plants can also aid in the surface stabilization of soils, preventing the windblown migration of soil with adsorbed contaminants.

Planting costs have been estimated to be in the range of $10,000 per acre, with monitoring costs parallel to those associated with other remediation technologies. Total phytoremediation costs are estimated to range from $60,000 to $100,000 per acre. The potential of phytoremediation is significant given proper design for its application. Contaminant type and distribution, soil chemistry, and climate are all important factors that must be considered.

BIBLIOGRAPHY

1. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL, p. 419.

BACTERIA ROLE IN THE PHYTOREMEDIATION OF HEAVY METALS

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INTRODUCTION

Rapid industrialization in the last century has led to the release of numerous contaminants, including heavy metals, to the environment. The release of heavy metals is of particular concern as they cannot be degraded, but only transformed from one form to another, and can accumulate in natural systems. Examples of heavy metals of particular significance include cadmium, copper, chromium, iron, lead, mercury, nickel, and zinc. They are released into the environment from a wide range of anthropogenic sources. Vehicles, industrial activities, building materials, and even the atmosphere contribute heavy metals to the water and soil, resulting in their occurrence at some sites in higher concentrations than is acceptable.

Heavy metals may remain dissolved in water or attach (referred to as sorption) to the mineral and organic components of soil. Although some heavy metals are required in minute quantities as micronutrients for the growth of plants and bacteria, at high concentrations they present a toxic threat to ecosystems. Bacteria and plants are susceptible to toxic effects of heavy metals, as are animals and humans who consume vegetation and crops grown in contaminated soils. Heavy metals are capable of bioaccumulation in plant and animal tissues and, therefore, can be biomagnified through the food chain.

Currently, heavy metal contaminated sites are treated by various immobilization and extraction methods. Pump-and-treat systems aim to wash heavy metals from the soil, using water alone, or metal-solubilizing compounds such as chelators and surfactants. Other methods involve thermally volatilizing or vitrifying contaminants in soil. At some sites, the soil is simply removed and dumped elsewhere. The existing treatment methods for contaminated soils are, in many cases, prohibitively expensive, which may postpone or preclude any treatment action. To gain wider acceptability and implementation, remediation technologies must be a low cost, sustainable, and effective alternative to physical and chemical treatment methods. Phytoremediation is one such emerging technology that can be used effectively for at-source contaminant mitigation.

The three basic components of phytoremediation systems are plants, bacteria, and the contaminated soil. Heavy metals are sorbed to the minerals in soil by cation exchange or to soil organic matter by complexation with organic acids. The complex interactions that have evolved between plants and bacteria in the rhizosphere (root zone) can be harnessed to remediate metal-contaminated soils. Bacteria and plants mobilize metals for uptake by excreting a vast array of organic compounds such as lipids, sterols, enzymes, and surfactants. Alternatively, they can immobilize metals via chemical transformation or precipitation of insoluble compounds. Labile metals can be sorbed to bacterial cells or taken up through plant cell membranes. Metals taken up by roots are translocated in the xylem (woody tissue) to the aboveground plant biomass, which can be harvested, thereby providing the basis for developing a decontamination technology using phytoremediation. Here we discuss the major processes by which bacteria and plants mobilize/immobilize heavy metals within the rhizosphere.

MOBILIZATION PROCESSES

The mobilization of metals from soil has a direct influence on their bioavailability to plants and hence the potential for their uptake and removal from the soil. There are a number of mechanisms by which bacteria and plants facilitate the dissolution of precipitates or the desorption of ions attached to mineral and organic fractions of soil.

Acidification/Protonation

Plant and bacterial exudates can alter the pH of soils and hence the bioavailability of contaminants and nutrients to both plants and bacteria (1). Soil acidification occurs due to proton efflux, the release of organic acids, or the addition of respiratory carbon dioxide to the soil (1). Free protons (H^+ ions) are added to the soil by a number of bacterial processes. Organic and amino acids are secreted by plant roots and over time may lower the pH of soils, increasing metal solubility. Bacterial respiration results in the addition of carbon dioxide to the soil, forming carbonic acid. The dissociation of acids in soil water causes the release of protons, which compete with metal ions for sorption or complexation sites. In this way, the protons may displace the metal cations into solution.

Plants too have a number of specialized mechanisms to increase the solubility of metals and nutrients. For example, iron is a micronutrient required for plant growth. To mobilize iron from the soil, plants may release protons to convert iron(III) to iron(II) and thus increase its solubility (2,3).

Solubilization by Biosurfactants

Biosurfactants are surface-active agents that are secreted by plants and bacteria within the rhizosphere (4). Microbially produced biosurfactants have many of the same properties as synthetic surfactants but have several advantages for *in situ* bioremediation. They are nontoxic to most plants and bacteria and are biodegradable, which prevents their accumulation in soil or groundwater. In addition, biosurfactants can be produced by bacteria localized around plant roots where they are needed.

Biosurfactants have both a hydrophobic and a hydrophilic region, which allows them to partition across interfaces of varying polarity. The hydrophobic region is often a nonpolar hydrocarbon chain, which reduces the surface tension at the interface (5). For example, it has been found that surfactin, a biosurfactant produced by *Bacillus subtilus,* reduced the surface tension of water from 72 to 27 mN/m at a concentration of only 0.005% (6). The lowering of the interfacial tension between the aqueous solution and substrate enables bacteria to access metals and degrade lipophilic substrates in the aqueous phase.

At low concentrations, surfactant molecules behave independently as monomers. On a solid surface, the surfactant molecules may form one or more layers (admicelles) with regions of similar polarity associated with each other. At concentrations above a nominal value, the surfactant molecules aggregate into micelles in the bulk phase, in addition to the interface. This value is dependent on the biosurfactant and is known as the critical micelle concentration (CMC) (7).

Biosurfactants have the capability to solubilize heavy metals that are sorbed to soil particles or soil organic matter. The surfactant molecules are adsorbed to the surface of the soil particle where they form complexes with attached metal ions (8). These complexes may then dissociate from the solid to the liquid phase, where similar surfactant molecules form micelles.

Plants produce surfactants such as lipids and sterols for root lubrication to aid root progression through the soil (9). These surfactants are also able to facilitate the desorption of contaminants and nutrients from soil particles. For example, saponins are plant-derived biosurfactants that are capable of binding to heavy metals such as cadmium, copper, lead, and zinc (10).

Chelation

Another mechanism by which bacteria and plants influence the bioavailability and toxicity of heavy metals is via the production of chelators. These are ligands that bind to metal ions forming chelates—ring-like structures that can increase the solubility of metals in solution. The production of chelates by microbes in the rhizosphere is greater than that in the bulk soil (11,12). Chelation

enhances the uptake of ions with larger valence than ions with lower valence; Parker et al. (13) found that chelators reduced the uptake of divalent metal ions while increasing the uptake of trivalent ions such as aluminum. In addition, dissociated organic anions such as citrate and oxalate may also be capable of forming complexes with metal ions sorbed to soil minerals or organic matter (1).

Chemical Transformation

Bacteria are capable of altering metal speciation between soluble and insoluble forms through reduction processes. The change in oxidation state of metals influences their solubility and hence their bioavailability. Reduction under anaerobic conditions is carried out by a range of heterotrophic bacteria. During respiration, these bacteria can use a metal cation as a terminal electron acceptor, reducing to a lower valence state (14), which can cause an increase in the solubility of metals such as iron and manganese since iron(II) and manganese(II) are more soluble than iron(III) and manganese(IV) (15). Similarly, the reduction of Hg(II) to Hg(0) within bacterial cells causes the diffusion of elemental mercury out of cells (1). However, in some cases reduction can decrease the available metal in solution, such as the reduction of chromium from VI to III valence results in lower solubility and mobility (1).

IMMOBILIZATION PROCESSES

Sorption

Binding to Cells. Bacteria have a net negative charge due to the presence of hydroxyl (OH^-), carboxyl (COO^-), and phosphate (PO_4^{3-}) functional groups on the membrane surface. This causes the attraction and sorption of free metal cations to negatively charged external sites on bacterial cells. The binding capacity is dependent on the type of bacteria. For example, the binding capacity of gram-positive bacteria is greater than that of gram-negative bacteria due to the difference in the structure and polymer content of membranes and the cell wall. The binding of metal ions by bacteria increases with temperature and is greater at lower pH (16).

Heavy metal cations can form complexes, which reduces their positive charge and increases their size, which causes the cations to be less favored for transport through plant and bacterial cell membranes and instead they are retained by the surface sites on cells.

Binding to Extracellular Molecules. Bacteria and plants excrete organic substances that are capable of binding heavy metals in ionic or solid forms. Simple organic molecules include acids and alcohols, which can attach to free metal ions. Macromolecules include long-chain organic acids such as humic and fulvic acids, which are capable of binding metal cations (17). Exopolysaccharides are a major component of biofilms and other microbial assemblages and are capable of trapping particulates and ions. Bacteria can also secrete specific metal binding proteins (metallothioneins) in response to the presence of toxic metals (1).

Uptake and Intercellular Sequestration

The uptake of heavy metal cations is an energetically favorable process for plant and bacterial cells due to their negative internal charge. Negative transmembrane potentials encourage the uptake of metal cations into the cell (13). Bacteria may store metals within inclusion bodies and thus render them temporarily unavailable and hence nontoxic.

Precipitation/Crystallization/Mineralization

Bacteria are capable of reducing metals to insoluble forms, lowering their bioavailability and hence toxicity to bacteria, plants, and animals. The bacterial reduction of chromium(VI) to chromium(III) immobilizes the metal in soil (1). Researchers have identified a strain of *Xanthomonas maltophyla* that is capable of catalyzing the reduction and precipitation of chromium as well as the transformation of other toxic metal ions including lead and mercury (18).

Volatilization

Biomethylation involves the microbial transfer of methyl ($-CH_3$) groups to a metal or metal-containing compound, often forming methylated species with increased volatility. Methylation of metals such as arsenic, lead, mercury, selenium, and tin can occur in either aerobic or anaerobic environments (1). Volatile methylated species can then escape from the soil into the atmosphere. However, methylated species of metals such as mercury and arsenic can be more toxic. For example, methylmercury is a neurotoxic compound formed via the methylation of ionic mercury. Some bacteria are capable of reducing mercury from its ionic to elemental form, increasing its volatility and decreasing its toxicity (2).

INTERACTIONS BETWEEN PLANTS, BACTERIA, AND CONTAMINANTS

Plants as Energy Sources for Microbes

The growth of bacteria in the rhizosphere is carbon limited (19). Most organic carbon in the rhizosphere is derived from plant sources. Root cap mucilage, root exudates, photosynthate, and plant debris provide organic carbon for microbial cell growth. Plant roots directly or indirectly foster rhizospheric bacteria by producing exudates that bacteria and fungi may use as a carbon source. Plant root exudates consist primarily of organic acids (of low and high molecular weight) as well as sugars and amino acids. These substrates can be easily degraded and utilized as an energy source by many types of soil bacteria, encouraging a higher concentration of soil microbes in the rhizosphere than in bulk soil (20). An increase in microbial biomass usually results in higher rates of contaminant degradation or mobilization due to the increased total activity of the rhizospheric community.

Transpiration Effects on Contaminant Movement

Plant root uptake of water influences the rate and direction of contaminant migration through the soil.

Soluble metals contained within the groundwater are drawn toward the roots by the transpiration stream. In this way, the contaminants move into the region where they may be taken up by the roots and the surrounding rhizospheric community, which facilitates access to contaminants by nonmotile bacteria and improves the possibilities for microbial action resulting in transformation or degradation (21). In addition, the network of plant roots intercepts contaminants drawn downward by the infiltration of rainwater. This reduces the loss of nutrients and contaminants from the upper regions of the soil.

Secondary Plant Metabolites

Secondary plant metabolites (SPMEs) comprise a wide range of organic compounds produced by plants and exuded by their roots. Although SPMEs are not essential for basic metabolic processes, they have an important role in the nutrition and defense of plants (22).

There are many theories as to the purpose of SPME production (23). It is generally accepted that many SPMEs are effectively natural pollutant analogues (24). The resemblance of many SPMEs to organic pollutants may encourage the bacterial production of enzymes that are capable of degrading both types of compounds. Thus, the plant reduces the time needed for bacteria to develop the enzymes required for the degradation of pollutants in the rhizosphere.

SPMEs are also produced by plants for defense against herbivory as well as insect and microbial attack (25). Allelopathic SPMEs are produced to reduce competition between plant species (26). SPMEs are also produced to act as chemical signals to other plants and microbes. However, this is not always to the benefit of the plant, as this trait can also encourage the growth of parasitic plants (27).

Cometabolism of Contaminants. Secondary plant metabolites may include enzymes that are intended for the degradation of one compound, but are also capable of degrading other, perhaps xenobiotic, compounds with no additional benefit to the plant in terms of energy or nutrition. In this case, the primary compound is referred to as a cometabolite as it provides the energy source for the degradation of the secondary compound (22). As cometabolism does not require the population to produce a specific enzyme for contaminant degradation, cometabolism of contaminants is improved by increasing the microbial biomass and diversity in the rhizosphere.

Exudates as Chemical Signals. Walton et al. (28) proposed the theory for the plant production of exudates as chemical signals to bacteria. When a plant detects the presence of a toxicant, it alters the composition of the root exudates produced. In turn, the plant root exudates alter the rhizospheric community in such a way as to increase the bacterial detoxification of the soil for the benefit of the plant, which may be achieved by the release of specific enzymes, cometabolites, or energy sources to increase the number and activity of rhizospheric bacteria or to change the bacterial exudates produced (28). Associations between plants and bacteria may be both specific and nonspecific and are thought to have evolved over time for the mutualistic benefits they offer.

Selection for Metal-Resistant Bacteria. Hyperaccumulating plant species may directly or indirectly increase the selection for metal-resistant bacteria in their rhizosphere. Hyperaccumulating plants are generally defined as variants capable of accumulating metals such as nickel, cobalt, copper, zinc, cadmium, manganese, and lead within tissues to concentrations 100 times or more greater than normal plants (29). Such plants usually prefer one particular metal, although some multimetal accumulators have been encountered. More than 400 hyperaccumulating species have been identified (30). One of the better known zinc hyperaccumulating species is *Thlaspi caerulescens*, which has been well researched for its phytoremedial potential. Higher ratios of metal-resistant bacteria are seen to exist around the roots of *T. caerulescens* than the nonaccumulating plant species growing in the same zinc-contaminated soil. This behavior is attributed to the release of metals for uptake via acidification of the plant rhizosphere, resulting in selection for bacteria that can tolerate higher zinc concentrations (31).

Plant Pathogens

Plants are subject to attack from insects and microorganisms. Insects eat plant tissues, such as leaves, or suck the sugar-rich phloem from the stalks. Bacteria can produce toxins that affect plant growth and hence reduce competition for soil nutrients. These bacterial phytotoxins may have been a reason for the evolution of detoxification mechanisms by plants and the production of allelopathic compounds as a defense mechanism. Bacteria also have a role as plant pathogens, causing disease to plant tissues and affecting the ability of plants to remove metals from soil. However, bacteria may also defend plants against attack from insects, fungi, and viruses. For example, the production of toxins by endophytic bacteria may protect plants from herbivory by chewing insects.

Nutrient Requirements

In many soils, the availability of nutrients is limited, which causes competition between bacteria and plants for nutrients. Bacteria are capable of forming mutualistic or antagonistic relationships with plants with respect to nutrient availability.

The presence of rhizospheric bacteria may have beneficial effects for plant biomass production. An increased microbial population results in greater mobilization of nonlabile nutrients and increased uptake by plant roots. Limiting nutritional elements are mobilized from soils by bacterial exudates. For example, siderophores (mugineic and avenic acids) are iron-chelating ligands that solubilize iron from the soil, which assists plants in assimilating iron and increases plant resistance to iron deficiency (12).

Some species of hyperaccumulating plants require heavy metals for normal growth, in concentrations that would be toxic to most species. Bacteria may assist these plants in meeting their high demand for metals. Studies

have shown that the total uptake of zinc by shoots of *Thlaspi caerulescens* was increased by a factor of 4 due to the presence of bacterial species, which increase was attributed to the twofold increase in the concentration of zinc in the shoots and a similar increase in the shoot biomass (12).

Root Area Augmentation

The presence of rhizospheric bacteria and plant mycorrhizal associations can increase the surface area of the plant root system. In addition, the presence of rhizospheric communities can also increase the biomass of plants. It has been found that bacterial seed inoculates increase plant root biomass, length, and exudate production (32). Hadas and Okon (33) demonstrated that the root growth of tomato seedlings was improved by inoculation with the bacteria *Azospirillum brasilense*. The roots had greater surface area due to the increased length and density of root hairs, with a subsequent increase in the uptake of water and minerals from the soil (33).

Soil Detoxification

Mutualistic relationships may develop between plants and bacteria living in contaminated soils. The presence of organic and inorganic contaminants may prevent the normal growth of plants and hence the supply of nutrients and energy for rhizospheric bacteria. Therefore, bacteria benefit from the nutritional gains brought about by their ability to detoxify soils. Where high concentrations of metals are present, the rhizospheric bacteria may mediate their immobilization or transformation, reducing metal bioavailability by binding metals to the negatively charged surface of bacteria, which may reduce their toxicity to plants. Additionally, rhizosphere communities may assist their host plants by mineralizing or degrading toxic organics to less hazardous forms.

CONCLUSION

At many sites around the world, heavy metals have built up to toxic concentrations in soils. High concentrations of soil metals are harmful to most forms of life including plants, bacteria, and humans. Bacteria interact with plants and heavy metal contaminants in a variety of ways to mediate the mobilization and immobilization of heavy metals within the soil. Plants may directly or indirectly stimulate these microbial processes through the release of a diverse range of root exudates. Recent research has shown that phytoremediation systems may be improved by building on the natural processes and interactions between plants and bacteria that occur in the rhizosphere. Phytoremediation may present a more sustainable solution to the worldwide problem of contaminated soils by further developing the remedial processes present in natural systems.

BIBLIOGRAPHY

1. Gadd, G.M. (2004). Microbial influence on metal mobility and application for bioremediation. *Geoderma*, in press.
2. Lasat, M.M. (2002). Phytoextraction of toxic metals: a review of biological mechanisms. *J. Environ. Qual.* **31**: 109–120.
3. Romheld, V. and Marschner, H. (1986). Mobilisation of iron in the rhizosphere of different plant species. *Adv. Plant Nutr.* **2**: 155–204.
4. Parkinson, M. (1985). Bio-surfactants. *Biotechnol. Adv.* **3**(1): 65–83.
5. Cameotra, S.S. and Bollag, J.-M. (2003). Biosurfactant-enhanced bioremediation of polycyclic aromatic hydrocarbons. *Crit. Rev. Environ. Sci. Technol.* **30**(2): 111–126.
6. Arima, K., Kakinuma, K., and Tamura, G. (1968). Surfactin, a crystalline peptidolipid surfactant produced by *Bacillus subtilis*: Isolation, characterization and its inhibition of fibrin clot formation. *Biochem. Biophys. Res. Commun.* **31**(3): 488–494.
7. Rosen, M.J. (1978). *Surfactants and Interfacial Phenomena*. John Wiley & Sons, Hoboken, NJ.
8. Mulligan, C.N., Yong, R.N., and Gibbs, B.F. (2001). Heavy metal removal from sediments by biosurfactants. *J. Hazard. Mater.* **85**(1–2): 111–125.
9. Curl, E.A. and Truelove, B. (1986). Root exudates. In: *The Rhizosphere*. E.A. Curl and B. Truelove (Eds.). Springer-Verlag, Berlin, pp. 55–90.
10. Hong, K.-J., Tokunaga, S., and Kajiuchi, T. (2002). Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils. *Chemosphere* **49**(4): 379–387.
11. White, P.J. (2001). Phytoremediation assisted by microorganisms. *Trends Plant Sci.* **6**(11): 502.
12. Whiting, S.N., De Souza, M.P., and Terry, N. (2001). Rhizosphere bacteria mobilize Zn for hyperaccumulation by *Thlaspi caerulescens*. *Environ. Sci. Technol.* **35**(15): 3144.
13. Parker, D.R., Chaney, R.L., and Norvell, W.A. (1995). Equilibrium computer models: applications to plant nutrition research. In: *Chemical Equilibrium and Reaction Models*. R.H. Leoppert, A.P. Schwab, S. Goldberg, and W.I. Madison (Eds.). Soil Science Society of America, pp. 163–200.
14. White, C. and Gadd, G.M. (1998). Reduction of metal cations and oxyanions by anaerobic and metal-resistant microorganisms: chemistry, physiology, and potential for the control and bioremediation of toxic metal pollution. In: *Microbial Life in Extreme Environments*. K. Horikoshi and W.D. Grant (Eds.). Wiley-Liss, Hoboken, NJ, pp. 233–254.
15. Lovley, D. (2000). Fe(III) and Mn(IV) reduction. In: *Environmental Microbe–Metal Interactions*. D. Lovley (Ed.). American Society of Microbiology, Washington, DC, pp. 3–30.
16. Goyal, N., Jain, S.C., and Banerjee, U.C. (2003). Comparative studies on the microbial adsorption of heavy metals. *Adv. Environ. Res.* **7**(2): 311–319.
17. Van Dijk, H. (1971). Cation binding of humic acids. *Geoderma* **5**(1): 53–67.
18. Blake, R.C. et al. (1993). Chemical transformation of toxic metals by a *Pseudomonas* strain from a toxic waste site. *Environ. Toxicol. Chem.* **12**: 1365–1376.
19. Grayston, S.J., Wang, S., Campbell, C.D., and Edwards, A.C. (1998). Selective influence of plant species on microbial diversity in the rhizosphere. *Soil Biol. Biochem.* **30**(3): 369–378.
20. Jones, D. (1998). Organic acids in the rhizosphere—a critical review. *Plant Soil* **205**: 24–44.
21. Harvey, P.J. et al. (2001). Phytoremediation of polyaromatic hydrocarbons, anilines and phenols. *Environ. Sci. Pollut. Resour.*: 1–18.

22. Singer, A.C., Crowley, D.E., and Thompson, I.P. (2003). Secondary plant metabolites in phytoremediation and biotransformation. *Trends Biotechnol.* **21**(3): 123–130.
23. Hadacek, F. (2002). Secondary metabolites as plant traits: current assessment and future perspectives. *Crit. Rev. Plant Sci.* **21**(4): 273–322.
24. Singer, A.C., Thompson, I.P., and Bailey, M.J. (2004). The tritrophic trinity: a source of pollutant-degrading enzymes and its implications for phytoremediation. *Curr. Opin. Microbiol.* **7**(3): 239–244.
25. Frey, M. et al. (1997). Analysis of a chemical plant defense mechanism in grasses. *Science* **277**: 696–699.
26. Bais, H. et al. (2003). Allelopathy and exotic plant invasion: from molecules and genes to species interactions. *Science* **301**: 1377–1380.
27. Bouwmeester, H.J., Matusova, R., Zhongkui, S., and Beale, M.H. (2003). Secondary metabolite signalling in host–parasitic plant interactions. *Curr. Opin. Plant Biol.* **6**(4): 358–364.
28. Walton, B.T., Hoylman, A.M., Perez, M.M., Anderson, T.A., Johnson, D.L., Guthrie, E.A., and Christman, R.F. (1994). Rhizosphere microbial communities as a plant defense against toxic subsances in soils. In: *Microbial Degradation of Organic Chemicals in the Rhizosphere*. T.A. Anderson and J.R. Coats (Eds.). American Chemical Society, Washington, DC, pp. 88–92.
29. Baker, A.J.M. and Brooks, R.R. (1989). Terrestrial higher plants which hyperaccumulate metallic elements—a review of their distribution, ecology and phytochemistry. *Biorecovery* **1**: 81–126.
30. Baker, A.J.M., McGrath, S.P., Reeves, R.D., and Smith, J.A.C. (2000). Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. In: *Phytoremediation of Contaminated Soil and Water*. N. Terry and G.S. Banuelos (Eds.). Lewis Publishers, Boca Raton, FL, pp. 85–107.
31. Delorme, T.A., Gagliardi, J.V., Angle, J.S., and Chaney, R.L. (2001). Influence of the zinc hyperaccumulator *Thlaspi caerulescens J. & C. Presl*. and the nonmetal accumulator *Trifolium pratense L.* on soil microbial populations. *Can. J. Microbiol.* **47**(8): 773–776.
32. Hofflich, G., Weihe, W., and Hect-Bucholz, C. (1995). Rhizosphere colonisation of different crops with growth promoting *Pseudomonas* and *Rhizobium* bacteria. *Microbiol. Res.* **150**: 139–147.
33. Hadas, R. and Okon, Y. (1987). Effect of *Azospirillum brasilense* on root morphology and respiration in tomato seedlings. *Biol. Fertil. Soils* **5**: 241–247.

PHYTOREMEDIATION OF LEAD-CONTAMINATED SOILS

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Several treatment technologies have been investigated for treating heavymetal-contaminated soils, such as lead. Recently, among the most promising methods is "phytoremediation," the use of certain plants to remove/accumulate or neutralize/degrade pollutants, of inorganic or organic nature. The systematic examination of plants, especially for removing lead from polluted soils has drawn serious attention, especially during the last decade. The overview of the specific technology and a brief description of the results obtained so far is briefly presented. Specific aspects that are of critical importance, such as the chemistry of soil and the interaction with the toxic metals, are also outlined.

SOURCES OF LEAD

Lead (Pb) is a bluish-gray metal that occurs naturally in minute amounts within the earth's crust. It has also been referred to as plumbum, lead metal, and pigment metal. The frequent use of this element in many industrial processes is the main reason for the widespread contamination (especially of soil) by lead. There are a variety of industrial processes that involve the production/use of lead, such as mining, smelting, manufacture of pesticides and fertilizers, dumping of municipal sewage, and burning of fossil fuels that contain a lead additive (leaded gasoline). Many commercial products and materials may also contain lead, including paints, ceramic glazes, television glass, ammunition, batteries, medical equipment, such as X-ray shields or fetal monitors, and electrical equipment. The applications of lead for roofing and for the production of ammunition have increased during the last 20 years. Lead battery recycling sites, of which 29 have been labeled as Superfund sites in the United States, and other manufacturers use more than 80% of the lead produced in the United States. On average, recycled lead products can satisfy only half of total U.S. lead requirements.

HEALTH EFFECTS

Lead has been listed as a potential carcinogen in the EPA Toxic Release Inventory (TRI). Inhalation and ingestion are the two main routes of exposure, whereas the health effects from both are the same. Pb accumulates in the body organs, such as the bones and the brain, which may lead to poisoning (plumbism), or even to death. The gastrointestinal tract, kidneys, and especially the central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration; children under the age of six are at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints, when exposed to lead.

CHEMISTRY OF LEAD-CONTAMINATED SOIL

The chemistry of metal interaction with the soil matrix is fundamental to the phytoremediation concept (Fig. 1). Once introduced into the soil matrix, lead is very difficult to remove due to a series of chemical reactions that are likely

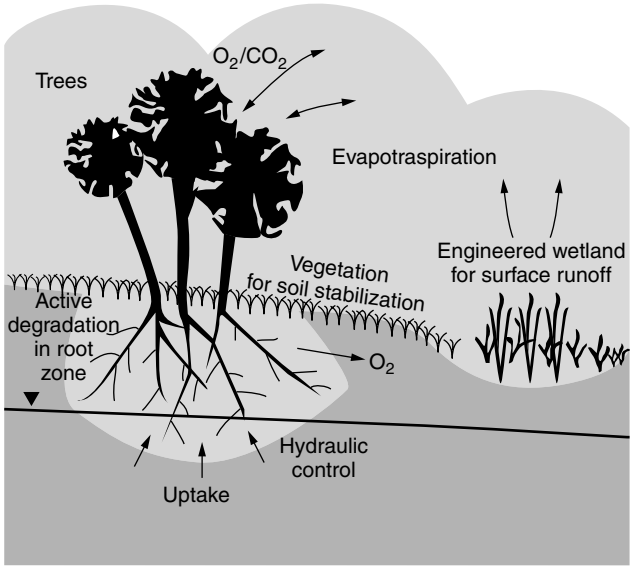


Figure 1. Plant processes that lead to environmental remediation.

to take place, such as mineralization. This transition metal resides within the upper 15–20 cm of the soil, where it is strongly bound by adsorption, ion exchange, precipitation, and complexation with existing organic matter. Lead found within the soil matrix can be classified into six general categories: ionic lead dissolved in soil water, exchangeable, carbonate, oxyhydroxide, organic, or the precipitated fraction. Sequential extractions of soil can be employed to isolate and quantify specific metallic forms, associated with different fractions (1).

The combinations of all these forms make up the total content of lead in soil. Water-soluble and exchangeable lead are the only fractions readily available for uptake by plants, whereas the oxyhydroxide, organically bound (occassionally), hydroxy carbonate, and precipitated forms of lead are the most strongly bound to the soil.

All these interactions that occur throughout the soil matrix are highly pH-dependent. The pH of soil has a significant effect on the mobility of lead from soil, as well as of other metals. The pH of soil generally ranges from 4.0–8.5. Under acidic conditions (pH values lower than 5.5), metal cations are more easily mobile, whereas anions tend to be sorbed to mineral surfaces. Metals become more available to plant roots under these conditions; however, due to the increase in toxic metal solubility, plant growth may be inhibited by phytotoxicity. The opposite occurs when the soil matrix is at an alkaline pH; anions are mobilized and cations are adsorbed to mineral surfaces or form precipitates, hence decreasing the bioavailability of metal cations and their subsequent plant uptake. The capacity of soil to bind lead increases with an increase in pH, cation exchange capacity (CEC), organic carbon content, soil/water E_h values ("mixed" redox potential), and phosphate levels (2).

Another important factor in the phytoremediation process is the presence of specific ionic species of lead, derived by respective hydrolytic reactions. Lead ions exist as Pb^{2+} at low (acidic) pH. As the pH increases (at pH values lower than 6), Pb^{2+} and $[Pb(OH)]^+$ cations are the principal species, but gradually several polynuclear species, including $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^+$, $[Pb_4(OH)_4]^{4+}$, and $[Pb_6(OH)_8]^{4+}$, form. They become abundant at even higher (alkaline) pH levels. Nevertheless, in a recent study, the existence of polynuclear species was seriously questioned; it was concluded that mononuclear complexes $Pb(OH)_q^{(2-q)+}$ (aq) (where $q = 1–4$) are the only hydrolyzed species likely to be significant under typical environmental and biological conditions (4).

The predominant insoluble lead compounds are lead phosphates, lead carbonates and hydroxy carbonates (this form exists when the pH is above 6), and lead (hydr)oxides. Lead sulfide (PbS) is the most stable solid form within the soil matrix and can be formed under reducing conditions, when increased concentrations of sulfides are present. Under anaerobic conditions, a volatile organolead compound (tetramethyl lead) can also be formed by microbial alkylation.

PROPOSED MECHANISMS FOR THE PHYTOREMEDIATION OF LEAD IN CONTAMINATED SOILS

Depending on the nature of the specific pollutant (organic or inorganic), the biology and the properties of the plant and other factors that could act synergistically, such as soil properties, it has been proposed that different mechanisms take place during phytoremediation.

Phytoextraction, rhizofiltration, and phytostabilization are the principal mechanisms that have been proposed, when the pollutants to be removed/treated are inorganic (e.g., toxic metals or radionuclides). Rhizodegradation, phytodegradation, and phytovolatilization are the main mechanisms proposed for the removal/treatment of organic pollutants, whereas the latter mechanism (phytovolatilization) has been also proposed for the removal of certain inorganic pollutants (e.g., Se, Hg, As). Hydraulic control, vegetative cover, and riparian corridors have been suggested as methods for treating inorganic or organic pollutants in contaminated soils; these methods are considered a combination of the aforementioned mechanisms, however, with certain differences that derive mainly from the way that these technologies are engineered (5).

The basic phytoremediation mechanisms, in which lead may be involved, are phytoextraction, rhizofiltration, and phytostabilization.

Phytoextraction

Phytoextraction is the uptake of contaminants by plant roots and their translocation within the plants; the contaminants are generally removed by harvesting the plants (e.g., Fig. 2 for nickel). This concentration technology leaves a much smaller mass to be disposed of than the excavation of soil (applications of *ex situ* treatment technologies), or other media. The specific technology is most often applied to metal-contaminated soil (5).

Lead hyperaccumulation by plants has not been documented in a natural setting. However, certain plants have been identified which can take up lead.

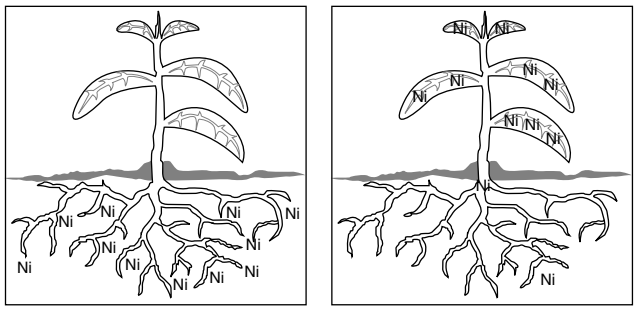

Ni
Ni
Ni

Table 1. Typical Plants and Mechanisms Used in Various Phytoremediation Applications Concerning Lead[a]

Mechanism	Media	Contaminants	Typical Plants
Phytostabilization	Soil, sediments	Metals (Pb, Cd, Zn, As, Cu, Cr, Se, U) Hydrophobic organics (PAHs, PCBs, dioxins, furans, pentachlorophenol, DDT, dieldrin)	Phreatophyte trees to transpire large amounts of water for hydraulic control Grasses with fibrous roots to stabilize soil erosion Dense root systems are needed to sorb/bind contaminants.
Phytoextraction	Soil, brownfields, sediments	Metals (Pb, Cd, Zn, Ni, Cu). Selenium (volatilization)	Sunflowers, Indian mustard, rapeseed plants, barley, hops, crucifers, serpentine plants, nettles, dandelions
Rhizofiltration	Groundwater, water and wastewater in lagoons or created wetlands	Metals (Pb, Cd, Zn, Ni, Cu) Radionuclides (^{137}Cs, ^{90}Sr, U) Hydrophobic organics	Aquatic Plants: — Emergents (bulrush, cattail, coontail, pondweed, arrowroot, duckweed) — Submergents (algae, stonewort, parrot, feather, Eurasian water milfoil, Hydrilla)

[a] References 5 and 6.

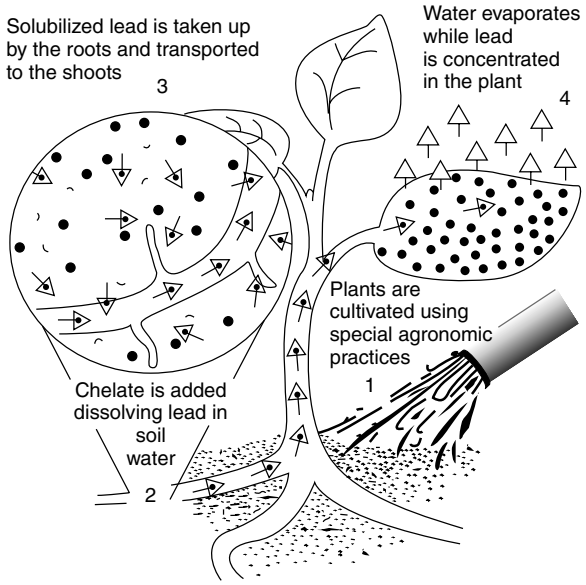


Figure 3. Enhancement of plant uptake of Pb through the use of synthetic chelates (2).

(such as EDTA) by several researchers was examined to overcome this drawback (Fig. 3).

The use of synthetic chelates in phytoremediation increases heavy metal uptake by the plants, through the increase of metal bioavailability, but also increases micronutrients availability, therefore decreasing the possibility of plant nutrient deficiencies. The goal of commercial phytoextraction is to remove or reduce the level of toxic metals within the contaminated soils (*in situ* treatment technology) to meet regulatory standards within 1 to 3 years following the application. The regulatory standard (achievement goal) for lead-contaminated soils set by the U.S. EPA is 500 mg of metal/kg of soil. Plants that can accumulate more than 1% of the target contaminant in the harvestable portion and can produce more than 20 metric tons of shoot biomass per hectare per year are usually required to achieve this goal.

Several researchers have found that this goal can be achieved by applying soil amendments and chemical chelates. Based on relevant studies, it has been shown that only 0.1% of the total amount of lead in contaminated soils exists in soluble form and, therefore, is considered bioavailable to plants for remediation. By adding synthetic chelators, the total amount of (bioavailable) lead in solution can be increased up to 100 times.

Increasing the mobility and bioavailability of lead in the soil through the application of certain chelators, organic acids, or other appropriate chemical compounds allows hyperaccumulation of metals in some plants. For lead, a number of different chelators have been tested, such as EDTA (ethylene dinitrilotetraacetic acid), CDTA (trans-1,2-cyclohexylene-dinitrilotetraacetic acid), DTPA (diethylene trinitrilopentaacetic acid), EGTA (ethylebis-[oxyethylene-trinitrilo]-tetraacetic acid), HEDTA (hydroxyethylethylene dinitrilotriacetic acid), citric acid, and malic acid. The addition of these chelates resulted in enhanced shoot lead concentrations (2). The soil additive EDTA can form hexahedral metal ion complexes with commonly found metals, such as Pb[II] or Fe[II], which can enhance their uptake by roots and translocation throughout the plant (7).

Although there are certain advantages in using synthetic chelates, environmental concerns for their impact on contaminated sites still need research. The major concern for using chelates to enhance phytoremediation and to increase the bioavailability of toxic metals, such as Pb, is the fear of lead leaching or running off into the ground or surface water, creating secondary contamination. By making the metals more soluble in the soil matrix, leaching is more probable and threatens to contaminate nearby water sources (2). The use of synthetic chelates necessitates careful mass balances to confirm that metals mobilized by chelators are not subsequently leached to groundwater.

The use of synthetic chelators (complex chemical compounds) is a questionable practice from the environmental standpoint. Natural chelators originating from plants or from microorganisms seem to be more promising. The

Table 2. Advantages and Disadvantages/Limitations of the Phytoremediation Process[a]

Advantages	Disadvantages/Limitations
Amenable to a variety of organic and inorganic compounds.	Restricted to sites with shallow contamination within rooting zone of remediative plants.
In situ/*ex situ* applications for treating contaminated soils.	May take up to several years to remediate a contaminated site.
In situ applications decrease the amount of soil disturbance, compared to conventional methods.	Restricted to sites with rather low contaminant concentrations.
Reduces the amount of waste to be landfilled (up to 95%).	Harvested plant biomass from phytoextraction may be classified as a hazardous waste.
In situ applications decrease the spread of contaminant via air and water.	Climatic conditions.
Does not require expensive equipment or highly specialized personnel.	Introduction of nonnative species may affect biodiversity.
Easy to implement and maintain.	Consumption of contaminated plant tissue is also of concern.
Low cost compared to conventional treatment methods.	
Environmentally friendly and aesthetically pleasing to the public.	

[a] Reference 2.

microbial protection of plants against phytotoxic concentrations, however, is often based on excluding heavy metals; therefore, it is uncertain whether an approach based on chemical chelators is practical for improving phytoremediation (8). Naturally secreted organic acids, such as mugenic and avenic acids, may exhibit the same mechanism (similar to EDTA) to scavenge soils for metals (7).

ADVANTAGES AND LIMITATIONS

The phytoremediation of lead involves a number of advantages and certain limitations. Both of them derive from the fact that the use of plants to treat lead-contaminated soils would affect the soil and the surrounding media; as a result, some other pollutants (e.g., other metals) might be treated as well. For this reason, the advantages and limitations of lead phytoremediation are generally regarded as similar to those found in all relevant phytoremediation applications.

The most important advantages are the low cost and the aesthetic result, which is the sight of plants. On the other hand, the most important limitations are that the biodiversity of the site might be altered and that the uptake of pollutants by the plants may change their biology (2,5,9). The specific factors that can be characterized as advantages or limitations of phytoremediation are summarized in Table 2.

CURRENT STATUS AND FUTURE TRENDS

Although the phytoremediation of lead-contaminated soils is a rather new technology, the initial results from the respective laboratory research in pilot plants as well as from field applications, can be characterized as rather promising (5). Nevertheless, a better insight that will illuminate the overall picture will be given after at least 10 years, when the field data would be adequate to help in drawing safe conclusions.

Although the research effort for already existing plants is ongoing, the use of genetic engineering for plant improvement has been proposed. However, before such plants can be used for the phytoremediation of contaminated sites, the questions that arise from these applications should be carefully answered in an appropriate time frame following extensive research.

BIBLIOGRAPHY

1. Tessier, A., Campbell, P., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**: 844–850.
2. Henry, R.J. (2000). *An Overview of The Phytoremediation of Lead and Mercury*. National Network of Environmental Management Studies (NNEMS), Washinghton, DC.
3. Baes, F.C. and Mesmer, E.R. (1976). *The Hydrolysis of Cations*. John Wiley & Sons, New York.
4. Perera, W.N., Hefter, G., and Sipos, P.M. (2001). An investigation of the lead (II)-hydroxide system. *Inorg. Chem.* **40**: 3974–3978.
5. EPA. (2000). *Introduction to Phytoremediation*. EPA Report Cincinnati, OH.
6. Schnoor, L.J. (1997). *Phytoremediation*. Technology Overview Report, TO-98-01. GWRTAC, Pittsburgh, PA.
7. Meagher, B.R. (2000). Phytoremediation of toxic elemental and organic pollutants. *Curr. Opin. Plant Biol.* **3**: 153–162.
8. Van Der Lelie, D., Schwitzguebel, J.P., Glass, D.J., and Vangronsveld, B.A. (2001). Assessing phytoremediation's progress in the United States and Europe. *Environ. Sci. Technol.* **35**: 446–452.
9. Miller, R.R. (1996). *Phytoremediation*. Technology Overview Report, TO-96-03. GWRTAC, Pittsburgh, PA.

PHYTOREMEDIATION OF METHYL *TERTIARY*-BUTYL ETHER

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(from *Phytoremediation: Transformation and Control of Contaminants*, Wiley 2003)

SUMMARY OF PRACTICAL IMPLICATIONS

The capability of plants to remediate methyl *tertiary*-butyl ether (MTBE) at contaminated sites is promising to the

point that at least one field test is underway and others anticipated. Both hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings and alfalfa (*Medicago sativa*) facilitate the removal of MTBE from saturated soil in the laboratory. The primary removal of MTBE is by soil volatilization facilitated by plant transpiration. Very little of the contaminant is metabolized or accumulated in laboratory studies. The MTBE that volatilizes and the small amount that diffuses from stems or transpires through leaves do not represent a risk in the atmosphere due to the rapid dispersion and degradation. Despite the different behavior of MTBE in groundwater, plants, and the atmosphere, concurrent phytoremediation of gasoline spills containing MTBE and other contaminants is expected to be very useful in the future.

INTRODUCTION

Methyl *tertiary*-butyl ether was first developed as a fuel oxygenate in the late 1970s to enhance the octane of gasoline and to improve air quality. In 1990, the U.S. Clean Air Act Amendments required fuel oxygenates to be added to gasoline in an effort to reduce atmospheric concentrations of carbon monoxide and ozone in some urban areas. The use of MTBE increased 16-fold from 1984 to 1993, to 24 billion pounds (approximately 10×10^6 metric tons). By 1998, MTBE was the fourth most common chemical product in the U.S. (Johnson et al. 2000). Oxygenates are added to over 30 percent of the gasoline used in the U.S., and MTBE is the most commonly used of these additives (Squillace et al., 1996). After formulation, MTBE constitutes up to 15 percent of gasoline by weight, giving rise to a daily usage of more than 10 million gallons (3.8×10^7 liters) in the U.S. (Johnson et al. 2000). However, continued use of MTBE is being questioned because of reports of adverse health effects, uncertainty about the efficacy of air pollution control, and the potential for contamination of groundwater (Anonymous 1997, Mehlman 1998). Several U.S. states have required that MTBE be phased out over time. A recent proposal was that the U.S. President use the authority under the Toxic Substances Control Act to ban MTBE across the U.S., but production continued in late 2000 at a rate of more than 11 million gallons or nearly 40 million liters per day.

As a part of the U.S. Geological Survey National Water Quality Assessment program from 1993 to 1994, 60 volatile organic compounds were analyzed for occurrence in groundwaters and surface waters. Of these 60 organic compounds, MTBE was the second most frequently detected chemical in samples of shallow groundwater from U.S. urban areas (Zogorski et al. 1998). Very little was detected in agricultural areas or deep groundwater wells. Surveys have reported finding MTBE in 5 to 10 percent of U.S. potable groundwater supplies (Stuckey 2000). Based on current distribution of MTBE sources and well pumping rates, Johnson et al. (2000) assessed the likelihood that more wells will become contaminated by MTBE. Although new and much more extensive databases are needed, the projected number of U.S. wells likely to experience contamination is in the thousands due to a large fraction of all community water supply wells lying within 1 kilometer of leaking underground storage tanks.

Methyl *tertiary*-butyl ether contamination of soil and groundwater can be separated into two categories: point sources, such as leaking underground storage tanks, and nonpoint sources, including infiltration and diffusion from urban air into shallow groundwater. General urban air contamination arises from fugitive emissions at gasoline stations and from gasoline-powered engines. Point sources are typically known quantifiable oxygenated gasoline spills onto the ground or leaks from underground storage tanks. Contamination by MTBE commonly occurs in conjunction with BTEX gasoline constituents (benzene, toluene, ethyl benzene, and xylenes). Gasoline from leaking underground storage tanks is the most frequent source of significant groundwater pollution with as much as one million gallons (approximately 4 million liters) of gasoline released into the ground each year (Hartley and Englande 1992), implying MTBE releases of hundreds of tons. It is estimated that out of three million underground storage tanks in use in the U.S., as many as 500,000 may be leaking petroleum into the ground (Hartley and Englande 1992). Actual leakage may be much higher than this implied level of 2 gallons per tank per year (8 liters per tank per year).

Properties of Methyl Tertiary-Butyl Ether

Methyl *tertiary*-butyl ether is an aliphatic ether with a molecular weight of 88.15 grams per mole (Fig. 1) (Squillace et al. 1997). This compound is volatile, colorless, and flammable (Caprino and Togna 1998). Because chemical structure influences many of the properties such as solubility, volatilization potential, and resistance to microbial degradation, it is useful to compare the physical and chemical properties of MTBE with those of the BTEX compounds with which it usually occurs in the environment (Table 1).

There is good evidence for microbial degradation of MTBE by several processes, as well as field data showing natural attenuation. Several processes for MTBE have been identified.

Anaerobic Microbial Transformation

Mormile et al. (1994) tested both pure and mixed cultures to anaerobically degrade MTBE. Two acetogens, *Acetobacterium woodii* and *Eubacterium limosum*, known to degrade phenyl methyl ethers, showed to MTBE transformation. However, the microbial cells consumed other gaseous substrates from the headspace of the incubation system and produced formate and acetate with no apparent toxicity caused by MTBE (Mormile et al. 1994). The capability of mixed cultures to anaerobically transform MTBE and *tertiary*-butyl alcohol was investigated under denitrifying and methanogenic conditions, with rates of transformation increasing with nutrients added (Yeh and Novak 1994). Methyl *tertiary*-butyl ether was shown to degrade in the soil taken from only one site out of three and only when nutrients were added. The degradation rates were much slower than those of the *tertiary*-butyl alcohol and complete degradation took

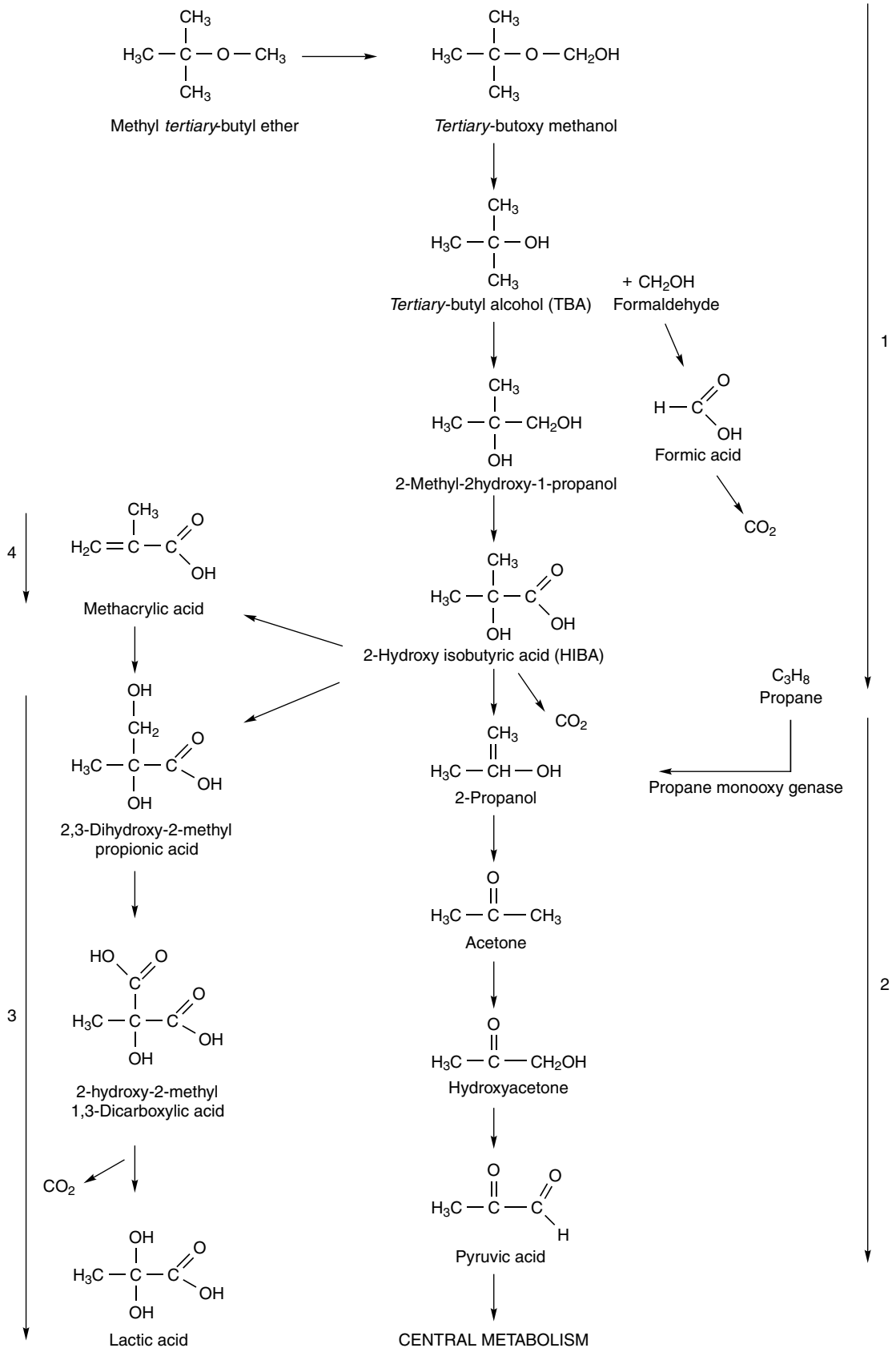


Figure 1. Methyl *tertiary*-butyl ether degradation pathway proposed by the investigation of propane oxidizing bacteria. Adapted from Steffan et al. (1997).

Table 1. Chemical and Physical Properties of Gasoline, Methyl *Tertiary*-Butyl Ether, Benzene, and Toluene

Property	Gasoline	Methyl *tertiary*-butyl ether	Benzene	Toluene
Molecular weight, grams per mole	≈100	88.15	78.11	92.13
Specific gravity	0.72	0.744	0.88	0.8669
	0.74	0.7404 to 0.7578	0.8765	
Boiling temperature, °C		53.6 to 55.2	80.1	110.6
Water solubility, milligrams per liter	100 to 200	43 000 to 54 300	1780	534.8
			1791	
Vapor pressure at 25 °C, millimeters mercury		245 to 251	95.19	28.4
Log K_{ow}		1.20	2.13	2.73
		0.94 to 1.30	1.56 to 2.15	2.11 to 2.80
Henry's law constant, atmospheres-cubic meters per gram mole		5.87×10^{-4}	5.43×10^{-3}	5.94×10^{-3}
		1.4×10^{-3}		
		3×10^{-3}		
		5.28×10^{-4}		
Dimensionless Henry's law constant (milligrams per liter of air) per (milligrams per liter of water)		0.0240	0.222	0.243
		0.0572		
		0.123		
		0.0216		
		mean: 0.0564		
Log K_{oc}		1.05	1.1 to 2.5	1.56 to 2.25
		$K_{oc} \approx 11$ cubic centimeters per gram	median = 1.9	
			$K_{oc} \approx 80$ cubic centimeters per gram	

K_{ow} is the dimensionless octanol–water partitioning coefficient.
K_{oc} is organic carbon normalized sorption coefficient.
Log is the base 10 logarithm.
Note: One atmosphere is 1.0133×10^{-5} pascals in the Henry's law constant and 1 millimeter of mercury of vapor pressure is 133.32 pascals. Adapted from Squillace et al. (1997) and references cited therein.

approximately 270 days. More recently Landmeyer et al. (1998) and Finneran and Lovley (2001) observed anaerobic degradation of MTBE under Fe(III) reducing conditions and Bradley et al. (2001) observed MTBE biodegradation under nitrate-reducing conditions

Aerobic Transformation in Mixed Cultures

Aerobic microbial transformation of MTBE was first successfully shown by Salanitro et al. (1994) using a mixed culture isolated from the sludge of an industrial chemical biotreatment operation. This culture, consisting of organisms from *Corynebacterium, Pseudomonades*, and *Achromobacters* was able to utilize MTBE at 2 milligrams per liter as a sole carbon source although none of the organisms were shown to grow alone on MTBE. Approximately 80 percent of the [^{14}C]-MTBE was mineralized to $^{14}CO_2$ or incorporated into new microbial cells after an incubation period of approximately 8 hours (Salanitro et al. 1994). *Tertiary*-butyl alcohol was observed as an intermediate. With 20 milligrams of MTBE per liter, little or no [^{14}C]-MTBE was metabolized to $^{14}CO_2$ or cellular material, suggesting that MTBE may be inhibitory to aerobes at high concentrations (Salanitro et al. 1994).

A consortium of aerobes from refinery activated sludge was also effective in transforming MTBE (Cowan and Park 1996), as was an aquifer consortium studied by Borden et al. (1997). Bradley et al. (1999) and Landmeyer et al. (2001) observed rapid metabolism of [^{14}C]-labeled MTBE using naturally occurring streambed microorganisms under mixed aerobic and anaerobic conditions in microcosms. Eweis et al. (1998) examined a compost-based biofilter microbial community and found MTBE degradation.

Aerobic Cometabolism

A fungus of the genus *Graphium* has been shown capable of cometabolizing MTBE with butane (Hardison et al. 1997), and Garnier et al. (1999) observed cometabolism with pentane by *Pseudomonas*. Steffan et al. (1997) reported indigenous propane-oxidizing bacteria isolated from contaminated and uncontaminated soils that could degrade MTBE. Isolate ENV425 that degrades MTBE was identified by fatty acid analysis to be most closely related to members of the genus *Nocardia*. All isolates were first grown with propane, then fed concentrations of MTBE in the range of 20 to 100 milligrams per liter, which was used as a sole carbon and energy source (Steffan et al. 1997). The cells were fed 20 milligrams per liter metabolized MTBE at a rate of at least 3.8 nanomoles per minute per milligram of cells without a significant lag period. Complete degradation occurred after approximately 4 hours, with *tertiary*-butyl alcohol accumulating nearly stoichiometrically, and with evolution of $^{14}CO_2$ from the methyl group. The microorganisms were capable of transforming *tertiary*-butyl alcohol at a rate of 1.8 nanomoles per minute per milligram of cells, about half that of

MTBE. Following 10 hours of transformation of *tertiary*-butyl alcohol, approximately 70 percent of the radiolabeled compound was still present in solution, suggesting the formation of water-soluble *tertiary*-butyl alcohol metabolites. Continued incubation showed 60 percent conversion to $^{14}CO_2$ after 24 hours and greater than 90 percent conversion after several days (Steffan et al. 1997). Figure 1 is a pathway for MTBE degradation proposed by Steffan et al. (1997).

Aerobic Transformation in Pure Cultures Lacking Other Substrates and Prior Induction

Four pure cultures of diverse genera have been shown capable of transforming at least a fraction of MTBE in a defined medium (Mo et al. 1997). The three strains investigated by Mo et al. (1997) represented *Methylobacterium, Rhodococcus*, and *Arthrobacter*. Also, a proteobacteria strain was derived from the biofilter examined by Eweis et al. (1998).

Potential Biotreatments for Methyl Tertiary-Butyl Ether

Salanitro et al. (2000) have successfully used bioaugmentation and oxygenation with a consortium designated MC-100 to enhance degradation of MTBE within an aquifer. Landmeyer et al. (2001) successfully used oxygenation only to enhance biodegradation of an MTBE-contaminated aquifer. Successful treatment was achieved in laboratory studies through cometabolism in an upflow fluidized-bed bioreactor (Stringfellow and Oh 2002) and in a vapor phase treatment using a trickling filter (Fortin and Deshusses 1999). In the latter case, contaminated soil from two different locations was used as an inoculum. Prince (2000) has reviewed most of the earlier literature on microbial MTBE degradation. Despite several instances of successful metabolism, MTBE appears to transform only slowly under typical field spill conditions, resulting in a need for additional cost-effective treatment methods.

A potentially useful alternative is phytoremediation. Plants have the benefit of absorbing large quantities of subsurface water by solar driven pumping (transpiration) and the roots support diverse microbial populations (Shimp et al. 1993, Davis et al. 1998a, Narayanan et al. 1999). Deep-rooted poplar (*Populus* spp.) trees have been studied in several contexts but there is little information on the capability to transpire or metabolize MTBE. Davis et al. (1998b) showed by use of Fourier transformed infrared spectroscopy that MTBE passes freely through hybrid poplars (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') in 1- to 2-day experiments although no effort was made to determine metabolic processes that might occur within the plant. Landmeyer et al. (2000) detected MTBE in cores of trees above a gasoline-contaminated aquifer but no effort was made to track the movement through the trees.

Rubin and Ramaswami (2001) have also investigated the uptake and phytoremediation of MTBE using hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34', & IC) cuttings. They reported transpiration of MTBE through plants with no evidence of MTBE transformation in the poplar (*Populus* spp.) saplings (Ramaswami and Rubin 2001).

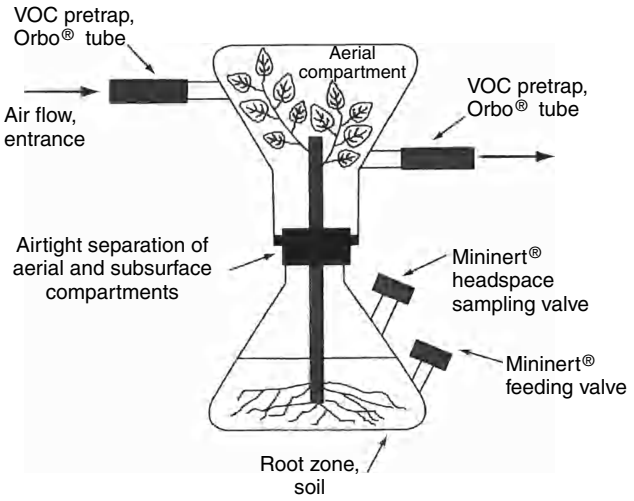


Figure 2. Schematic of the reactor design used to investigate hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings growing in soil.

UPTAKE OF METHYL TERTIARY-BUTYL ETHER BY HYBRID POPULUS IN HYDROPONIC SOLUTION

Experimental Setup

To determine the potential for hybrid poplars (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') to take up, metabolize, and translocate MTBE, a hydroponic experiment was performed, measuring the capability of hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings to remove [^{14}C]-MTBE from aqueous solution. Uptake of [^{14}C]-radiolabeled MTBE by hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings was investigated in a manner similar to methods pioneered by Burken (1993) and Burken and Schnoor (1996). A schematic of the reactor design is provided in Fig. 2. However, in the first experiment, there was no attempt made to collect gases volatilizing from plant leaves. The study included varying concentrations of MTBE in solution to determine any toxic response. Hydroponic studies used one-quarter-strength Hoagland's inorganic nutrient solution, fed to the root zone of batch reactors containing hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings. Eight-inch (200-millimeter) long cuttings (0.75 to 1 inches or 19 to 25 millimeters in diameter) were affixed with pre-drilled screw caps and pre-drilled Teflon®-lined septa. Teflon® tape was wrapped around the stem and acrylic caulk was used to seal the caps and septa to the cutting. Hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings were first rooted in hydroponic solution until a vascular root system appeared, then placed in 1-liter bioreactors containing 400 milliliters of nutrient solution. The bioreactors consisted of a 1-liter Erlenmeyer flask modified by attaching a sampling port to the bottom and top of each flask. The cuttings were maintained in a laboratory growth chamber at 28 °C under artificial grow lights that provided a photon flux at the leaf surface of 100 to 160 micromoles of photons per square meter per second, the full photosynthetically active range.

Controls were included in triplicate to distinguish the uptake of MTBE by hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings from losses out of the system. First, a capped control with only nutrient solution and [^{14}C]-MTBE was included to determine the contribution of bio-degradation possibly occurring inside the hydroponic solution and sorption to the glass. To determine loss of compound through leaks in the system, controls were used with solid glass rods in place of a tree cutting. Finally, two sets of planted cuttings were cut off just above the cap to create decapitated controls, which were necessary to observe the effect of an excised tree on [^{14}C]-MTBE removals. Two sizes of cuttings were used; the first was approximately the same diameter as the glass rod and the second was similar to the intact tree reactors.

After being sealed, all reactors were spiked with a combination of [^{14}C]-radiolabeled MTBE ("hot," *i.e.*, radioactive), 6 microcuries per reactor, and pure MTBE ("cold," *i.e.*, nonradioactive) to a total aqueous concentration of 10.18 milligrams per liter, (creating a cold:hot MTBE ratio of 12 037:1). Concentrations of cold MTBE were then increased to 100, 1000, and 10 000 milligrams per liter. Reactors were prepared for all concentrations in triplicate. Samples were collected daily to monitor the disappearance of [^{14}C]-MTBE from hydroponic solution. Transpiration was measured gravimetrically each day, and replacement nutrient solution was added through the lower Mininert® port. Prior to adding nutrient solution, all headspace gas surrounding the root system was removed through a series of traps to capture any MTBE that was present in the headspace above the hydroponic solution. The air was pumped out through an activated carbon trap capturing pure compound and other organic metabolites (Orbo® tube 32, large, Supelco), and a trap that allowed air to bubble through 1 molar sodium hydroxide (NaOH) to capture any carbon dioxide (CO_2). To extract the trapped MTBE, the activated carbon was placed into 4-milliliter glass vials and submerged in 2 milliliters of methanol (Fisher) for 24 to 48 hours. Samples of 100 microliters were taken and injected into 15 milliliters of Scintiverse® for counting on a liquid scintillation counter. One milliliter samples were taken from the sodium hydroxide (NaOH) in the carbon dioxide (CO_2) traps and injected into an Ultima Gold scintillation cocktail (Packard) for scintillation counting.

After 10 days, total [^{14}C]-uptake was quantified in the roots, lower stem, upper stem, leaves, and petioles of the hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings *via* oxidation to $^{14}CO_2$ in a R.J. Harvey Bio-Oxidizer, and subsequently by scintillation counting. Oxidation efficiency was determined to be 92 percent and was calibrated with pre- and post-analysis efficiency testing.

Results from Hydroponic Solutions

Based on recorded observations of visual symptoms, biomass, and transpiration rate, MTBE was found not toxic to hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings at concentrations as high as 1000 milligrams of MTBE per liter. However, the trees dosed with 10 000 milligrams of MTBE per liter died after only a few days. Transpiration rate correlated well with biomass measurements and was a good measure of growth and vitality. Hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings were healthy and grew well in all experiments at concentrations as high as 1000 milligrams of MTBE per liter.

Figure 3 displays removal of [^{14}C]-MTBE from solution by the full and excised cuttings as well as the controls. The data for the full ($n = 5$) and excised ($n = 3$) cuttings are shown as an average with the error bars representing one standard deviation. Uptake of MTBE occurred immediately in all planted reactors and continued throughout the investigation. For the five planted reactors, 66.98 ± 6.09 percent of the total MTBE was removed from hydroponic solution at the end of the 10-day experiment.

Methyl *tertiary*-butyl ether removal after 10 days for the excised cuttings was 42.97 ± 3.32 percent. The data from the toxicity portion of the experiment yielded a comparable result for the cuttings dosed with 10 000 milligrams per liter—51.52 ± 2.29 percent was removed from solution after 11 days. The removal rate was similar for the excised cuttings ($k = 0.060 \pm 0.002$ per day and the correlation coefficient $r^2 = 0.994$), and for the cuttings that died at 10 000 milligrams of MTBE per liter ($k = 0.067$ per day) as evidenced by the first order rate coefficients. The reproducibility of the removal rates and percent removed from solution are a strong indication that the cause is attributable to movement of MTBE through the dead stem as opposed to leaks from the enclosed system. Excised cuttings are apparently capable of volatilizing MTBE (and very little water) from solution to the atmosphere.

After 10 days, the experiment was terminated and the cuttings were sacrificed. The various components were bio-oxidized and the radioactivity measured with the liquid scintillation counter to determine the amount of radiolabeled compound in the plant tissue. Figure 4

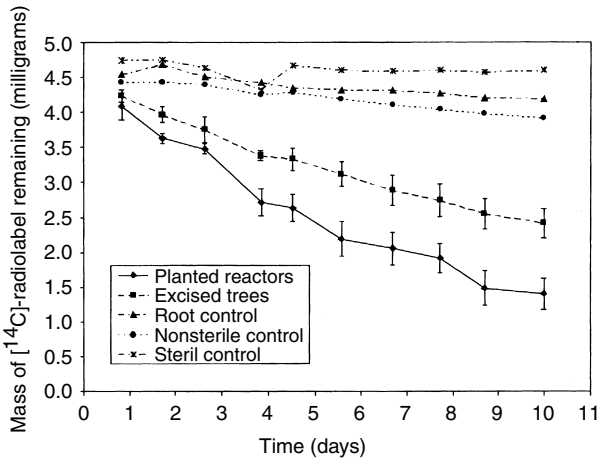


Figure 3. Hydroponic experiment with hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings: mass of methyl *tertiary*-butyl ether remaining in aqueous solution as determined by liquid scintillation counting. At time = 0, 4.3 milligrams of methyl *tertiary*-butyl ether was added for an initial concentration of 10.2 milligrams per liter in solution. Error bars on the data for full trees ($n = 5$) and excised trees ($n = 3$) represent one standard deviation.

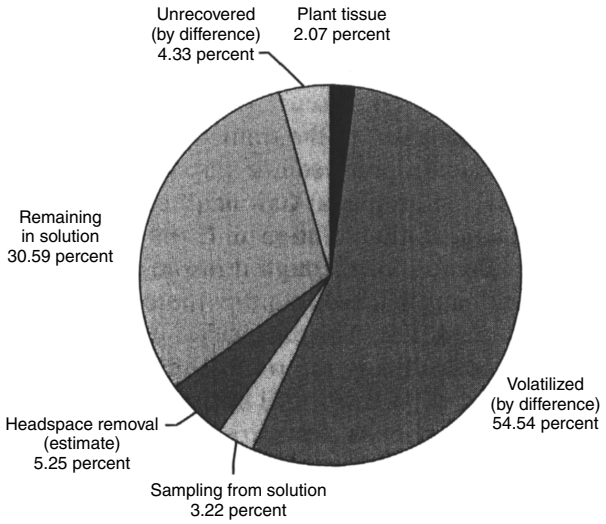


Figure 4. Hydroponic experiment: graph depicting [^{14}C]-radiolabel distribution and recovery results for the reactors containing hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings as determined by liquid scintillation counting at the termination of the 10-day investigation. Results are given as a percent of the total [^{14}C]-MTBE initial spike (6 microcuries) added to reactors at time = 0. The amount of radiolabel that was reported as volatilized was determined as the difference in the amount remaining in solution at the termination of the experiment between the unsterilized and planted reactors. The amount reported as unrecovered was the difference between the unsterilized and sterile reactors.

summarizes the radiolabel recoveries for the full cutting and displays the overall mass balance. The amount of MTBE volatilized through plants was found to be 54.5 percent. This was estimated by the difference in the amount of radiolabel remaining in solution between the planted cuttings and the sterile controls. This estimate assumes that any removal from the excised tree reactors was due to uptake and not to leaks (Winnike 1998). However, leaks of MTBE through the septums and seals can be substantial, and leaks have been shown to rival transpiration of MTBE through leaves in such experiments (Hong et al. 2001).

The average [^{14}C]-radiolabel remaining in solution was 33.02 ± 6.09 percent. This is approximately twice as much as that found in the toxicity investigations in the same reactors at the same concentration. This value was expected to be similar due to the similar experimental conditions and duration. The reason for this difference lies in the relationship between cumulative transpiration and uptake of MTBE. A comparison of average transpiration rates shows that the cuttings in the toxicity experiment transpired more (32.3 ± 11.24 milliliters per day) than the cuttings in the hydroponic experiment (26.5 ± 10.0 milliliters per day). Because the leafy portion was exposed to the atmosphere, the amount of radiolabeled MTBE transpired through the leaves was not measured directly.

UPTAKE EFFICIENCY AND TOXICITY

Methyl *tertiary*-butyl ether was taken up by the plants and translocated up the vascular system of the plant in the transpiration stream. The efficiency of uptake of MTBE from hydroponic solution by hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings was estimated by the change in MTBE mass in the solution and the volume fraction of water transpired each day. Because of the high transpiration rates of all cuttings, it was necessary to add nutrient solution to the reactors daily, diluting the initial concentration of MTBE. This resulted in a continual decrease in concentration and mass of MTBE in the root compartment. For chemicals that are readily taken up and not transformed in the roots, the efficiency of uptake is identical to the dimensionless transpiration stream concentration factor (*TSCF*). The *TSCF* is defined as the chemical concentration in the xylem water divided by the chemical concentration in the external solution (Briggs et al. 1982). The TSCF was estimated to be in the range of 0.5 to 0.8 for MTBE for hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings based on

$$U = (TSCF)\ (C)\ (T) \tag{1}$$

in which U is the rate of mass uptake (milligrams per day), C is the concentration in solution (milligrams per milliliter), and T is the rate of transpiration (milliliters per day). The concentrations used to estimate *TSCF* were based on initial experimental concentrations of 10, 100, and 1000 milligrams per liter. The *TSCF* value was not calculated for the toxic concentration of 10 000 milligrams per liter.

UPTAKE OF METHYL TERTIARY-BUTYL ETHER BY HYBRID POPULUS PLANTED IN SOIL

Experimental Setup

To assess the capability of hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings to remove MTBE from soil, an Iowa agricultural silt-loam soil (Nodeway-Ely series) was taken from an uncontaminated field site with a fraction organic matter of 0.025 (Burken 1993). The soil was air-dried, pulverized, and passed through a 2-millimeter sieve. The cuttings were allowed to root hydroponically for 2 weeks until a full vascular root system developed. Four cuttings were transplanted to individual reactors containing 500 grams of air-dried soil, and 180 milliliters of nutrient solution was added intermittently to the flask to achieve uniform soil moisture content (Fig. 2). The reactors were initially at 100 percent saturation and acclimated for 7 days. During this time, the trees transpired and the soil-water saturation level was reduced 70 to 90 percent.

After this acclimation, the leafy portion of the cutting was enclosed by attaching an inverted 1-liter Erlenmeyer flask modified with an inlet port for air flow near the top and an outlet near the bottom. The perimeter of the open end was sealed with acrylic caulk to fit snugly around the screw cap. Parafilm® tape was used to seal this joint, and a Mininert® valve was placed on the top sampling port of the bottom flask to create a fully encapsulated system. Reactors were treated with doses of 3.95 milligrams of

cold MTBE and 7.1 microcuries of [^{14}C]-MTBE mixed with the feed water (resulting in a ratio of cold:hot MTBE of 10 069:1). Air was purified and pumped through the aerial portion of the reactor at 1.0 to 3.0 liters per minute. The air inlet and outlet ports of the Erlenmeyer flask were fitted with activated carbon traps to capture [^{14}C] transpired through the plants (two traps were used in series on the outlet port to ensure capture). The scrubbed air then passed through traps to capture any $^{14}CO_2$ that was mineralized by soil microorganisms or by the plant in the aerial portion of the reactor.

Results with Hybrid Populus in Soil

The primary goal of this test was to quantify volatilization of [^{14}C]-MTBE from leaf tissue. By enclosing the leafy portion of the cutting, a total mass balance was achieved. The total recovery was lower than expected (67.4 ± 6.3 percent). However, this test provided valuable information with regard to the major pathways for MTBE removal. The unrecovered portion seemed to be partially the result of leaks from the enclosed reactor vessel (Fig. 2). The four planted cuttings remained healthy throughout the test, which was terminated after 33 days because the leaves grew too large and were pressing into the sides of the aerial compartment. The longer duration of this experiment (compared to the prior experiment in hydroponic solution) was possible because of slower growth of the cuttings in the soil. Transpiration was monitored by gravimetric analysis.

The rate of transpiration varied widely throughout the test because of excess humidity in the aerial compartment. As humidity increased to high levels, transpiration decreased dramatically due to aerodynamic resistance. In addition, the average transpiration rates for all reactors were significantly lower than under hydroponic conditions as a result of the decreased water availability in the soil. Although [^{14}C]-MTBE uptake was not quantified daily, the fluctuation in transpiration rates very likely influenced the rate of MTBE uptake from the soil water. The full set of transpiration data is provided in Winnike (1998).

Radiolabel recoveries on a percent mass basis are presented in Fig. 5. Because only liquid scintillation counting was utilized, it was uncertain whether the radiolabel recovered was [^{14}C]-MTBE or a [^{14}C]-metabolite. Only a small percentage of the initial [^{14}C]-radiolabel remained in the soil (4.75 ± 1.76 percent), indicating that 33 days were adequate to remove a majority of the MTBE from the soil. In subsequent tests, the vast majority of the radiolabel exists as parent compound, MTBE, in hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') tissues.

The [^{14}C]-radiolabel that was transpired constituted the most significant flux of MTBE movement (55.55 ± 1.85 percent). Assumedly the recovered radiolabel from the activated carbon traps was [^{14}C]-MTBE. Subsequent analyses in the laboratory indicated that MTBE was predominant over other potential metabolites such as *tertiary*-butyl alcohol. The air also bubbled through a sodium hydroxide (NaOH) trap to capture $^{14}CO_2$ from the mineralization of MTBE. A small percent of the initial MTBE input was recovered as $^{14}CO_2$ (1.62 ± 0.63 percent), which indicates that either hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings or microorganisms in the soil were able to mineralize a portion of the MTBE to carbon dioxide (CO_2).

The headspace in the root compartment was sampled and analyzed for both [^{14}C] and $^{14}CO_2$ prior to watering and at the end of the test. This amount was shown to be fairly significant with recoveries of 0.63 ± 0.55 percent and 2.03 ± 1.85 percent for [^{14}C] and $^{14}CO_2$, respectively. The observed range of 0.41 to 4.50 percent demonstrates the high variability in $^{14}CO_2$ recovery. The amount of [^{14}C] remaining in plant tissue was approximately 3 percent. On the basis of total plant mass, the leaves contained 14.72 ± 4.02 milligrams of MTBE per kilogram, the petioles 11.10 ± 3.86 milligrams of MTBE per kilogram, and roots ± 3.76 milligrams of MTBE per kilogram. The leaves contained the largest total percentage (34.27 ± 9.55 percent) and the roots accounted for the smallest (11.14 ± 2.12 percent).

CHANNEL TESTS WITH ALFALFA

Tests were carried out in a 6-channel system (Zhang et al. 1998). Table 2 provides information on the experimental system and the tests that were conducted. The results are described fully elsewhere (Zhang et al. 1998, Zhang 1999, Zhang et al. 1999, 2000, 2001). Table 3 and Fig. 6 show that vegetation affects the upward movement of MTBE from the saturated zone to the soil surface. Channel 4 has a much smaller fraction of MTBE and water moving to the soil surface. The recovery of MTBE was larger for Channel 4, which was barren of vegetation and unseeded with microbial cultures capable of biodegrading MTBE. As shown in Table 3, the measured loss of MTBE to the atmosphere at the soil surface was much greater than that which entered the plant and then passed into the atmosphere. The fraction of water that was lost as vapor to the atmosphere was considerably larger than the measured fraction of MTBE that entered the atmosphere (Zhang et al. 1999). The total recoveries of MTBE in the vegetated channels were less than 100 percent for all of the tests. The incomplete recovery of MTBE was probably due to enhanced rhizosphere biodegradation in the soil. Microcosm experiments with soils from the channel system were conducted, and a disappearance rate for MTBE of up to 5 milligrams per kilogram of soil per day was observed.

The water transpired daily by the plants increased from the time the alfalfa (*Medicago sativa*) was cut until the next harvest as shown in Fig. 7. The transpiration rate was on average 5 millimeters per day (0.5 cubic centimeter per square centimeter per day) at the end of July 1999. This value was in agreement with predicted transpiration rates (Davis et al. 1998a). Figure 8 provides information on the concentration of MTBE in the plant water as a function of plant height. Experiments conducted with plant stems show that MTBE diffuses through the stem surface into the atmosphere (Zhang et al. 2001). The estimated values of the diffusivity for MTBE range from 8×10^{-8} to 8×10^{-7} square centimeters per second for alfalfa (*Medicago sativa*) plant stems (Zhang et al. 2001).

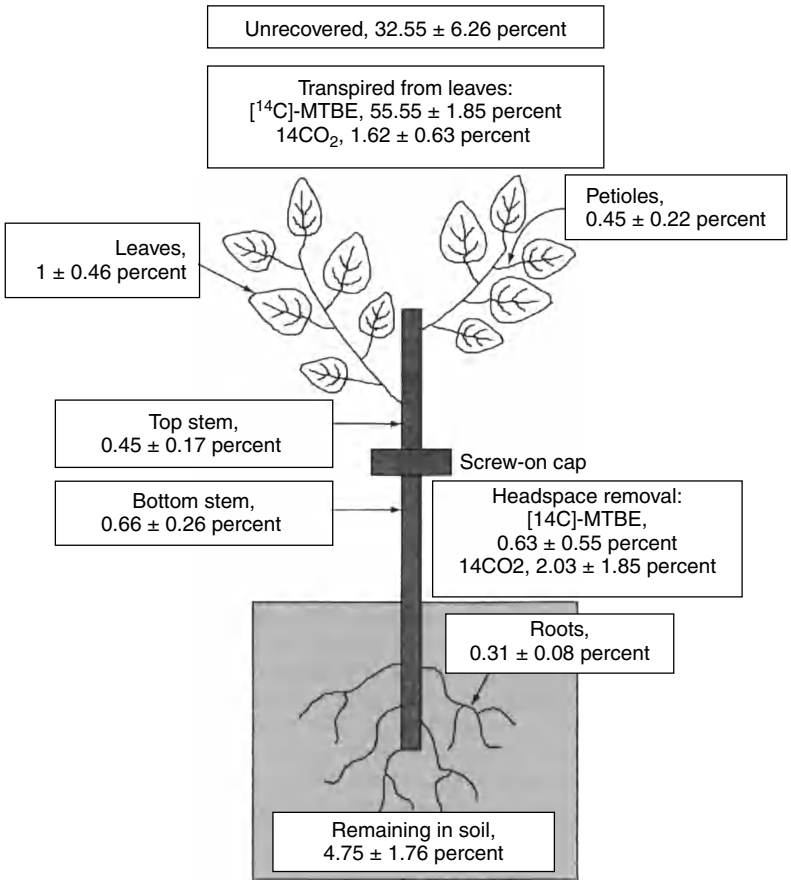


Figure 5. Schematic and mass balance of methyl *tertiary*-butyl ether uptake by hybrid poplars (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') in soil reactor.

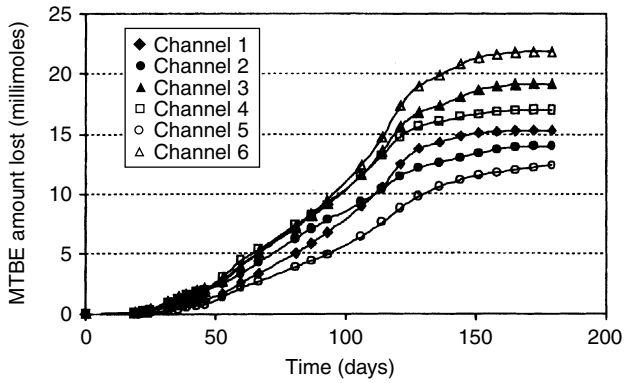


Figure 6. Cumulative loss of methyl *tertiary*-butyl ether to the atmosphere through the soil surface for each of six channels. Tests conducted from June 30 to December 25, 1998.

Table 2. Experimental Conditions and Treatments in Each Channel for the Six-Channel Experimental System

	Planted with 10 alfalfa (*Medicago*) *sativa* plants	Air sparged at 0.24 liter per channel per day	Additional bacteria (2 liters of suspension added on June 20, 1998)
Channel 1	Yes	Yes	#33 (*Rhodococcus*)
Channel 2	Yes	No	#33 (*Rhodococcus*)
Channel 3	Yes	No	No
Channel 4	No	No	No
Channel 5	Yes	No	#41 (*Arthrobacter*)
Channel 6	Yes	Yes	#41 (*Arthrobacter*)

Note: Channel dimensions were 1.1 meters long, 0.65 meter deep, and 0.10 meter wide. The soil was alluvial silty sand soil (with less than 10 percent silt) collected near a landfill in Riley County, Kansas. The system was illuminated with 12 cool white fluorescent lights (40 watts) at a height of 0.50 meter above the soil; light intensity was approximately 160 micromoles of photons or microeinsteins per square meter per second. The channels were fed with an MTBE-water solution of 0.84 millimole per liter at 1 per day from June 30, 1998 to September 20, 1998 (83-day duration). Distilled water was fed from September 21 to December 25, 1998 (96-day duration) and the channels fed with an MTBE-water solution of 0.84 millimole per liter at 1 per day from Feb. 6, 1999 until the data in Figs 7 and 8 were collected during the summer of 1999. Strain #33 (*Rhodococcus*) and Strain #41 (*Arthrobacter*) were obtained from C.F. Kulpa (Mo et al. 1997, Zhang et al. 1999).

FATE OF METHYL TERTIARY-BUTYL ETHER IN THE ATMOSPHERE

Site-specific determinations are necessary to ensure that the amount of MTBE transferred to the atmosphere does not exceed air quality standards. This analysis takes into account the total amount of compound volatized per unit time and the mixing zones in the atmosphere. This can be compared to the large quantities of MTBE introduced into the atmosphere because of gasoline pumping at refueling stations and engine operation. The MTBE introduced to the atmosphere caused by phytoremediation is significantly less.

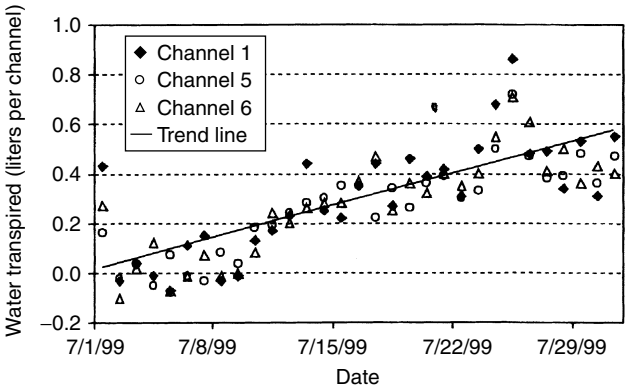


Figure 7. Water transpired daily by alfalfa (*Medicago sativa*) in three channels during July 1999; plants were cut back to 60 millimeters on July 1.

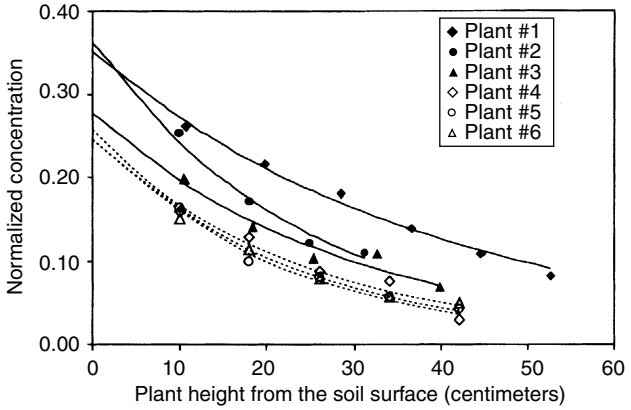


Figure 8. Methyl *tertiary*-butyl ether dimensionless concentration in plant water as a function of alfalfa (*Medicago sativa*) stem position from the soil surface. Dimensionless feed concentration of methyl *tertiary*-butyl ether is 1 which corresponds to 0.84 millimoles per liter.

The MTBE released to the atmosphere is rapidly dissipated. The published information on the degradation half-life of MTBE in the atmosphere indicates that MTBE readily degrades chemically because of the hydroxyl radicals (OH^-) present. Squillace et al. (1997) have reviewed the fate of MTBE in the atmosphere and report that the half-life of MTBE can be as short as 3 days at 25 °C.

The following method to estimate the concentration of MTBE being released through vegetation is based on mass balance considerations. If the MTBE flows upward into the unsaturated zone together with the water drawn up by transpiration, the air required to hold the associated water vapor is the critical control volume. For example, consider the case in which there is 88 milligrams of MTBE per liter in the groundwater, and the water and MTBE move into the atmosphere together at 25 °C where the vapor pressure of water is 3173 pascals (23.8 millimeters of mercury) or a mole fraction of 0.0313 at saturation in air with 1×10^5 pascals (1 atmosphere) pressure. A liter of water contains 55.6 gram moles which requires 43,434 liters of air to dissolve the water under saturation conditions at 25 °C and 1×10^5 pascals (1 atmosphere) of pressure. The 88 milligrams of MTBE per liter is 1 millimole per liter in water, but only $0.001/1776 = 0.56$ parts per million by volume in air. Thus, the concentration of MTBE in air is diluted because of the water vapor dissipation process that partially controls the rate of evapotranspiration. Because (1) MTBE concentrations in groundwater are often much smaller than 88 milligrams per liter, (2) the air is usually not saturated with water vapor, and (3) the ambient air contains some water vapor, the values of MTBE in the atmosphere as a result of phytoremediation are very small. This is especially true compared to values at a refueling station where MTBE vapors in equilibrium with the liquid fuel may be as high as 50,000 parts per million by volume.

FIELD STUDIES

The basic processes observed at the laboratory scale (*i.e.*, biodegradation, volatilization, and transpiration), also take place at a field scale. Salanitro et al. (2000) observed aerobic biodegradation in the field with and without bioaugmentation using MTBE-degrading microorganisms. Wilson et al. (2000) reported biodegradation under anaerobic conditions. Hong et al. (2001) demonstrated the beneficial contributions of vegetation with respect to plume control. Landmeyer et al. (2000) reported the uptake of MTBE into vegetation.

Phytoremediation is an effective technology for remediation of fuel-contaminated sites as shown elsewhere in this book. Based on the results of laboratory and field studies reviewed in this chapter, vegetation increases the rate of evapotranspiration and the upward movement of MTBE into the unsaturated zone and the atmosphere. The beneficial effects of vegetation for MTBE are similar to those for BTEX compounds in fuel-contaminated soils; however, MTBE tends to persist longer in the atmosphere compared to BTEX compounds because MTBE is more resistant to photochemical degradation. Furthermore, MTBE is more mobile in soil and groundwater, and MTBE is not degraded readily in the root zone. Where these different properties of BTEX and MTBE are taken into account, simultaneous phytoremediation of shallow groundwater plumes from fuel spills should be feasible at many sites (see Weaver et al. this book).

CONCLUSIONS

Methyl *tertiary*-butyl ether is a compound of concern because of possible carcinogenic effects, persistence in soil and groundwater, and potential resistance to degradation by microorganisms. The widespread occurrence of this compound in groundwater is relatively recent, and conventional treatment is either ineffective or expensive. Phytoremediation provides an inexpensive, esthetically pleasing, and effective alternative for treating numerous organic contaminants. These investigations show that hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings and alfalfa (*Medicago sativa*) are capable of cleaning up water and soil contaminated with MTBE. Specific conclusions are as follows:

- Hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings tolerate concentrations of MTBE of at least 1000 milligrams per liter. The concentrations observed in the environment near a source of MTBE contamination can be as high as 200 milligrams per liter and hybrid poplars (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') could effectively take up MTBE at this concentration without apparent toxic effects.
- Small hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings are effective at removing MTBE from hydroponic solution. Tests demonstrated that cuttings dosed with 10, 100, and 1000 milligrams per liter were able to achieve an MTBE removal of 30.6 percent remaining in solution within 10 days from 400-milliliter reactors.
- Small hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings and alfalfa (*Medicago sativa*) are effective at removing MTBE from soil. Hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') cuttings removed 95.2 ± 1.8 percent within 33 days when MTBE was initially at a soil water concentration of 22 milligrams per liter (soil concentration of 7 milligrams per kilogram). The evapotranspiration rate and amount of MTBE volatilized are considerably larger in alfalfa (*Medicago sativa*) vegetated soil compared to soil without vegetation. The evapotranspiration rate is small after alfalfa (*Medicago sativa*) plants are cut back; the rate increases nearly linearly with time as the plants increase in size over 29 days.
- The primary removal mechanism for MTBE was volatilization into the soil gas and atmosphere. When soil volatilization was not possible, significant amounts also transpired through hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') leaves and stem. Shown to move with water into the plant (*TSCF* of 0.5 to 0.8), MTBE also volatilized through the stem of excised small hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') plants and alfalfa (*Medicago sativa*) stems. Removal occurred at a slower rate than for actively transpiring hybrid poplar (*Populus deltoides* × *Populus nigra* 'DN34' 'Imperial Carolina') and alfalfa (*Medicago sativa*) plants. However, the volatilization is typically expected to be very small, especially compared to the MTBE volatilized at gasoline refueling stations. The small amount of MTBE that does volatilize into the atmosphere disperses and degrades photochemically with a half-life on the order of days.

This research provides evidence that phytoremediation could be a potential alternative for the remediation of MTBE contaminated sites.

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READING LIST

Anonymous (1997). Fueling the debate. *Environ. Health Persp.* **105**(10): 1042–1043.

Borden, R.C., Daniel, R.A., LeBrun, L.E., and Davis, C.W. (1997). Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. *Water Resour. Res.* **33**: 1105–1115.

Bradley, P.M., Landmeyer, J.E., and Chappelle, F.H. (1999). Aerobic mineralization of MTBE and *tertiary*-butyl alcohol by streambed microorganisms. *Environ. Sci. Technol.* **33**: 1877–1879.

Bradley, P.M., Chapelle, F.H., and Landmeyer, J.E. (2001). Methyl *t*-butyl ether mineralization in surface-water sediment microcosms under denitrifying conditions. *Appl. Environ. Microbiol.* **67**(4): 1975–1978.

Briggs, G.G., Bromilow, R.H., and Evans, A.A. (1982). Relationships between lipophicity and root uptake and translocation of non-ionized chemicals by barley. *Pestic. Sci.* **13**: 495–504.

Burken, J.G. (1993). *Vegatative uptake by Populus spp. and mineralization of atrazine in variable soil types*. Masters thesis. University of Iowa, Iowa City.

Burken, J.G. and Schnoor, J.L. (1996). Phytoremediation: plant uptake of atrazine and role of root exudates. *J. Environ. Eng.* **122**(11): 958–963.

Caprino, L. and Togna, G.I. (1998). Potential health effects of gasoline and its constituents: a review of current literature (1990–1997) on toxicological data. *Environ. Health Persp.* **106**(3): 115–125.

Cowan, R.M. and Park, K. (1996). Biodegradation of the gasoline oxygenates MTBE, ETBE, TAME, TBE and TAA by aerobic mixed cultures. *Hazard. Ind. Wastes* **28**: 523–530.

Davis, L.C., Banks, M.K., Schwab, A.P., Narayanan, M., Tracy, L.E. Erickson, and J.C., (1998a). Plant-based remediation. In: *Bioremediation: Principles and Practice. Vol. 2, Biodegradation Technology Developments*. S.K. Sikdar and R.L. Irvine (Eds.). Technomic, Lancaster, Pennsylvania, pp. 183–219.

Davis, L.C., Vanderhoof, S., Dana, J., Selk, K., Smith, K., Goplen, B., and Erickson, L.E. (1998b). Movement of chlorinated solvents and other volatile organics through plants monitored by Fourier transform infrared (FT-IR) spectrometry. *J. Hazard. Sub. Res.* 4–1: 1–26.

Eweis, J.B., Schroeder, E.D., Chang, D.P.Y., and Scow, K.M. (1998). Biodegradation of MTBE in a pilot-scale biofilter. In: *Natural Attenuation: Chlorinated and Recalcitrant Compounds*. G.B. Wickramanayake and R.E. Hinchee (Eds.). Battelle Press, Columbus, Ohio, pp. 341–346.

Finneran, K.T. and Lovley, D.R. (2001). Anaerobic degradation of methyl *tert*-butyl ether (MTBE) and *tert*-butyl ether (TBE). *Environ. Sci. Technol.* **35**: 1785–1797.

Fortin, N.Y. and Deshusses, M.A. (1999). Treatment of methyl *tert*-butyl ether vapors in biotrickling filters. 1. reactor startup, steady-state performance and culture characteristics. *Environ. Sci. Technol.* **33**: 2980–2986.

Garnier, P.M., Auria, R., Auger, C., and Revah, S. (1999). Cometabolic biodegradation of methyl *t*-butyl ether by *Pseudomonas aeruginosa* grown on pentane. *Appl. Microbiol. Biotechnol.* **51**(4): 498–503.

Gomez, M.M., Abernathy, C.O., and Du, J.T. (1997). *Drinking water health advisory for methyl tertiary-butyl ether*. American Chemical Society Division of Environmental Chemistry Preprints of Papers, Washington, DC, pp. 370–372.

Hardison, L.K., Curry, S.S., Ciuffetti, L.M., and Hyman, M.R. (1997). Metabolism of diethyl ether and cometabolism of methyl *tert*-butyl ether by a filamentous fungus, a *Graphium* sp. *Appl. Environ. Microbiol.* **63**: 3059–3067.

Hartley, W.R. and Englande, A.J., Jr. (1992). Health risk assessment of the migration of unleaded gasoline—a model for petroleum products. *Water Sci. Technol.* **25**: 65–73.

Hong, M.S., Farmayan, W.F., Dortch, I.J., Chiang, C.Y., Schnoor, S.K., and McMillan, J.L. (2001). Phytoremediation of MTBE from a groundwater plume. *Environ. Sci. Technol.* **35**: 1231–1239.

Johnson, R., Pankow, J., Bender, D., Price, C., and Zogorski, J. (2000). MTBE: To what extent will past releases contaminate community water supply wells. *Environ. Sci. Technol.* **34**: A210–A217.

Landmeyer, J.E., Chapelle, F.H., Bradley, R.M., Pankow, J.F., Church, C.D., and Tratnyek, P.G., (1998). Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993–1998). *Ground Water Mon. Rem.* **18**: 93–102.

Landmeyer, J.E., Vroblesky, D.A., and Bradley, P.M. (2000). MTBE and BTEX in trees above gasoline-contaminated ground water. In: *Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds*. G.B. Wickramanayake, A.R. Gavaskar, J.T. Gibbs and J.L. Means (Eds.). Battelle Press, Columbus, Ohio, pp. 17–24.

Landmeyer, J.E., Chapelle, F.H., Herlong, H.E., and Bradley, P.M. (2001). Methyl *tert*-butyl ether biodegradation by indigenous aquifer microorganisms under natural and artificial oxic conditions. *Environ. Sci. Technol.* **35**: 1118–1126.

Mehlman, M.A. (1998). Editorial: pollution by gasoline containing hazardous methyl *tertiary*-butyl ether (MTBE). *Arch. Environ. Health* **53**(4): 245–246.

Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, X., and Kulpa, C.F. (1997). Biodegradation of methyl *t*-butyl ether by pure bacterial cultures. *Appl. Microbiol. Biotechnol.* **47**: 67–72.

Mormile, M.R., Liu, S., and Suflita, J.M. (1994). Anaerobic biodegradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions. *Environ. Sci. Technol.* **28**: 1727–1732.

Narayanan, M., Erickson, L.E., and Davis, L.C. (1999). Simple plant-based design strategies for volatile organic pollutants. *Environ. Progress* **18**: 231–242.

Prince, R.C. (2000). Biodegradation of methyl *tertiary*-butyl ether (MTBE) and other fuel oxygenates. *Crit. Rev. Microbiol.* **26**: 163–178.

Ramaswami, A. and Rubin, E. (2001). Measuring phytoremediation parameters for volatile organic compounds: focus on MTBE. *Pract. Periodical Hazard. Toxic Radioact. Waste Manag.* **5**: 123–129.

Rubin, E. and Ramaswami, A. (2001). The potential for phytoremediation of MTBE. *Water Res.* **35**: 1348–1353.

Salanitro, J.P., Diaz, L.A., Williams, M.P., and Wisniewski, H.L. (1994). Isolation of a bacterial culture that degrades methyl *t*-butyl ether. *Appl. Environ. Microbiol.* **60**: 2593–2596.

Salanitro, J.P., Johnson, P.C., Spinnler, G.E., Maner, P.M., Bruce, H.L. Wisniewski, and C. (2000). Field-scale demonstration through aquifer bioaugmentation and oxygenation. *Environ. Sci. Technol.* **34**: 4152–4162.

Schnoor, J.L., Licht, L.A., McCutcheon, S.C., Wolfe, N.L., and Carreira, L.H. (1995). Phytoremediation of organic and nutrient contaminants. *Environ. Sci. Technol.* **29**(7): 318–323.

Shimp, J.F., Tracy, J.C., Davis, L.C., Lee, E., Huang, W., Schnoor, L.E. Erickson, and J.L. (1993). Beneficial effects of plants in the remediation of soil and groundwater contaminated with organic materials. *Crit. Rev. Environ. Sci. Technol.* **23**(1): 41–77.

Squillace, P.J., Zogorski, J.S., Wilber, W.G., and Price, C.V. (1996). Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993–1994. *Environ. Sci. Technol.* **30**: 1721–1730.

Squillace, P.J., Pankow, J.F., Korte, N.E., and Zogorski, J.S. (1997). Review of the environmental behavior and fate of methyl *tert*-butyl ether. *Environ. Toxicol. Chem.* **16**(9): 1836–1844.

Steffan, R.J., McClay, K., Vainberg, S., Condee, C.W., and Zhang, D. (1997). Biodegradation of the gasoline oxygenates methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *tert*-amyl methyl ether by propane-oxidizing bacteria. *Appl. Environ. Microbiol.* **63**: 4216–4222.

Stringfellow, W.T. and Oh, K.C. (2002). Initiation of MTBE biotreatment in fluidized-bed bioreactors. *J. Environ. Eng.* **128**(9): 852–861.

Stuckey, H.T. (2000). The benefits and problems associated with MTBE. *Environ. Protect.* **11**(7): 49–52.

Wilson, J.T., Cho, J.S., Wilson, B.H., and Vardy, J.A. (2000). *Natural attenuation of MTBE in the subsurface under methanogenic conditions*. EPA/600/R-00/006. National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. (http://www.epa.gov/ORD/NRMRL/mtbe/MTBEreport.pdf).

Winnike, S.K. (1998). *Phytoremediation of methyl tert-butyl ether (MTBE) by hybrid poplar trees*. Masters thesis. University of Iowa, Iowa City.

Yeh, C.K. and Novak, J.T. (1994). Anaerobic biodegradation of gasoline oxygenates in soils. *Water Environ. Res.* **66**: 752–774.

Zhang, Q. (1999). *Phytoremediation of methyl tert-butyl ether (MTBE) in groundwater–experimental and modeling studies*. Ph.D. dissertation. Kansas State University, Manhattan, Kansas.

Zhang, Q., Davis, L.C., and Erickson, L.E. (1998). Using vegetation to treat methyl *tert*-butyl ether contaminated groundwater. In: *Proceedings of the 1998 Conference on Hazardous Waste Research–Bridging Gaps in Technology and Culture*. U.S. Environmental Protection Agency Hazardous Substance Research Center: Great Plains/Rocky Mountains, Kansas State University, Manhattan, Kansas. Held in Snowbird, Utah, May 18–21. pp. 262–272 (http://www.engg.ksu.edu/HSRC).

Zhang, Q., Davis, L.C., and Erickson, L.E. (1999). An experimental study of phytoremediation of methyl *tert*-butyl ether (MTBE) in groundwater. *J. Hazard. Sub. Res.* **2**: 4–1 to 4–19. (http://www.engg.ksu.edu/HSRC).

Zhang, Q., Davis, L.C., and Erickson, L.E. (2000). Plant uptake of methyl *tert*-butyl ether (MTBE) from groundwater. In: *Environmental and Pipeline Engineering 2000*. R.Y. Surampalli (Ed.). American Society of Civil Engineers, Reston, Virginia, pp. 166–173.

Zhang, Q., Davis, L.C., and Erickson, L.E. (2001). Transport of methyl *tert*-butyl ether (MTBE) through alfalfa plants. *Environ. Sci. Technol.* **35**: 725–731.

Zogorski, J.S., Delzer, G.C., Bender, D.A., Squillace, P.J., Baehr, T.J. Lopes, A.L., Stackelberg, P.E., Landmeyer, J.E., Lico, C.J. Boughton, M.S., Pankow, J.F., Johnson, R.L., and

N.R. Thomson (1998). MTBE: summary of findings and research by the U.S. Geological Survey. In: *1998 Annual Conference of the American Water Works Association*, Denver, Colorado.

PHYTOREMEDIATION OF SELENIUM-LADEN SOILS

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Selenium (Se) is a naturally occurring metalloid that is toxic at high concentrations but is also a nutritionally essential element. In the 1980s, Se-contaminated water at the natural wildlife refuge at Kesterson Reservoir, California was responsible for widespread reproductive failure, developmental defects, and death in migratory aquatic birds and fish. The environmental and health impacts of this incident have resulted in extensive research on the behavior of Se in soils and plants. The cost of using conventional remediation technologies for cleaning up Se-contaminated soils is very high, so recent research has focused on phytoremediation of Se from contaminated soils. Selenium accumulation by plants and its subsequent volatilization are very effective in remediating Se-contaminated soil and water. Natural hyperaccumulator plants such as *Astragalus* growing in seleniferous soils accumulate high concentrations of Se in their tissues. However, the main drawback of using these plants for phytoremediation is their slow growth rate and low biomass. This has prompted researchers to investigate the possibility of developing genetically engineered plants with better Se phytoextracting capacity. Understanding the speciation and bioavailability of Se in soils and the biochemistry of Se in plants and microorganisms is the first step toward developing effective phytoremediation strategies for Se-laden soils.

INTRODUCTION

Selenium is a naturally occurring metalloid, essential for animals, humans, and microorganisms in trace amounts (1). It provides protection against diseases such as liver necrosis, muscular dystrophy, Keshan disease, infertility, and white muscle in livestock (2). At higher doses, it is toxic to animals and humans. The concentration range of Se from trace element requirement to lethality is very narrow. The minimal nutritional requirement for animals is about 0.05–0.10 mg Se/kg dry forage feed, but to 2–5 mg Se/kg dry forage is toxic (3). A chronic form of Se poisoning in livestock is 'alkali disease' caused by ingestion of plants containing high concentrations of Se. Excess Se in diet causes birth defects and sterility in animals; loss of hair, teeth, nail, fatigue; and even death in humans (4).

Selenium is found primarily in sedimentary rock formations in drier areas of the world. It is chemically very similar to sulfur (S); it has five valence states; selenide (2−), elemental selenium (0), thioselenate (2+), selenite (4+), and selenate (6+) (5). Environmental speciation of Se depends on redox conditions and pH; selenate is the major species in aerobic and neutral to alkaline environments, but selenide and elemental Se dominate under anaerobic conditions. Selenium complexes with metals and nonmetals, forming both organic and inorganic compounds (3). Interest in Se has grown during the past couple of decades, primarily due to the Kesterson Reservoir controversy in the 1980s. Selenium-contaminated water at the natural wildlife refuge at Kesterson Reservoir, California, was responsible for reproductive failure, developmental defects, and death in migratory aquatic birds (6) and fish (7). Scientists, regulators, politicians, and the general U.S. public became aware of the dangers of Se contamination as a result of this incident. Selenium toxicity is encountered in several arid and semiarid regions of the world that have seleniferous, alkaline soils derived from weathering of seleniferous rocks and shales. Se leaching from these soils is accelerated by irrigation, and it accumulates in high concentrations in drainage water, mainly as selenate. Selenium is also released into the environment by various industries such as oil refineries and electrical utilities (3).

Conventional remediation technologies for cleaning up Se-contaminated soils depend on physicochemical and electrochemical approaches, which are often prohibitively expensive. Moreover, these methods produce hazardous by-products, which must be transported to landfills, thereby adding to the remediation cost. Phytoremediation is the use of plants to extract, accumulate, and volatilize Se (8). It offers a cheaper, safer, and environmentally friendly solution for cleaning up Se-contaminated soils. This article provides an overview of the various sources of Se contamination, factors affecting Se bioavailability in soils, Se biochemistry and the mechanism of Se accumulation in plants, and future directions in the improvement of phytoremediation through biotechnology.

SOURCES OF SELENIUM CONTAMINATION

Selenium contamination in the environment arises from both natural and anthropogenic sources. Soils that are derived from shale rocks contain high concentrations of Se. As a result of irrigation, Se is leached into the subsurface drainage water and is eventually channeled into evaporation ponds. Evaporation and continual drainage into these ponds, builds up the amount of bioavailable Se to very high concentrations, which can be very damaging to wildlife, which was first demonstrated by the environmental disaster at the Kesterson Reservoir in California (9). Selenium-contaminated irrigation drainage water represents one of the most serious problems confronting agriculture in the western United States and other parts of the world whose geological and environmental conditions are similar (9).

Anthropogenic Se contamination develops from aqueous discharges of electrical power plants, coal ash leachates, oil refinery effluents, and other industrial wastewater (4). Selenium is widely used in electronics, photography, and in the production of steel, glass, ceramics, pigments, paints, pharmaceuticals, rubber, fungicides, and insecticides (10).

Of the 1430 hazardous waste sites on the United States Environmental Protection Agency's National Priorities List, at least 376 have measurable levels of Se (11).

SELENIUM IN SOILS

Most uncontaminated soils contain 0.10 to 2 ppm of total Se (12). Excessive amounts of Se is present only in the semiarid and arid regions of the world in soils derived from cretaceous shales. However, total Se in soils is not a reliable index of the actual amount available to plants. Normal soils contain <50 ppb of water-soluble Se. The chemical form of Se in soils largely determines its mobility and bioavailability to plants and animals. Selenium species in soil solution can be present primarily in three oxidation states; selenates, selenites, and selenides (12). In the oxidized alkaline soils of western San Joaquin Valley, California, selenate is the dominant soluble species constituting 98% of the soluble Se, but selenites and organic Se species are also present. The solubility and mobility of Se in soils depend on processes such as adsorption, precipitation, and transformation, which in turn depend on the chemical species of Se, pH, and redox conditions. Several studies have shown that selenite is sorbed onto soil to a much greater extent than selenate (13), which makes it less bioavailable than selenate. Selenate generally adsorbs weakly onto clays, iron oxides, and other soil phases at neutral to alkaline pH. The low solubility of Se in acid or neutral soils can be attributed to its occurrence as selenite in combination with ferric iron as ferric selenite. In soils containing reactive ferric oxides, ferric selenite–ferric hydroxide adsorption complexes are formed. Oxidation of selenite to selenate in alkaline soils is favored by a decrease in the stability of ferric hydroxide–selenite complexes (12). Oxyanions such as NO_3^- can facilitate the oxidation of Se, resulting in high levels of soluble selenate in drainage effluents from agricultural lands.

The three major mechanisms of Se transformation in soil are: oxidation–reduction, methylation–demethylation, and volatilization. Oxidation leads to mobilization, and reduction results in immobilization of Se. Methylation and volatilization lead to the loss of Se from the soil. A number of microorganisms are capable of forming volatile, alkylated Se compounds from inorganic forms of Se, which are less toxic. Dimethylselenide (DMSe) is the major metabolite of Se volatilization, although other products such as dimethyldiselenide (DMDSe), methaneselenone, methaneselenol, and dimethylselenide sulfide may also be produced (14).

SELENIUM IN PLANTS

Plant Uptake and Transport

Selenium is taken up from soils by plants primarily as selenate or selenite. Selenate is accumulated in plant cells against its likely electrochemical potential gradient through a process of active transport (3). Selenate competes directly with sulfate for uptake, indicating that both anions are taken up by the sulfate transporter protein in the root plasma membrane. Kinetic and expression studies have indicated that sulfate transporters belong to two main classes, transporters that have either high or low affinity for sulfate. The high-affinity transporter is the primary transporter involved in sulfate uptake and is expressed mainly in the roots. The low-affinity transporter is expressed both in roots and shoots and may be involved in intercellular transport of sulfate (3). Unlike selenate, there is no evidence that the uptake of selenite is mediated by membrane transporters. Selenate is taken up by the sulfate transporter, so sulfate salinity drastically inhibits plant uptake of selenate (15).

Plant Assimilation and Volatilization

After uptake, it is believed that selenate is transported to chloroplasts, where it is processed by the S assimilation pathway (1). Selenate is activated by ATP sulfurylase enzyme, forming adenosine 5′-phosphoselenate (APSe), which is a major rate-limiting step for selenate assimilation in plants. APSe is then reduced to selenite by adenosine 5′-phosphosulfate (APS) reductase, which in turn is nonenzymatically reduced to selenide by glutathione. Selenocysteine is synthesized from O-acetyl serine and selenide by cysteine synthase enzyme (1). Selenoamino acids, such as selenocysteine and selenomethionine, are nonspecifically incorporated into proteins, thereby leading to Se toxicity (3). Selenomethionine can be converted to DMSe and then volatilized. Recently, Se volatilization by plants has received attention as a possible method of phytoremediation of Se-contaminated soils.

Selenium Hyperaccumulators and Nonaccumulators

Plants differ in their ability to accumulate Se in their tissues. Certain plants can hyperaccumulate Se in their shoots when grown in seleniferous soils. Such plants, called Se hyperaccumulators, include a number of species such as *Astragalus, Stanleya, Morinda, Neptunia, Oonopsis*, and *Xylorhiza* (3). They can accumulate several hundreds to several thousands of milligrams of Se/kg dry weight in their tissues, whereas nonaccumulators contain less than 25 mg Se/kg dry weight. Secondary Se accumulators include plants such as Indian mustard and canola, which can accumulate several hundred milligrams of Se/kg tissue when grown in soils contaminated with moderate levels of Se.

The pathway for the assimilation of inorganic forms of Se to selenocysteine in Se accumulators, it is believed, is the same as for nonaccumulators (3). The main difference between Se accumulators and nonaccumulators is that accumulators metabolize selenocysteine into various nonprotein selenoamino acids. The best characterized Se accumulator is *Astragalus bisulcatus*. In this plant, selenocysteine is methylated to methylselenocysteine, which prevents its nonspecific incorporation into proteins and helps to confer Se tolerance (16).

PHYTOREMEDIATION

Phytoremediation is the use of plants to remove, contain, or render harmless certain environmental pollutants (4).

It offers a cheaper, safer, and environmentally friendly solution for cleaning up Se-contaminated areas. Plants can be used in conjunction with microbial activity to extract, accumulate, and volatilize Se (8). There are several different types of phytoremediation, which can be classified as

- Phytoextraction, which uses the ability of certain plants to take up contaminants from soil and water and accumulate them in their tissues. Such tissues can then be harvested and removed from the site. Phytoextraction is facilitated by hyperaccumulator plants that grow naturally on heavy metal and metalloid-rich soils (17). Several plant species have been evaluated for their efficiency in phytoremediation, particularly certain species of *Astragalus* (18). However, these are slow growing plants, and the Se accumulated can be leached back into the soil from the leaves by rainfall (3). Another disadvantage of phytoextraction is that the accumulated Se in plant tissues could become available to animals and birds.
- Phytostabilization, which uses plants to immobilize contaminants chemically and physically at the site, thereby preventing their movement to surrounding areas (19).
- Phytofiltration, which takes advantage of the ability of plant roots to absorb or adsorb environmental contaminants, mostly metals, from water and waste streams.
- Phytodetoxification, which involves the ability of plants to change the chemical species of the contaminant to a less toxic form. For example, plants can take up toxic hexavalent chromium and convert it to nontoxic trivalent chromium (15).
- Phytovolatilization, which uses plants and their associated microbes to metabolize certain contaminants to volatile forms, which are removed from the environment. For Se, phytovolatilization is an innovative and potentially effective remediation technology for several reasons.
  1. Volatilization minimizes the production of Se-laden plant material, thereby reducing the risk that contaminants move into the local food chain.
  2. DMSe, the major component of volatile Se resulting from phytovolatilization, is 600 times less toxic than selenate or selenite (20).

The ideal plant species for phytoremediation is one that can accumulate and volatilize large amounts of Se, grow rapidly, produce a large biomass in Se-contaminated soil, tolerate salinity and other toxic environmental conditions, and provide a safe source of forage for Se-deficient livestock (3). Indian mustard (*Brassica juncea*) has most of these preferred characteristics (21). These plants can also be genetically engineered to improve their Se-remediation capacity. Pilon-Smits et al. (22) were able to overexpress the gene encoding ATP sulfurylase in Indian mustard, which resulted in transgenic plants that accumulated two- to three-fold more Se per plant compared to wild-type plants.

GENETIC ENGINEERING TO ADVANCE SELENIUM PHYTOREMEDIATION

Phytoremediation by genetically unaltered plant species is limited by both environmental and biological factors. Hyperaccumulators can accumulate high concentrations of Se in their tissues, but phytoremediation using hyperaccumulators is often very slow due to their slow growth rate and low biomass (23). These limitations can be overcome by conventional plant breeding techniques, but developing accumulators that have suitable characteristics may take decades. Genetic engineering has the potential to produce accumulators with suitable traits for phytoremediation within a short time (4). Genetic engineering could be used to create plants that are more tolerant to contaminants, have greater efficiency in extracting pollutants, or have greater capacity for accumulating and detoxifying pollutants.

Manipulation of the Sulfate Assimilation Pathway

The most popular genetic engineering strategy is to overexpress appropriate genes in suitable plants by inserting extra copies of coding DNA under the control of constitutive or inducible promoter elements. Overexpression of genes involved in rate-limiting steps of Se assimilation and volatilization pathways should enhance such processes in transgenic plants (4), which requires thorough understanding of the mechanisms of Se uptake and metabolism in plants. Plants metabolize Se through the S assimilation pathway, so overexpressing various genes in this pathway is likely to result in increased assimilation and volatilization of Se in transgenic plants. For example, overexpression of sulfate transporter genes could greatly increase plant uptake of Se. Overexpression of ATP sulfurylase gene (coding for ATP sulfurylase protein constituting the rate-limiting step in the S and Se assimilation pathway) or overexpressing the methionine S-methyltransferase gene (coding for the first enzyme in the biochemical pathway resulting in the formation of DMSe, the major volatile form of Se produced by plants) could result in enhanced phytoremediation capacity in transgenic plants. Transformation of Indian mustard with a gene encoding ATP sulfurylase from *Arabidopsis* under the control of a constitutive promoter resulted in higher levels of ATP sulfurylase activity and increased Se accumulation in these plants (22).

Introduction of Genes from Selenium Hyperaccumulators

A second strategy is to introduce additional metabolic pathways into the plant by overexpressing unique genes from Se hyperaccumulator plants. Hyperaccumulators have a unique ability to reduce the toxic effects of Se by depleting the intracellular concentrations of selenocysteine and selenomethionine, which disrupt plant metabolism when incorporated into enzyme proteins. In hyperaccumulators, the levels of selenocysteine and selenomethionine are reduced by the presence of metabolic pathways that lead to the accumulation of Se in nonprotein amino acids (4). Neuhierl and Boeck (24) purified a methyl transferase enzyme from *A. bisulcatus*, which specifically methylated selenocysteine. When the gene encoding the *A.*

bisulcatus methyl transferase was transferred to *E. coli*, the bacteria had increased Se tolerance and reduced incorporation of Se into protein (25).

Introduction of Microbial Genes

Microbes are also likely to provide a new library of genes capable of conferring Se tolerance and phytoremediation capacity on plants. Overexpression of microbial genes has been successfully used in the past to increase heavy metal tolerance in plants (4). Identification and use of these genes to transform plants can enhance the capacity of plants for uptake, detoxification, and volatilization of Se.

Overexpressing Transcription Factors

Overexpression of ATP sulfurylase that catalyzes the rate-limiting step in the Se assimilation pathway results in increased accumulation of Se (22). Many other genes in the S/Se assimilation pathway could be similarly overexpressed, or a similar effect could be achieved by overexpressing a single transcription factor responsible for activating a number of coregulated genes (4). In the Se assimilation pathway, the expression of three genes, ATP sulfurylase, sulfate permease, and APS reductase are regulated similarly (4). It is possible that a common transcription factor can be used to modulate the expression of these genes, resulting in increased Se assimilation in plants.

SUMMARY AND FUTURE DIRECTIONS

The consequences of elevated Se accumulation at the Kesterson Reservoir National Wildlife Refuge in California fueled extensive research on the behavior of Se in soils and plants. Conventional remediation technologies for cleaning up Se-contaminated soils are often prohibitively expensive. On the other hand, Se accumulation and volatilization by plants have been effective in remediating Se-contaminated soil and water (26,27). Selenium volatilization is a particularly attractive option because toxic inorganic Se is converted to a volatile gas DMSe, which is about 600 times less toxic than inorganic Se. Although a number of Se hyperaccumulators are known, their slow growth rate and low biomass make them less than satisfactory for phytoremediation. To enhance the Se remediation potential of plants, understanding the speciation and bioavailability of Se in soils and the biochemistry of Se assimilation and volatilization in plants and microorganisms is of paramount importance.

Recent molecular studies have revealed numerous details of Se physiology and biochemistry in plants. Overexpression of genes encoding transporters and enzymes involved in the uptake, assimilation, and volatilization of sulfate has been highly successful in elucidating the role of these proteins in Se metabolism. Identification of the rate-limiting steps in the Se assimilation pathway will aid in enhancing the phytoremediation capacity of plants by genetic engineering. The role of rhizosphere bacteria in Se volatilization by plants also needs to be further elucidated, because it is well known that plants volatilize relatively low amounts of Se in the absence of bacteria. Primary Se accumulators are a potential source of genetic material that could be used to alter Se metabolism in economically important plants, but secondary accumulators, such as Indian mustard, which are fast growing and have high biomass can also be genetically engineered to improve their phytoremediation capacity.

Disposal of Se-containing vegetation is another problem that needs further study. Se is an essential trace element in humans and animals, so one solution is to use seleniferous plant materials as a forage blend in Se-deficient regions. Plants used for phytoremediation of Se may also be used to generate useful by-products such as fibers for the production of paper and building materials and energy for heat production.

BIBLIOGRAPHY

1. Ellis, D.R. and Salt, D.E. (2003). Plants, selenium and human health. *Curr. Opin. Plant Biol.* **6**: 273–279.
2. Navarro-Alarcon, M. and Lopez-Martinez, M.C. (2000). Essentiality of selenium in the human body: Relationship with different diseases. *Sci. Total Environ.* **249**: 347–371.
3. Terry, N., Zayed, A.M., de Souza, M.P., and Tarun, A.S. (2000). Selenium in plants. *Annu. Rev. Plant Physiol. Plant. Mol. Biol.* **51**: 401–432.
4. Berken, A., Mulholland, M.M., LeDuc, D.L., and Terry, N. (2002). Genetic engineering of plants to enhance selenium phytoremediation. *Crit. Rev. Plant Sci.* **21**: 567–582.
5. Frankenberger, W.T., Jr. and Engberg, R.A. (Eds.). (1998). *Environmental Chemistry of Selenium*. Marcel Dekker, New York.
6. Ohlendorf, H.M., Hoffman, D.J., Salki, M.K., and Aldrich, T.W. (1986). Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium from irrigation drain water. *Sci. Total Environ.* **52**: 49–63.
7. Saiki, M.K. and Lowe, T.P. (1987). Selenium in aquatic organisms from subsurface agricultural drainage water, San Joaquin Valley, California. *Arch. Environ. Contam. Toxicol.* **19**: 496–499.
8. Banuelos, G.S. (2000). Factors influencing field phytoremediation of selenium-laden soils. In: *Phytoremediation of Contaminated Soil and Water*. N. Terry and G.S. Banuelos (Eds.). Lewis, Boca Raton, FL, pp. 41–59.
9. Ohlendorf, H.M., Hothem, R.L., Aldrich, T.W., and Krynitsky, A.J. (1987). Selenium contamination of the grasslands. A major California, USA, waterfowl area. *Sci. Total Environ.* **66**: 169–184.
10. Kerr, J.A. (1998). Selenium. In: *The Electronic Encyclopedia* (TM). Academic American Encyclopedia on CD-ROM, Grolier Electronic, Danbury, CT.
11. Agency for Toxic Substances and Disease Registry. (1996). *Toxicological Profile of Selenium*. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.
12. Adriano, D.C. (1986). *Trace Elements in Terrestrial Environments*, 2nd Edn. Springer-Verlag, New York.
13. Gissel-Nielsen, G., Gupta, U.C., Lamand, M., and Westermarck, T. (1984). Selenium in soils and plants and its importance in livestock and human nutrition. *Adv. Agron.* **37**: 397–460.
14. Thompson-Eagle, E.T. and Frankenberger, W.T. (1992). Bioremediation of soils contaminated with selenium. In: *Advanced Soil Science*. R. Lal and B.A. Stewart (Eds.).

Soil Restoration Series, 17, Springer-Verlag, New York, pp. 261–310.

15. Zayed, A.M., Lytle, C.M., and Terry, N. (1998). Accumulation and volatilization of different species of selenium by plants. *Planta* **206**: 284–292.
16. Wang, Y., Boeck, A., and Nuehierl, B. (1999). Acquisition of selenium tolerance by a selenium non-accumulating *Astragalus* species via selection. *Biofactors* **9**: 3–10.
17. Kumar, N.P.B.A., Dushenkov, V., Motto, H., and Raskin, I. (1995). Phytoextraction: The use of heavy metals to remove heavy metals from soils. *Environ. Sci. Technol.* **29**: 1232–1238.
18. Parker, D.R., Page, A.L., and Thomason, D.N. (1991). Salinity and boron tolerances of candidate plants for the removal of selenium from soils. *J. Environ. Qual.* **20**: 157–164.
19. Berti, W.R. and Cunningham, S.D. (2000). Phytostabilization of metals. In: *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment*. I. Raskin and B.D. Ensley (Eds.). Wiley-Interscience, New York, pp. 71–88.
20. Wilbur, C.G. (1980). Toxicology of selenium: A review. *Clin. Toxicol.* **17**: 171–230.
21. Zayed, A.M., Pilon-Smits, E.A.H., deSouza, M.P., Lin, Z.Q., and Terry, N. (1999). Remediation of selenium-polluted soils and waters by phytovolatilization. In: *Phytoremediation of Metal-Contaminated Water and Soils*. N. Terry and G. Banuelos (Eds.). CRC Press, Boca Raton, FL, pp. 61–83.
22. Pilon-Smits, E.A.H. et al. (1999). Overexpression of ATP sulfurylase in Indian mustard leads to increased selenate uptake, reduction and tolerance. *Plant Physiol.* **119**: 123–132.
23. Cunningham, S.D., Shann, J.R., Crowley, D.E., and Anderson, T.A. (1997). Phytoremediation of contaminated water and soil. In: *Phytoremediation of Soil and Water Contaminants*. E.L. Kruger, T.A. Anderson, and J.R. Coats (Eds.). *ACS Symposium Series* No. 164, American Chemical Society, Washington, DC.
24. Neuhierl, B. and Boeck, A. (1996). On the mechanism of selenium tolerance in selenium accumulating plants: Purification and characterization of a specific selenocysteine methyltransferase from cultured cells of *Astragalus bisulcatus*. *Eur. J. Biochem.* **239**: 235–238.
25. Neuhierl, B., Thanbichler, M., Lottspeich, F., and Boeck, A. (1999). A family of S-methylmethionine-dependent thiol-selenol mthyltransferases: Role in selenium tolerance and evolutionary relation. *J. Biol. Chem.* **274**: 5407–5414.
26. Banuelos, G.S., Terry, N., Zayed, A., and Wu, L. (1995). Managing High Soil Selenium with Phytoremediation. *Proc. 12th, Annu. Natl. Meet. Am. Soc. Surf. Min. Reclam.*, Gillette, WY.
27. Terry, N. and Zayed, A.M. (1998). Phytoremediation of selenium. In: *Environmental Chemistry of Selenium*. W.T. Frankenberger, Jr. and R.A. Engberg (Eds.). Marcel Dekker, New York, pp. 633–656.

SOIL PIPES AND PIPE FLOW

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Natural soil pipes are subsurface cavities of diameter greater than 1 mm that are continuous in length such that they can transmit water, sediment, and solutes through the soil and bypass the soil matrix. Soil pipes are larger versions of soil macropores. Pipes can be up to several meters in diameter, several hundred meters long, and occur in a broad range of environments. They are most common in soils that are subject to cracking in dry periods or are highly dispersible. Soils that have a significant amounts of swelling clays also commonly contain soil pipes (e.g., montmorillonite, illite, and bentonite). Piping is common in arid and semiarid areas where shrinking and desiccation cracking are common. Piping is also common in highly organic soils in humid uplands (e.g., blanket peats). However, soil pipes are found in virtually all climates, in organic and mineral soils, and on disturbed and undisturbed land.

PIPE INITIATION

The wide range of environments in which soil pipes are found reflects the wide range of pipe initiation and development processes (Fig. 1) (1). The initiation of piping is discussed in detail by Jones (2), although there have been relatively few process measurements (3,4). The following factors are considered important in the initiation and development of piping: climate, biota, human activity, pedogeomorphic context, role of soil chemistry (influenced by sodium salts and influenced by systems exhibiting base deficiency), soil texture, erodibility, soil structure and hydraulic conductivity, clay minerals, cracking potential, and dispersivity. The dual need for water supply and desiccation means that pipes are most frequent in semiarid and temperate marine environments (1). Flow through desiccation and biotic and mass movement cracks may enhance the macropores into pipe networks. Jones (5) demonstrates that the vast majority of catchments examined that have piping in Britain, for example, face south, suggesting that desiccation cracking may be very important in the formation of piping there. Gilman and Newson (6) observed that vertical cracks in both the roof and floor of peat pipes were a common feature in mid-Wales during the drought summer of 1976 and suggested that this allowed more water to reach deeper levels and created permanent extensions of the pipe networks when rewetting took place. Faunal activity in many areas, it has been shown, results in active soil pipe formation and affects subsurface movement of water (4,7).

PIPE IDENTIFICATION

Until recently, it has been difficult to find and define soil pipe networks because pipes are often visible only at stream banks or where the pipe roof has collapsed and created a surface opening (Fig. 1b) or formed a gully. Therefore, it is difficult to map the route of a soil pipe or to know its diameter, depth, and length across a hillslope. In some soils, a change in surface vegetation may often indicate the presence of a pipe (8). Jones and Crane (9) extensively mapped 4.4 km of pipes in a drainage area of only 0.23 km^2 by a dye tracing and ground survey. Pipe locations were identified mainly by observation of collapse features, of water jets emerging from pipes, and the sound of flowing water (2). However, these techniques do not give

(a)



(b)



(c)



Figure 1. Natural soil pipes. (**a**) large pipe outlet with coarse sediment delivered from its base; (**b**) collapsed surface undermined by pipe erosion; (**c**) typical pipe outlet in blanket peat. Holden, J. and Burt, T.P. (2002) Piping and pipeflow in a deep peat catchment. *Catena* **48**: 163–199.

a detailed or complete picture of the subsurface network and can result in underestimates of pipe density. Often, destructive techniques (e.g., soil trenches) must be used to investigate the pipes (2), and there have been few other attempts to locate and map subsurface piping accurately.

Holden et al. (10) demonstrated that ground penetrating radar (GPR) could be used to sense soil pipes remotely (Fig. 2). The radar transmits short pulses of high-frequency (10–10,000 MHz) electromagnetic energy through the ground surface, which is reflected from boundaries between soil layers or from internal irregularities whose electrical properties are different. Thus, soil pipe cavities can be identified by radar when it crosses over them. GPR work has shown that pipe network densities are much greater than can be detected from surface observation alone. On its own, the radar can detect only subsurface cavities, but when used in conjunction with tracers (e.g., sodium chloride), it can establish the hydrologic connectivity of soil pipes (11), which will be detected by alterations in the reflection of the electromagnetic signal if the electrical conductance of the water in the soil pipe suddenly changes below the radar. Thus, it is possible to determine how pipes are connected to others within a complex subsurface drainage network.

PIPE MORPHOLOGY

The size (mean diameter) of pipes is the most recorded measure of pipe geometry often measured only at outlet locations. However, pipe size can vary significantly just a few meters upslope from the outlet. All areas have a range of pipe sizes, often within the same pipe network. The largest pipes, however, tend to develop in arid and semiarid areas (12). Some evidence suggests that small rounded pipes tend to evolve into larger flat-bedded or rectangularly shaped pipes (2). Fiberscopes have recently been developed to examine internal structures of soil pipes, although these have usually been restricted to short distances from a pipe outlet (13). The average cross-sectional area of pipe outlets per kilometer of stream bank is often taken as a good measure of piping intensity along a stream bank (14), although many reports are of pipes not directly connected to the stream. Pipes can be at any depth within a soil profile, although they are more common at the interface between two distinct soil horizons (especially at organic—mineral interfaces), where there is a sharp transition in hydraulic conductivity or erodibility. In blanket peat, however, pipes have been found that undulate



Figure 2. Ground penetrating radar being used in the field to detect soil pipes. Photo by Vincent Holden.

throughout the soil profile. Pipe floors can run counter to the surface topography such that hydraulic pressures are required to transport the water upward through those sections. An example of a typical vertical section through a soil pipe network is shown in Fig 3. Pipes thus provide rapid connectivity of water, sediment, and solutes throughout the soil profile. Soil pipes are rarely isolated conduits; they often form complex networks that have meandering and anastomosing forms (2,10). Thus, they can extend the stream channel network many hundreds of meters upslope and rapidly transmit water and sediment from great distances away from the stream channel itself.

PIPE HYDROLOGY

Laboratory work (15), modeling (16), and field measurement (17,18) have shown that piping can be a very important hydrologic phenomenon, particularly in humid temperate regions (2,6,14,19). Jones and Crane (9) reported, for example, that 49% of stream flow in the Maesnant catchment, mid-Wales, United Kingdom, was generated through the pipe network. Holden and Burt (10) found that 10% of the discharge in peat catchments moved through the pipe network but at times (depending on antecedent conditions), this could be as high as 30%. Three broad categories of pipe flow can be identified: perennial, ephemeral, and seasonal. There is typically a great variety of hydrologic response between one pipe and another, even within a small area, although some pipe outlets can simply be connections to the same pipe network as others. Jones (20) reports that piping doubles the dynamic source area for rapid runoff response in the upper Maesnant, mainly by linking points well beyond the riparian zones of seepage to the stream.

It is likely that there are several sources of pipe-flow water: overland flow entering collapse features where pipes are open to the surface; water flowing through cracks and root channels to enter the pipe network; diffuse seepage from pipe walls into the pipe system, and groundwater springs forcing water upward from below (Fig. 3). Pipes often receive water more quickly than would be expected from diffuse seepage through soil layers (8,10), and it certainly does not seem that pipe flow in all catchments is restricted by the long time it takes for rainwater to infiltrate down as far as the level of pipes. Nevertheless, Sklash et al. (21), using isotope analysis, showed that pipes in some catchments may transmit predominantly 'old' water (water from previous storms) that is richer in deuterium during storm flow. In an adjacent catchment, however, there was strong chemical evidence that storm flow in the pipes was dominated by fresh storm rainfall. In semiarid zones, pipe flow can occur while the surrounding soil or bedrock remains relatively dry (12).

PIPE EROSION AND WATER QUALITY

Piping, a form of subsurface erosion, has been associated with gully and rill development in many parts of the world. Particular associations were noted in Australia and New Zealand during 1940s soil erosion surveys. Alluvial and loess soils are particularly prone to such pipe–gully coupling. Some pipes are subject to 'episodic cut and fill' in that they can collapse and block the route for water before eventually unblocking and allowing water to flow through them again (17). Thus, pipe discharge can be highly erratic. Pipes can provide the stream system with sediment that is very different from that expected from overland flow because they often connect and erode deeper soil layers (Fig. 3). If piping is very active, then sediment losses from hillslopes can be severe and can cause problems for soil conservation workers. However, very few measurements of pipe-flow sediments have been made around the world. Hauser and Zotl (22) measured 0.5 kg of sand per week from one pipe that had an average discharge of 0.16 $L\,s^{-1}$ in the Sarmatian mountains of Graz, Austria, and badland pipe sediment loads, it is thought, are an order of magnitude higher than overland flow concentrations (2). Because it is subsurface, pipe erosion can occur, even when the hillslope is densely vegetated (23).

The role of piping in major mass movement is as yet uncertain. There have been some instances where pipes have been identified as the cause of subsidence or landslides, others where pipes are thought to have developed after the mass movement, and still further cases

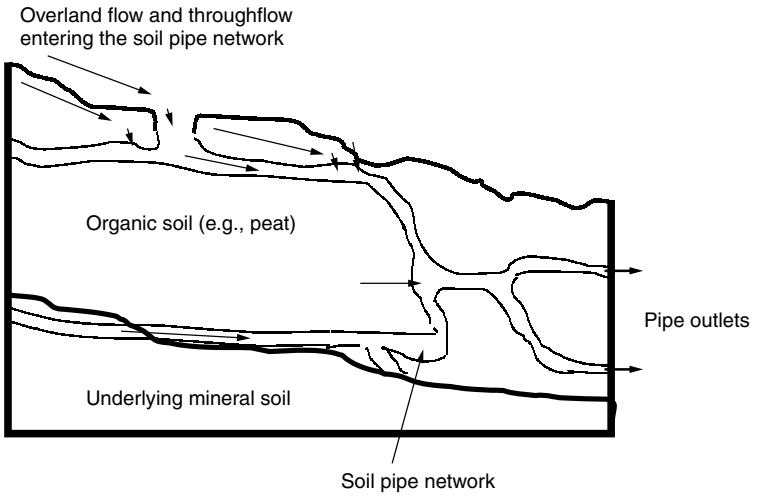


Figure 3. Schematic of a short vertical section through a soil pipe network.

where pipes it is thought, have prevented mass movement. In many circumstances, water flow is too great to be freely transmitted along these subsurface tunnels, and a pressure head builds back up the pipe. If a heavy rainstorm occurs, it is possible that restrictions in the dimensions of the pipes that act as bottlenecks will impede flow. Hence, water builds back up the pipe, and large pressures may build up within the slope. At the same time, pipes might provide a drainage path for water, prevent the buildup of gravitational forces on the slope, and thus prevent mass movements in some areas.

In some catchments, measurements of pipe flow chemistry have failed to determine any significant difference from that of overland flow, suggesting that the sources of the water were the same (24). Piping may therefore exacerbate problems of acid runoff by reducing soil buffering effects as a result of more rapid transmission, reduced soil residence times, and reduced contact between weathering mineral surfaces. Drainage and aeration of large sections of hillslope can also encourage release of sulfates and organic acids, particularly from peaty soils, which increases the acidity of the runoff. Therefore, many pipes tend to issue more acidic water during storms and contribute to acid flushes in streams that can increase acid rain impacts on fish and microfauna.

BIBLIOGRAPHY

1. Bryan, R.B. and Jones, J.A.A. (1997). The significance of soil piping processes: inventory and prospect. *Geomorphology* **20**: 209–218.
2. Jones, J.A.A. (1981). The nature of soil piping: a review of research. *British Geomorphological Research Group Monograph Series 3*, GeoBooks, Norwich, MA.
3. Torri, D. and Bryan, R. (1997). Micropiping processes and biancana evolution in Southeast Tuscany, Italy. *Geomorphology* **20**: 219–235.
4. Onda, Y. and Itakura, N. (1997). An experimental study on the burrowing activity of river crabs on subsurface water movement and piping erosion. *Geomorphology* **20**: 279–288.
5. Jones, J.A.A. (1994). Soil piping and its hydrogeomorphic function. *Cuaternario y Geomorfologia* **8**: 77–102.
6. Gilman, K. and Newson, M.D. (1980). *Soil Pipes and Pipeflow; A Hydrological Study in Upland Wales*, *British Geomorphological Research Group Research Monograph No. 1*, GeoBooks, Norwich, MA.
7. Banerjee, A.K. (1972). Morphology and genesis of pipe structure in ferralitic soils of Midnapore District, West Bengal. *Journal of the Indian Society of Soil Science* **20**: 399–402.
8. Jones, J.A.A., Wathern, P., Connelly, L.J., and Richardson, J.M. (1991). Modelling Flow in Natural Soil Pipes and its Impact on Plant Ecology in Mountain Wetlands. In: *Hydrological Basis of Ecologically Sound Management of Soil and Groundwater (Proceedings of the Vienna Symposium, August 1991)*. IAHS publication 202, pp. 131–142.
9. Jones, J.A.A. and Crane, F.G. (1984). Pipeflow and pipe erosion in the Maesnant experimental catchment. In: *Catchment Experiments in Fluvial Geomorphology*. T.P Burt and D.E. Walling (Eds.). GeoBooks, Norwich, MA, pp. 55–72.
10. Holden, J. and Burt, T.P. (2002). Piping and pipeflow in a deep peat catchment. *Catena* **48**: 163–199.
11. Holden, J. (2004). Hydrological connectivity of soil pipes determined by GPR tracer detection. *Earth Surface Processes and Landforms to be published*.
12. Bryan, R.B. and Yair, A. (Eds.). (1982). *Badland Geomorphology and Piping*. GeoBooks, Norwich, MA.
13. Terajima, T., Sakamoto, T., and Shirai, T. (2000). Morphology, structure and flow phases in soil pipes developing in forested hillslopes underlain by a Quaternary sand-gravel formation, Hokkaido, northern main island in Japan. *Hydrological Processes* **14**: 713–726.
14. Jones, J.A.A., Richardson, J.M., and Jacob, H.J. (1997). Factors controlling the distribution of piping in Britain: a reconnaissance. *Geomorphology* **20**: 289–306.
15. Sidle, R.C., Kitahara, H., Terajima, T., and Nakai, Y. (1995). Experimental studies on the effects of pipeflow on throughflow partitioning. *Journal of Hydrology* **165**: 207–219.
16. Nieber, J.L. and Warner, G.S. (1991). Soil pipe contribution to steady subsurface stormflow. *Hydrological Processes* **5**: 329–344.
17. Zhu, T.X. (1997). Deep-seated, complex tunnel systems—a hydrological study in a semiarid catchment, Loess Plateau, China. *Geomorphology* **20**: 255–267.
18. Carey, S.K. and Woo, M. (2001). Spatial variability of hillslope water balance, Wolf Creek basin, subarctic Yukon. *Hydrological Processes* **15**: 3113–3132.
19. Uchida, T., Kosugi, K., and Mizuyama, T. (1999). Runoff characteristics of pipeflow and effects of pipeflow on rainfall-runoff phenomena in a mountainous watershed. *Journal of Hydrology* **222**: 18–36.
20. Jones, J.A.A. (1987). The effects of soil piping on contributing area and erosion pattern. *Earth Surface Processes and Landforms* **12**: 229–248.
21. Sklash, M.G., Beven, K.J., Gilman, K., and Darling, W.G. (1996). Isotope studies of pipeflow at Plynlimon, Wales, UK. *Hydrological Processes* **10**: 921–944.
22. Hauser, A. and Zotl, J. (1955). Die morphologische Bedeuntung der unterirdischen Erosion durch Gesteinausspulung. *Petermans Mitt.* **99**: 18–21.
23. Jones, J.A.A. (1990). Piping effects in humid lands. In: *Groundwater Geomorphology; the Role of Subsurface Water in Earth-Surface Processes and Landforms*. C.G. Higgins and D.R. Coates (Eds.). Geology Society of America Special Paper 252, pp. 111–137.
24. Cryer, R. (1980). The chemical quality of some pipeflow waters in upland mid-Wales and its implications. *Cambria* **6**: 28–46.

LOW FLOW GROUNDWATER PURGING AND SURGING

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Groundwater monitor wells are installed primarily as tools to measure the dissolved concentrations of contaminants in groundwater in and around facilities where the release

of contaminants has occurred or where the potential exists for such a release to occur (i.e., adjacent to landfills). These wells are installed with the intention of obtaining an accurate assessment of the conditions in the formation adjacent to the well. A significant body of literature and guidance documentation exists concerning the location, drilling, installation, and development of those wells to that end. However, it has become evident that the quality of the data yielded from monitor wells is dependent on screen length and location (addressed during design and installation), purging method, and purge volume. The question becomes how does one collect samples from groundwater monitoring wells that generate representative results?

The regulatory community and those involved in the design and operation of remediation systems are seeking an accurate answer to that question. However, interest is also generated from the economic pressures to reduce the cost of sampling and monitoring procedures. Standard groundwater sampling procedures involve purging three to five well volumes with a pump or a bailer, which entails expense in the form of time (often for two technicians) and disposal of the purge water. These two issues have driven recent research by the scientific community, as well as the regulatory community, which is also beginning to act by introducing new protocols for the acceptable sampling of wells.

The use of screened hydraulic probes is recognized as an accurate sampling method and as the yardstick for comparison with various monitor well sampling techniques. Their practical use is of value for initial plume delineation and assessment in aid of the design of a monitor well network; however, they are impractical as a long-term monitoring system. The groundwater monitor well is essential for that role.

For conventional purge techniques, wherein three to four well casing volumes of water were removed during purging, it was determined that water in a monitor well was "static" and in time grew "stagnant." The purging of the well casing volumes was to remove the old and "stagnant" water, which allowed for representative aquifer water to enter the well bore for sampling.

Concerns were twofold: (1) the assumption that the mechanisms at work within the well bore that would attenuate the contaminant concentrations such as vaporization and/or biodegradation supported by oxygen diffusion; and (2) the assumption that with time, formation conditions will improve, contaminant concentrations will decrease, and samples will demonstrate that trend.

Recent studies have shown that conventional purging procedures can activate two phenomena that to give false results: vertical mass averaging within the well bore and the introduction of water lower in the formation through vertical (upward) flow paths. Vertical heterogeneity of contaminant concentrations within the well bore occurs when zones of striking hydraulic conductivity contrast are present. Contaminants preferentially flow through the more permeable units intersected by the well screen. Gross purging then simply mixes the entire well bore. Low flow discrete level sampling has been devised to address this specific phenomena. The induction of vertical uncontaminated groundwater flow from beneath a partially penetrating well is a problem in formations at the opposite end of the hydrodynamic spectrum, which are coarsely granular (sand and gravel) and relatively homogenous.

Field testing shows that low flow purging at specific vertical points within the well bore yields results that are similar to sampling via the conventional purging methods. Bailing is likely to produce the lowest concentrations, and low flow pumping slightly higher, but both tend to produce results that are significantly lower than actual concentrations within the adjacent formation. In general, it appears that the more vigorously a well is purged, the more likely it is that the samples will underrepresent contaminant concentrations within the adjacent formation. A detailed description of low flow (minimal drawdown) groundwater sampling is described by the U.S. Environmental Protection Agency.

Physical and chemical processes can potentially impact a monitor well in a static or stagnant state. The processes that could effect the concentration of dissolved components or the degree of mixing of heterogenetic water within a well bore column include:

- The groundwater flow rate through the surrounding formation and its influence via advective flow within the well
- The vertical profile of the contaminant concentration and hydraulic conductivity contrast within the adjacent formation
- Vaporization and volatilization across the air water interface at the top of the well
- Diffusion of oxygen through the air–water interface into the well bore stimulating biodegradation Diurnal and seasonal temperature fluctuations
- Diffusional transport vertically within the well bore as well as horizontally from the adjacent formation
- Barometric pumping, which under some conditions can cause water level fluctuations (and mechanical mixing) in wells located in unconfined aquifers
- Seismic activity
- Tidal forces
- Local heavy auto, truck, or train traffic

In aggregate, these forces impact all monitor wells to various degrees depending on the geologic and geographic site conditions. In some instances, "static" conditions are dynamic enough to ensure that water in a monitor well is representative of the adjacent formation.

Consequently, some regulatory bodies have begun to consider the use of non-purge or low-purge (the EPA) methods of sampling. In California, the Cal/EPA allows non-purge sampling in cases where:

- The monitor well is screened in an unconfined (water table) aquifer
- The screened interval extends above the top of the water table

- The monitor wells are located in moderate-to-high recovery aquifers consisting of sands or gravels

Purging is still required when:

- The well is new and has been sampled less than two times (this also assumes the well underwent an adequate development purge at installation)
- Chlorinated hydrocarbons, PNAs, diesel, or metals are the contaminant
- Slow recovering wells within fine-grained sediments (clays and silts) are used
- Monitor wells associated with sparging or soil vapor extraction activity are used

LOW FLOW TECHNIQUES

Low flow refers to the velocity with which water enters the pump intake and is imparted to the groundwater in the immediate area of the well screen. Low flow does not necessarily refer to the flow rate of groundwater discharged on the surface, which can be affected by flow regulators or restrictions. Flow rates from 0.1 to 0.5 L/min are used; however, on more porous formations, up to 1.0 L/min have been used (1).

Advantages of low-flow sampling (1) include:

- Groundwater samples are representative of the mobile load of contaminants present.
- Minimal disturbance occurs, which minimizes sampling artifacts.
- Less operator variability and greater operator control are provided.
- Reduced stress occurs on the aquifer when minimal drawdown sampling is performed.
- Reduced need exists for filtration and, consequently, less time sampling occurs.
- Smaller purging volume decreases waste disposal costs and sampling time.
- Better sample consistency exists.

Some of the disadvantages include higher initial capital costs, greater setup time in the field, additional training time, resistance to change by regulators or consultants, and the concern that the new data will trigger regulatory action based on new, more accurate concentration data (1). In some settings, low flow purging and sampling is appropriate simply because of the physical setting: low permeability formations where recharge rates are less than 0.1 L/min and fractured rock formations where representative samples may come from selectively oriented fracture networks.

The desire by the regulatory and regulated community to obtain accurate results, the realization of the problems associated with sampling, and the costs associated with conventional approaches are likely to drive the development and implementation of new standard protocols for the sampling of monitor wells. It also presents an opportunity for the development and application of new technology and approaches.

BIBLIOGRAPHY

1. Puls, R.W. and Barcelona, M.J. (1996). *Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures*. EPA Groundwater Issue, Office of Research and Development, Office of Solid Waste and Emergency Response, EPA/540/S-95/504, April.

GROUNDWATER QUALITY

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The value of groundwater lies in its widespread occurrence and availability and also its consistent good quality. Groundwater, on the whole, is cleaner than most surface water and maintains a nearly uniform temperature.

As groundwater moves through the subsurface, physical, chemical, and biological processes interact to change its original quality. The earth materials through which groundwater moves act as natural filters to screen out some bacteria and some impurities from the water. Groundwater is usually clear and colorless and of excellent sanitary quality, making it drinkable directly as withdrawn, which does not mean, however, that groundwater is completely free of impurities. In fact, all groundwater contains some dissolved minerals.

Water is a universal solvent (1). From the time rain falls to the ground and begins to run off or pass into and through the soil and rocks, it dissolves these materials and thus picks up various mineral constituents. These dissolved minerals are rarely harmful to health and may give the water a pleasant taste.

The dissolved minerals include sodium, calcium, magnesium, and potassium, which combine with bicarbonates, sulfates, and chlorides. The character of the earth materials mainly determines the composition of groundwater. The longer the period contact of water with rocks, the more minerals are dissolved.

The most common groundwater quality problems are caused by natural hydrogen sulfide (2). A high content of dissolved mineral salts may affect the taste of drinking water and have laxative effects.

Hardness is caused by a high concentration of calcium and magnesium. It can cause scale formation in kettles, pipe systems, boilers, and tanks. The most common negative effect of hardness is its tendency to prevent soap from lathering and to form soap scum. Water hardness can be alleviated at a fairly reasonable cost by installing a water softener. It is not desirable, however, to remove all the minerals that make water hard. Water that is too soft is likely to corrode water distribution systems and tanks as well as to produce a flat, unpalatable taste and render the water less beneficial to the health of most people.

Excessive iron is another common natural problem. Iron concentrations in excess of 0.3 mg/L (milligrams per liter) do not normally cause health problems but are of concern for aesthetic and taste reasons. Water that has a high concentration of iron has a metallic taste and causes reddish stains on fixtures, cookware, and laundry.

Cascading or spraying the water into the air so that it is exposed to oxygen can reduce an excessive iron content. High levels of manganese cause problems similar to those caused by excessive iron. The stains caused by manganese are black and are harder to remove than iron stains.

Iron bacteria in groundwater do not damage health but are a nuisance because they clog the pores in the aquifer near wells and well screens, thereby reducing well yields. Bacteria also produce red-to-brown slime in toilet tanks and plumbing. Iron bacteria can be killed by pouring a small amount of disinfecting solution such as chlorine bleach into the water.

Hydrogen sulfide gas is recognizable by its "rotten egg" smell and taste (3). It is a poisonous gas that can build up in a small, enclosed area such as a well pump house. A person who works in a poorly ventilated space may become nauseated or even lose consciousness. Water containing hydrogen sulfide is corrosive to plumbing systems, a condition that can be reduced by aeration or by chlorination and filtration.

Water quality is commonly characterized as "safe" or "good." "Safe" water typically means that the water is free from bacteria and disease-causing organisms, as well as from minerals and substances that can have adverse health effects. The term "good quality" water is a relative term whose meaning depends on the intended use of the water. Sanitary quality can be assessed by periodically analyzing water samples for coliform bacteria and nitrate. These substances do not normally occur in groundwater and their presence may indicate contamination.

Coliform bacteria are useful indicators of harmful microorganisms. According to the drinking-water standards of the United States, safe drinking water should not contain more than one coliform bacterium per 100 mL (6 cu in.) of water. If coliform bacteria occur in well water in numbers that indicate the water is unsafe, the water should be disinfected either by chlorinating or by boiling before drinking until further sample analyses indicate that the water is safe to drink. Sources of bacteria are septic tanks and leach fields and surface water contaminating the well.

High nitrate levels may indicate organic contamination from nearby sources of nitrate, such as barnyard drainage, animal waste storage, and percolation from agricultural land, fertilizers, and septic tanks (4). The U.S. national limit for nitrate-nitrogen concentration is 10 mg/L, which is equivalent to 45 mg/L of nitrate (2). The European standard is 11.4 mg/L nitrate-nitrogen (50 mL/L as nitrate. The main reason for this limit is the risk to (young) infants (blue babies) from drinking high nitrate waters.

Well water can be analyzed by either a country or state public health environmental laboratory or by a qualified private laboratory. Municipal authorities (local health departments) have sources on where water may be analyzed. Routine tests for coliform bacteria or inorganic contaminants, such as nitrate and salts, are relatively inexpensive. However, analyses for inorganic and organic industrial chemicals and pesticides can be very expensive. Those concerned about possible contaminants in their water supplies can contact their local health departments. Specialists from these departments can help determine if a cause for concern exists before extensive and potentially expensive water testing is performed. Keeping accurate records of the water tests ensures proper documentation of the water-quality history of a particular well. Even without obvious signs of contamination, it is advisable to have well water analyzed at least once a year.

If water contamination persists even after several tests, an alternative drinking-water supply should be used or a new source obtained. Leading causes of bacterial and nitrate contamination are poor well construction and poor well location. In most cases, nitrate contamination is limited to the shallow part of the water-bearing formation. When the contaminant is a volatile organic compound (VOC), it may cause problems, by drinking and also by inhalation and absorption through the skin.

BIBLIOGRAPHY

1. Hem, J.D. (1985). *Study and Interpretation of the Chemical Characteristics of Natural Water*. USGS Water-Supply Paper 2254.
2. Fetter, C.W. (2001). *Applied Hydrogeology*. Prentice-Hall, Englewood Cliffs, NJ, p. 598.
3. Moore, J.E. et al. (1995). *Groundwater-a Primer*. American Geological Institute, p. 53.
4. Waller, R.M. (1988). *Ground Water and The Rural Homeowner*. US Geological Survey, p. 36.

RADIAL WELLS

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Radial wells have a radial or horizontal component that comprises the well screen. Types of radial wells include collector wells, horizontal directionally drilled (HDD) wells, and slant or horizontal wells. The most common type of radial wells are collector wells, which have the basic design of a vertical shaft (or caisson) with horizontal screen laterals to collect groundwater. The vertical shaft typically extends to depths from 9 to 46 m (30 to 150 ft) and has a 5-m inside diameter. The laterals are typically tens to hundreds of meters in length and have a diameter of 305 mm (12 in.). The number of laterals designed for the well is dependent on aquifer characteristics (such as hydraulic conductivity) and water demand. Advances in radial well design have allowed for up to 500 m of horizontal well screen (total of all laterals) to be developed in formations where vertical wells can accommodate only 20 m of well screen. Radial wells take advantage of natural filtration through the aquifer materials, which reduces chemical treatment costs.

The lateral well screens are usually installed near the bottom of shallow aquifers in order to exploit the maximum saturated thickness of the aquifer. The laterals are installed by jacking the well screens through precast ports in the vertical shaft at one or more elevations (Fig. 1).

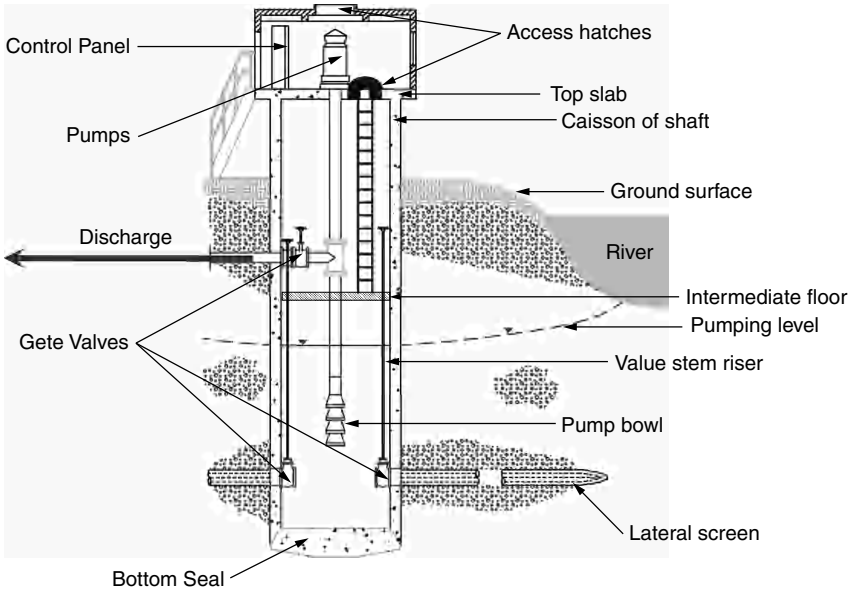


Figure 1. Lateral well schematic (after Bennett & Williams, Inc.).

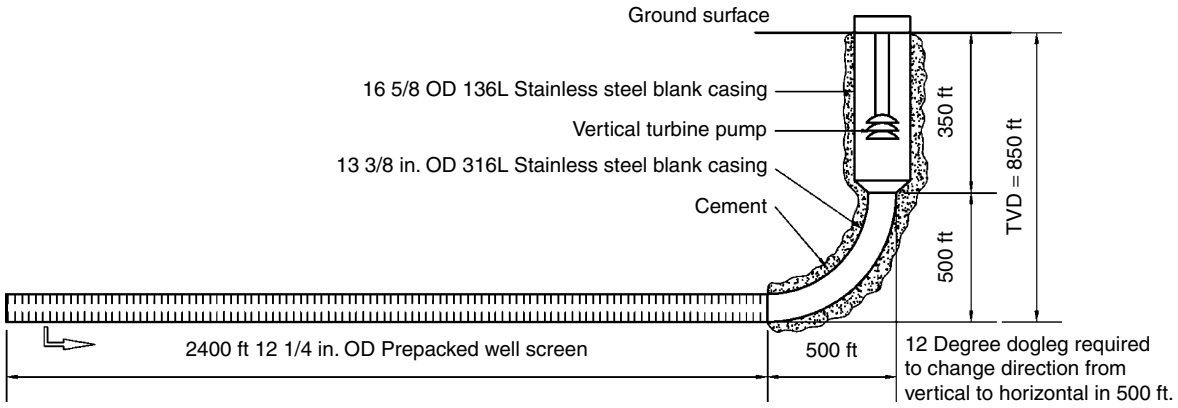


Figure 2. Horizontal directionally drilled (HDD) well.

Radial wells are reported to require less maintenance than conventional vertical wells, as the longer horizontal screens reduce water velocity entering the screen slots, thereby maximizing well efficiency and reducing well head losses and clogging. Existing radials wells can be rehabilitated with the installation of new laterals.

Radial wells are used in applications such as municipal production wells, dewatering operations, and inducing surface water infiltration for groundwater recharge.

An emerging technology in the groundwater supply industry is the use of horizontal directionally drilled (HDD) wells (Fig. 2). HDD technology is widely used in the oil and gas industry; however, HDD technology has not yet been completely transferred to the groundwater supply industry for routine or wide-scale applications. HDD wells utilize a "mud motor" technology along with sophisticated downhole navigation systems to "guide" the drill first vertically and then horizontally (or a combination of both). The application of HDD technology is in its infancy in the water well industry; however, there is potential for specialized applications such as desalination plant intake systems, or specialized recharge or enhancement of a shallow aquifer's saturated thickness. HDD wells may be constructed to extend to over 1000 m.

RECHARGE IN ARID REGIONS

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Groundwater recharge in arid regions or deserts is a process that requires a favorable combination of hydrologic factors. Accordingly, recharge, in arid regions occurs more rarely and supplies annual quantities of water to the groundwater table lower than typical of more humid regions. Many of the processes by which recharge occurs, such as surface infiltration, stream channel loss, and seepage from impounded water bodies, however, are common to both regions.

DEFINITION OF ARID REGIONS

By definition, the aridity of a region is determined by the ratio of mean annual precipitation to mean annual potential evapotranspiration (PET). As shown in Fig. 1, arid regions in both the Northern and Southern Hemispheres are situated mostly between 10° and 35° latitude worldwide. Regions that have average annual precipitation (P) totaling less than 250 mm (10 in) make up an estimated 25% of the worldwide land areas outside of the polar regions (1). Arid regions are sometimes further classified as hyperarid, arid, or semiarid, according to the ranges in the P/PET ratio (Table 1).

VARIABILITY OF PRECIPITATION AND RECHARGE

For several reasons, estimates of mean annual precipitation are difficult to relate directly to recharge in arid regions. Largely, this difficulty develops from characteristically high temporal and spatial variability in both the distribution of precipitation and recharge in arid regions.

Table 1. Arid Region Subclassifications

Arid Region Subclassifications[a]	P/PET Ratio
Hyperarid	< 0.03
Arid	0.03 to < 0.20
Semiarid	0.20 to < 0.50

[a] After Reference 2.

Longer term recharge to precipitation ratios (R/P) for various arid regions in the United States generally are typically less than 5% (3–5).

High temporal variability of precipitation exists across seasonal and multiyear time frames. Average annual precipitation depths for arid regions result from large variances between extreme high and low annual totals. For example, average annual precipitation falling on the town of Arica, located in the Atacama Desert region of Chile, during a 17-year period was only 0.5 mm (0.02 in). Interestingly, this average resulted from just three measurable showers in a 17-year period (6). Such variability in precipitation infers even greater temporal variability in recharge in arid regions.

Similarly, the spatial variability of precipitation in arid regions can be high. If convective, as opposed to frontal, storms characteristically supply a significant percentage of the annual precipitation within an arid region, the areal distributions of rainfall from individual storms can be highly variable. Adjacent gauging stations can indicate significant differences in the total precipitation recorded during any given storm or during an entire year, and in the next year, a completely different pattern could be observed. Recharge, a process that requires a sufficient precipitation threshold to overcome evapotranspiration losses and soil moisture deficits in the soil, can be significantly affected by such spatial variability in precipitation.

Recharge in arid regions might be further limited due to areal variations in hydrogeologic and topographic factors. In arid regions where topographic relief is high, recharge often occurs along mountain fronts, where precipitation is greater and where there may be sustained runoff from snowpack. Other studies have shown that, in some

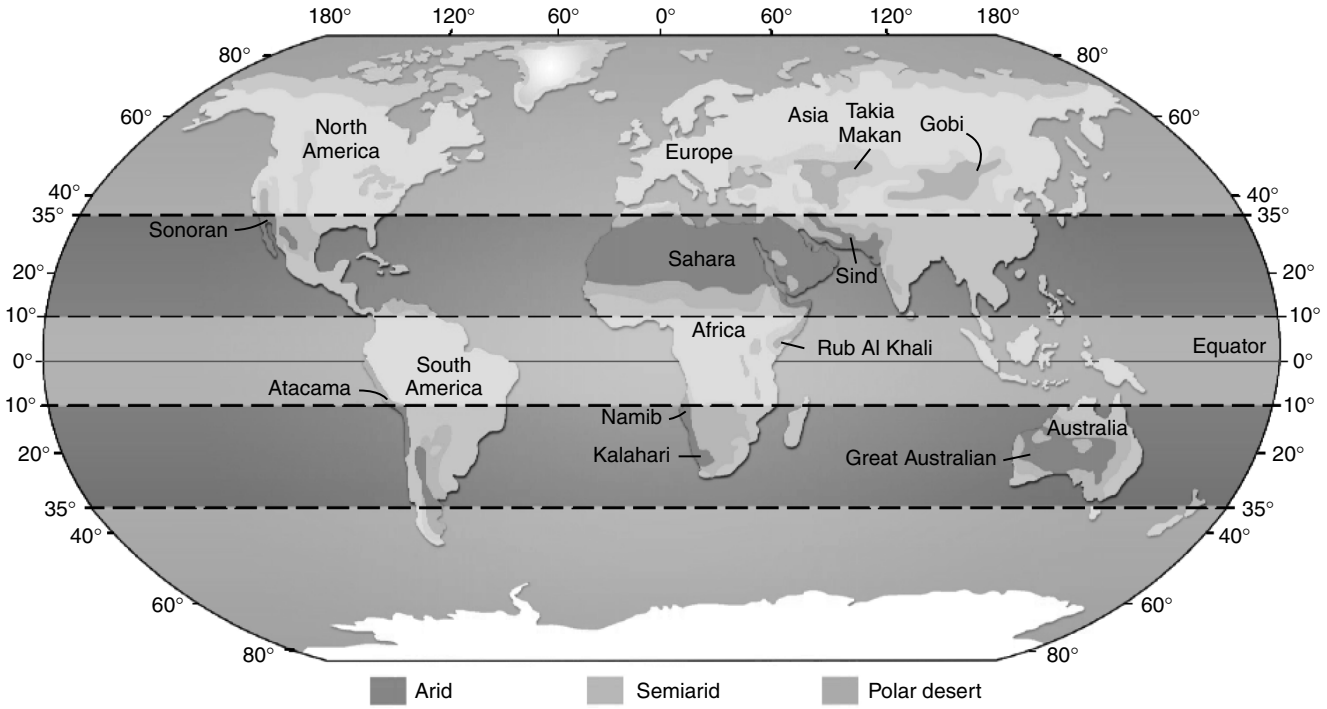


Figure 1. Worldwide pattern of arid regions (copyrighted Fig. 13–15 in Reference 1). Figure preparation/revision by Hargis and Associates, Inc., San Diego, CA.

mountainous areas, "mountain block recharge" occurs as a result of diffused infiltration through thin or absent soils overlying fractured bedrock (7). Recharge can also occur along incised alluvial channels during ephemeral or intermittent runoff. In certain low-lying areas or depressions, precipitation or runoff waters might be detained, thereby providing localized recharge through sediments or fractures. In highland areas, exposures of fractured bedrock can facilitate infiltration during precipitation or runoff, creating perched groundwater zones or deeper infiltration to the regional water table. Thus, the overlay of spatial and temporal variability of precipitation onto the areal variability of recharge areas further increases recharge variability temporally and spatially.

CONDITIONS FAVORING RECHARGE

For recharge to occur in any region, certain initial conditions must be satisfied. First, there must be sufficient surface water to infiltrate into the soil. Such conditions may result from sufficient precipitation (in terms of depth, intensity, and/or duration), runoff, or water impoundment. Second, the moisture storage potential of underlying soils must be satisfied. In other words, the void spaces in the soil matrix must become saturated. Once these conditions are met, recharge to the groundwater table becomes possible through deep percolation of soil water. Subsurface soil or bedrock conditions, however, such as fractures or heterogeneities, can sometimes locally short-circuit these overall requirements, thereby providing more direct "conduits" to the water table.

Recharge from runoff in ephemeral streams in the southwestern United States is depicted in Fig. 2. During wet seasons, sustained runoff in the alluvial channel may result in infiltration, provided there is sufficient vertical permeability in the underlying sediments. This infiltration locally recharges the groundwater table along the course of the ephemeral stream (wash or arroyo). A typical wet season recharge event is depicted in Fig. 3. During dry seasons, phreatophytes rely on the availability of shallow soil water and groundwater in the vicinity of the ephemeral stream channel, discharging groundwater by evapotranspiration. Another fraction is lost to direct surface evaporation from soils.

PRECIPITATION VERSUS EVAPOTRANSPIRATION

Theoretically, soil moisture is recharged during periods when precipitation exceeds potential evapotranspiration ($P >$ PET). As discussed earlier, such conditions are rare in arid regions, which is further illustrated in the monthly average relationship between precipitation and pan evaporation (E), shown in Fig. 4. This comparison shows a site in Tucson, Arizona, elevation ~730 m (~2400 ft) above mean sea level (msl), and at Sierra Ancha, Arizona, elevation ~1555 m (5100 ft) msl. Using the average annual value of evaporation for each site as an estimate for the average annual potential evapotranspiration, the P/E ratios for Tucson and Sierra Ancha during the timeframe

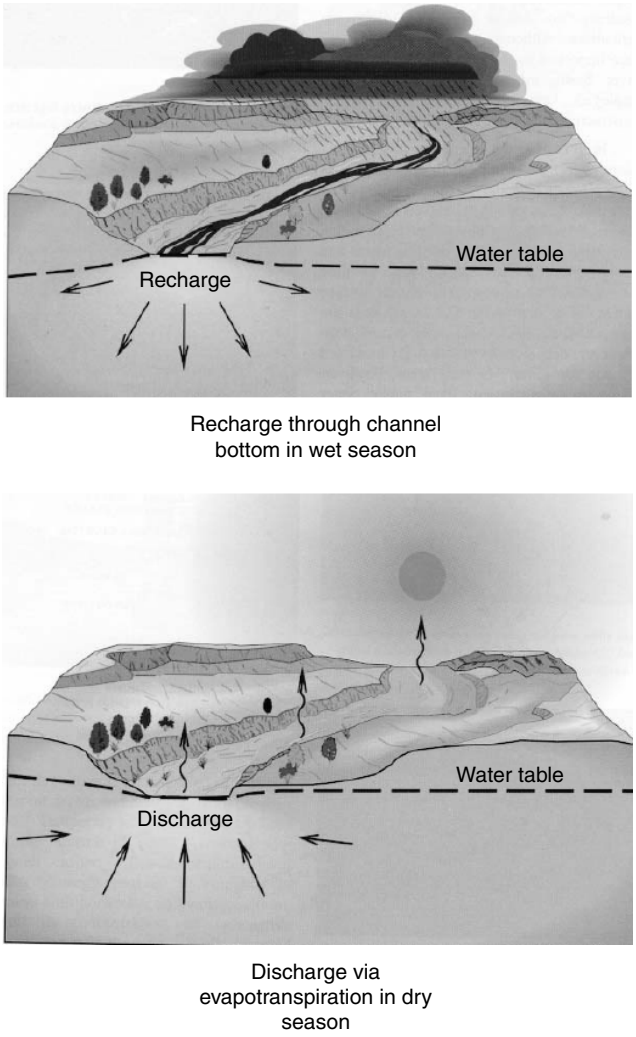


Figure 2. Recharge from runoff in ephemeral streams.

from 1963 through 1966 were approximately 0.15 and 0.37, respectively. The arid region subclassifications of these sites, according to Table 1 and based on the limited records evaluated, would be arid and semiarid, respectively.

From these plots, it can be seen that the recharge potential in arid regions can vary significantly with seasonal conditions. The effect of elevation differences on the P/E ratios is also evident. Both stations indicate a bimodal (double-peaked) distribution of precipitation during the year, indicating higher precipitation typically in the winter and summer months. On average, a greater amount of precipitation falls during the summer months, but the lower rate of evaporation better favors recharge potential during winter months, which is evident from the closer convergence of the P and E curves on the Tucson plot and the crossover of the two curves on the Sierra Ancha plot.

During the period of record (1963–1966), the monthly average values show that there was always a soil moisture deficit at the Tucson station, whereas a soil moisture recharge potential was present during the winter months at Sierra Ancha. These patterns help to

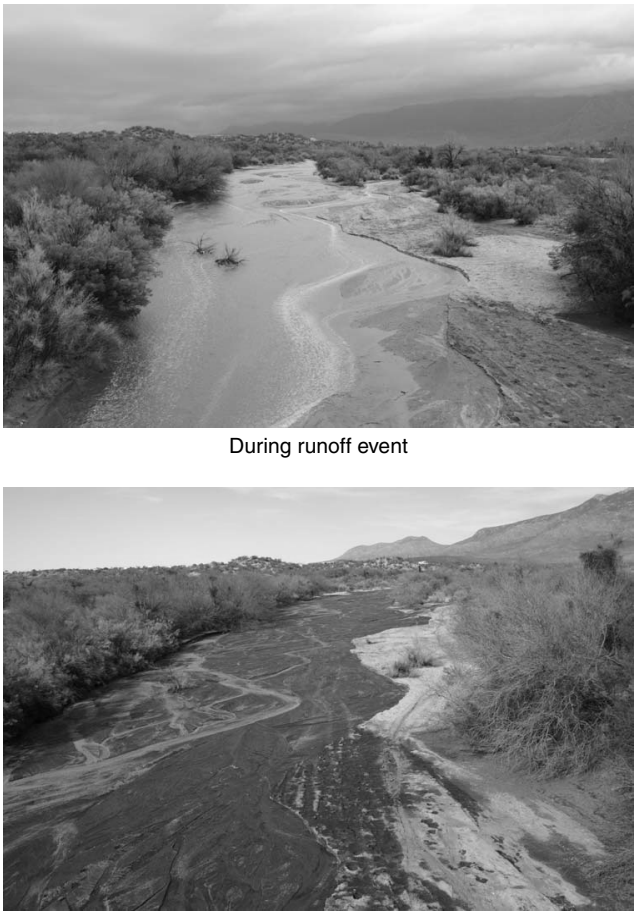


Figure 3. Wet season recharge in Cañada del Oro Wash near Tucson, Arizona.

understand the conditions favoring recharge, but it should be understood that longer term variability might overlay these patterns. Long-term variability results from extreme conditions of drought and precipitation, earlier said to affect the calculation of average values of precipitation and evapotranspiration in arid regions. The example in Fig. 4 is based on averages calculated over a 4-year period. The averages of total annual precipitation for Tucson and Sierra Ancha during these 4 years were 340 mm (13.37 in) and 692 mm (27.25 in), respectively. Longer term records for these stations indicate lower averages of 283 mm (11.13 in) and 676 mm (26.60 in), respectively (8).

RECHARGE ESTIMATION

Recharge is a component of the hydrologic budget often calculated from a water budget equation, whereas other variables, such as precipitation, evaporation, runoff, and use quantities, usually represent field-measured parameters. Another method of estimation involves calibration of groundwater flow models against field measurements of groundwater levels. Generally, these models simulate the water budget dynamics of the study area.

Research is being performed to improve methods for quantifying recharge in arid regions. Methods under investigation include interpreting stable and radioactive isotopic signatures. The most common methods employ ratios between stable isotopes of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) or simply the graphical relationship between ^{2}H and ^{18}O to estimate the "isotopic age" of the water, and therefore the time since it was recharged (9). Other common methods are based on the decay constants of various radioisotopes such as tritium (^{3}H), carbon (^{14}C), and chlorine (^{36}Cl) (9,10). Recent research has examined silicon (^{32}Si) to estimate long-term recharge rates based on the "loss" of the isotope by adsorption during infiltration (11).

Other methods under current investigation for estimating recharge in arid areas include microgravity networks, temperature profiling, geochemical profiling, and various remote-sensing techniques. Microgravity networking employs finely gridded gravity instrumentation to assess seasonal and long-term changes in the mass of groundwater in storage under a basin (12). Temporal changes in the gravity profile measured across the network infer changes in the volume of groundwater stored in the underlying aquifer and hence, recharge and discharge.

Temperature profiling is based on the difference in the temperature of recharging waters versus ambient soil and groundwater. Research is focusing on both natural and artificial recharge from infiltration through stream channels as well as more diffuse recharge mechanisms. To accomplish this, multilevel temperature probes are emplaced at successive depths within soil borings drilled in known or suspected recharge areas.

Geochemical methods also require depth profiling in the soil column beneath suspected recharge areas. The concept relies on interpreting changes in soil chemistry from water movement during infiltration. Such changes result from either deposition or dissolution of minerals along the infiltration pathway. For example, using a combination of field-measured chloride data and numerical simulations, researchers have estimated long-term recharge cycles in the Badain Jaran Desert in China as far back as 1000 years (13).

Remote sensing techniques involve interpretation of tones, colors, and spectral hues observable in bare soils as well as due to vegetation densities and spectral variations. Such differences can be interpreted from photographic or scanned imagery and infer regions where shallow subsurface water is present. Infrared techniques employ either thermal- or near-infrared spectra. Thermal techniques detect temperature differences in soil moisture variations, whereas near-infrared relies on vegetation inferences.

BIBLIOGRAPHY

1. Skinner, B.J, Porter, S.C., and Botkin, D.B. (1999). *The Blue Planet, An Introduction to Earth System Science*, 2nd Edn. John Wiley & Sons, New York.
2. UNESCO. (1979). Map of the world distribution of arid regions: explanatory note. In: *Understanding Water in a Dry Environment: Hydrological Processes in Arid and SemiArid Zones*. International Association of Hydrogeologists, Balkema, Lisse, The Netherlands, Vol. 23.

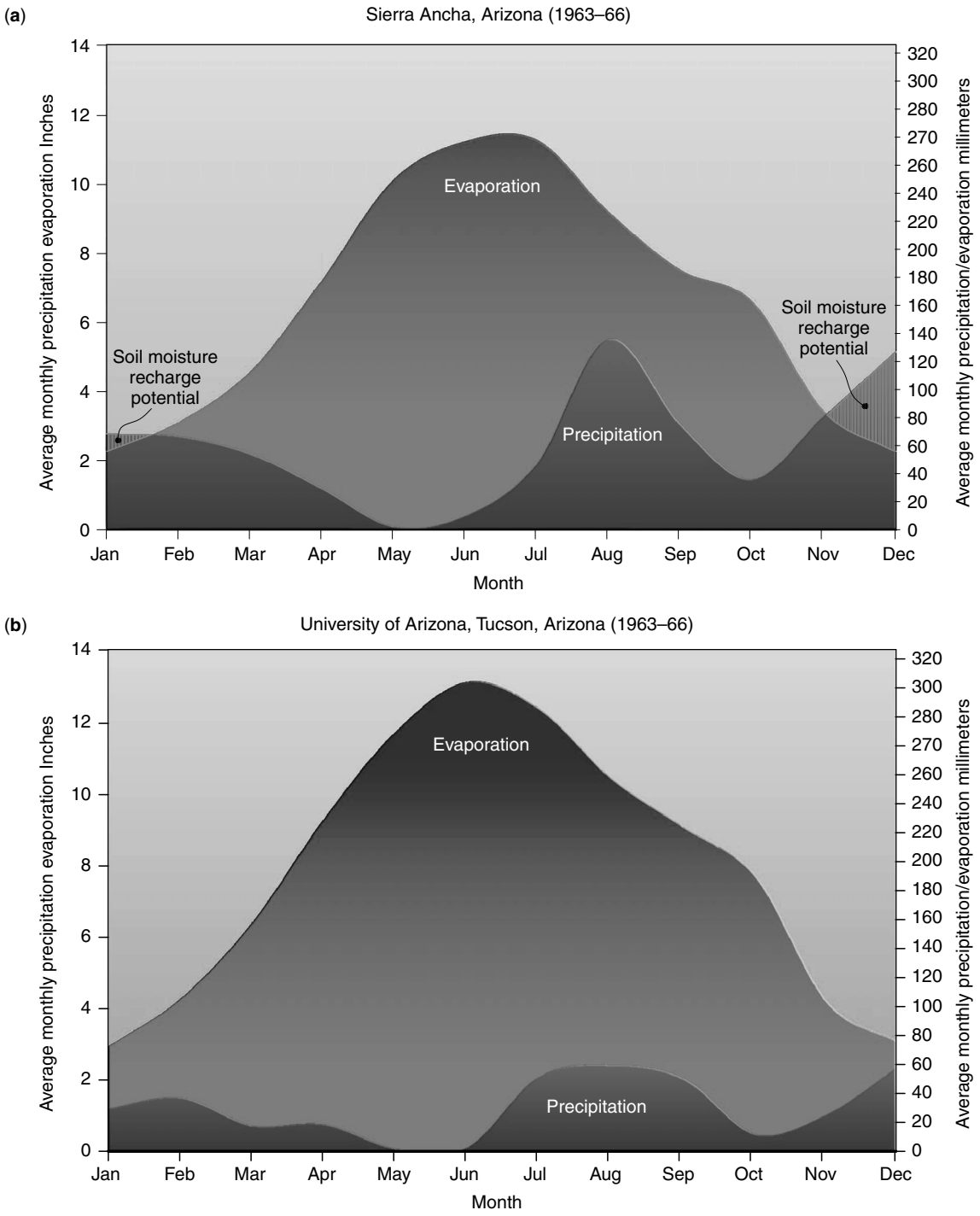


Figure 4. (**a**) Relationships between average monthly precipitation and evaporation at Tucson and Sierra Ancha, Arizona; (**b**) Comparison of soil moisture recharge potential in Tucson vs. Sierra Ancha, Arizona (data from Sellers & Hill, 1974) (Ref. 14).

3. Harshbarger, J.W. (1959). Geohydrology of Arid Lands: Arizona—A Case Study. In: *Arid Lands Colloquia, 1958–1959*. University of Arizona Press, Tucson, AZ. Available: http://alic.arid.arizona.edu/sonoran/documents/harshbarger/alc_geohydrology.html.

4. Sophocleous, M. (Ed.). (1998). *Perspectives on Sustainable Development of Water Resources in Kansas*. Kansas Geological Survey: Bulletin 239. Lawrence, KS.

5. Hevesi, J.A., Flint, A.L., and Flint, L.E. (2002). *Preliminary Estimates of Spatially Distributed Net Infiltration and Recharge for Death Valley Region, Nevada-California*. U.S. Geological Survey: Water-Resources Investigations Report 02-4010.

6. McDonald, J.E. (2002). *Climatology of Arid Lands*. Available: http://alic.arid.arizona.edu/sonoran/documents/alc_climatology_aridlands.html.

7. Long, A. and Estoe, C. (2003). *Mountain-Block Recharge*. Research abstract for work sponsored by SAHRA. Available: http://www.sahra.arizona.edu/research/TA2/2_5.html.
8. Sellers, W.D., Hill, R.H., and Sanderson-Rae, M. (1985). *Arizona Climate, One Hundred Years, 1885–1985*. University of Arizona, Tucson, AZ.
9. Davis, S.N., Campbell, D.J., Bentley, H.W., and Flynn, T.J. (1985). *Ground Water Tracers*. National Ground Water Association, Dublin, OH.
10. Faure, G. (1986). *Principles of Isotope Geology*, 2nd Edn. John Wiley & Sons, New York.
11. Ekwurzel, B. and Einloth, S. (2003). *Quantifying Groundwater Recharge Using ^{32}Si*. Research abstract for work sponsored by SAHRA. Available: http://www.sahra.arizona.edu/research/TA2/2_4.html.
12. Pool, D.R. and Schmidt, W. (1997). *Measurement of Ground-Water Storage Change and Specific Yield Using Temporal-Gravity Method Near Rillito Creek, Tucson, Arizona*. U.S. Geological Survey: Water Resources Investigation Report 97-4125.
13. Jinzhu, M., Ding, L., Jiawu, Z., and Edmunds, W.M. (2003). Groundwater recharge and climatic change during the last 1000 years from unsaturated zone of SE Badain Jaran Desert. *Chin. Sci. Bull.* **48**(14): 1469–1474.
14 Sellers, W.D. and Hill, R.H. (1974). *Arizona Climate, 1931–1972.* University of Arizona Press, Tucson, AZ.

SUB-SURFACE REDOX CHEMISTRY: A COMPARISON OF EQUILIBRIUM AND REACTION-BASED APPROACHES

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INTRODUCTION

The study of subsurface redox chemistry has gained importance because of increased awareness of the relationships between chemical speciation and contaminant behavior in the environment. The oxidation state of a redox component can affect its solubility, sorption to soil, and toxicity. Knowledge of redox processes is therefore fundamental to understanding the fate and transport of organic and inorganic constituents in both pristine and contaminated environments.

Redox reactions involve oxidation, and accompanying reduction, of the reacting species because of transfer of electrons. Such reactions, directly or indirectly, determine the fate and transport of several biologically important elements such as carbon, nitrogen, and sulfur in the soil environment. Elements of environmental significance undergoing redox reactions include heavy metals like lead and zinc, which are multivalent and readily undergo a change in valence.

Redox reactions in natural environments can be biotic or abiotic. Most redox processes encountered in natural aquatic systems are biologically catalyzed or at least indirectly affected by living microorganisms. In subsurface systems, such as groundwater aquifers with microbial activity, the redox state is significantly influenced by microbe-mediated redox reactions. In such environments, a sequence of distinct redox zones can develop depending on the composition of aquifer materials and aqueous constituents and the relative rates of redox reactions and the transport of products or reactants.

Frequently, redox reactions in subsurface environments are evaluated with equilibrium thermodynamics. Although equilibrium thermodynamics is useful for visualizing the potential relationships between the oxidized and reduced phases of various elements, in many cases, redox equilibrium is not established because of the presence of living organisms, dependence of redox transformations on biological catalysis, and the slow kinetics of oxidation and reduction reactions (1). Time spans for attainment of equilibrium for dissolution/precipitation of secondary phases and redox reactions may range from a few hours to years. Many groundwaters are not well posed, and speciation calculations for numerous groundwaters have shown that various redox couples typically exist in a state of disequilibrium. When disequilibrium exists, geochemical model based on equilibrium thermodynamics will provide incorrect speciation results for the redox species. Reliable predictions of solid-phase dissolution/precipitation and redox reactions require knowledge of reaction kinetics. This article presents a comparison of equilibrium and reaction-based kinetic approaches for evaluating subsurface redox chemistry.

MODELING APPROACHES

The two approaches that compute the distribution of chemical species in the subsurface are the kinetic and equilibrium models. Both approaches use the concept of components and species to model systems with multiple chemical reactants. Components are a set of linearly independent chemical entities such that every species can be written as the product of a reaction involving only the components, and no component can be written in terms of components other than itself. For a given system, the set of components is not unique, but once it has been defined, the representation of species in terms of this set of components is unique. The number of components is selected such that it is the minimum number of the set of species necessary to describe the composition of all phases and species in the chemical system.

Equilibrium models focus on the final equilibrium state of a solution composed of several components in a closed system (2). Implicit in this approach is the assumption that the modeled reactions are fast and fully reversible, which results in natural systems with areas where thermodynamic equilibrium has been established, at least locally. Both of the above conditions are frequently violated, as many redox reactions are slow and irreversible. For example, consider the oxidation of organic matter, which is usually an irreversible reaction,

and the diagenesis of sedimentary rock, which occurs over decades. The equilibrium composition of soil systems is generally calculated using two methods—the equilibrium constant method (3) and the free energy minimization technique (4). The equilibrium constant method uses the mass action principle to relate the redox species involved in specific reactions. The equilibrium composition is obtained by solving the mass action relations used along with the mass balance equations for different components. The free energy minimization technique involves combining the chemical potential of each species with the mass balance equation for each component. The equilibrium composition is obtained by minimizing the free energy of the system (5). Of these two methods, the equilibrium composition approach has been more commonly adopted in the models developed to date.

Kinetic formulations, typically used in reactive transport modeling, describe the transformation of redox species using rate expressions for reactions affecting specific redox species. These reactions may include sorption to soil, degradation, dissolution/precipitation, complexation, and volatilization to gaseous phase. Additionally, these reactions may be biotic, thereby requiring an additional consideration of biological growth and accompany organic matter degradation. The kinetic models can be grouped, on the basis of the logic coupling the transport and reaction equations, into two categories: two-step and one-step methods. The two-step methods involve solving the transport equations followed by the chemical reaction equations at each time step, whereas the one-step methods involve incorporating the chemical reaction equation into the transport equation and solving the resulting set of nonlinear equations explicitly or implicitly. The use of the kinetic approach to model redox reactions in groundwater systems is a relatively recent development, and much work is continuing in this area.

Equilibrium Models

The equilibrium models describe multispecies reactive chemical transport based on principles of thermodynamics, and they can describe complexation, sorption to soils, and removal via precipitation in batch and flow through systems at equilibrium. The approaches used by different investigators to model redox processes in groundwater systems can be grouped into four categories (2): effective internal approach, external approach, oxygen fugacity approach, and redox couple approach. The first three approaches assume that the system has achieved thermodynamic equilibrium, whereas the last approach handles redox processes under partial equilibrium conditions.

The effective internal approach (6,7) is based on the principle of conservation of electrons, although free electrons do not exist in the aqueous phase (2). Therefore, a redox reaction involving the loss of an electron through oxidation must be accompanied by a simultaneous reaction involving the gaining of electron through reduction. The sum of the valence states of each species in the system remains constant as chemical redox reactions progress. For redox-sensitive species, their redox states equal their valences.

The external approach (8), unlike the internal approach, considers hypothetical electron activity as an aqueous component. For computational purposes, the redox reactions are considered mathematically equivalent to complexation reactions in which the hypothetical electrons are incorporated as a component (2). Reduction half-reactions involve higher valence species reacting with the hypothetical electrons to form lower valence species. For each set of redox species, the ionic species in the highest oxidation state is chosen as master component and all other oxidation states are formed from it.

The oxygen fugacity approach uses oxygen fugacity as a redox parameter in the system (9). The mass balance equation of oxygen provides an additional equation to solve the system of chemical speciation equations involving redox reactions. The use of oxygen fugacity as a redox potential indicator can be illustrated using the following half-cell reaction for water:

$$2H_2O(l) = O_2(g) + 4H^+ + 4e^- \quad (1)$$

Then the redox potential (Eh) and the oxygen fugacity (f_{O_2}), using the equilibrium constant $K_{O_2(g)/H_2O(l)}$ for the half-reaction, can be related by (10)

$$\log(f_{O_2}) = \left(\frac{4F}{2.303RT}\right) Eh - 4\log\{H^+\} + 2\log\{H_2O(l)\} + \log K_{O_2(g)/H_2O(l)} \quad (2)$$

where the terms within {} represent the activities of the enclosed species.

The fourth concept, called the redox couple approach (6,9), assumes that partial equilibrium conditions prevail in the system. This approach separates each redox couple into two master species that give rise to two mass balance equations. After the complete calculation of chemical speciation, the redox potential is determined from the activities of this couple and its equilibrium constant (2). Redox couples may be preferred for modeling the redox processes if the analytical data for the couples are available. As the subsurface system may have more than one redox couple, the redox couple approach can test whether these redox couples are at equilibrium with each other. The applicability and validity of redox sequence concept can also be tested. If the aqueous solution exists at a single redox potential, the redox sequence concept requires that all redox reactions in the aqueous solution be at thermodynamic equilibrium. Using the concept of redox zones, the dominant redox couple, which controls the redox potential in a given redox zone, can determine the redox potential of the system. The use of redox zones for classifying the subsurface environment is an important concept in the numerical simulation of subsurface redox chemistry.

Kinetic Models

If the reactions are insufficiently fast, because of chemical kinetics or mass diffusion limitations, relative to the macroscopic transport processes affecting solute concentration (e.g., advection, hydrodynamic dispersion), the assumption of thermodynamic equilibrium, or even local

equilibrium, may not apply. In subsurface environments, with the exception of aqueous redox reactions, it is usually valid to model most homogeneous aqueous-phase reactions (including complexation and acid-base reactions) using equilibrium thermodynamics as they are characterized by rapid rates, especially in comparison with subsurface flow. However, increasing evidence suggests that heterogeneous reaction processes (such as adsorption, biodegradation, and precipitation/dissolution) may need to be described by a kinetic model. In a kinetic model for flow-through systems, algorithms have been proposed that integrate the flow processes (advection and dispersion) with the transformation processes. A flow chart that illustrates a typical algorithm adopted for this purpose is presented in Fig. 1.

Various kinetic formulations have been proposed for adsorption, biodegradation, and precipitation of species present in soils. Some common kinetic equations used in the literature for these processes are discussed below.

Adsorption. The kinetic formulations for adsorption to soils include those based on mass transfer, first-order reaction, and nth-order reaction (11).

$$\text{Mass transfer}: \quad \frac{\partial C_s}{\partial t} = \alpha(f(C_w) - C_s) \tag{3}$$

$$\text{First-order reaction}: \quad \frac{\partial C_s}{\partial t} = k_1 \frac{\theta}{\rho_b} C_w - k_2 C_s \tag{4}$$

$$\text{nth-order reaction}: \quad \frac{\partial C_s}{\partial t} = k_1 \frac{\theta}{\rho_b} C_w^n - k_2 C_s \tag{5}$$

where α is a mass transfer coefficient, θ is the soil porosity, ρ_b is the soil bulk density, $f(C_w)$ is some function of the concentration of dissolved chemical, C_w [M/L^3], k_i ($i = 1,2$) are reaction rate constants, and C_s is the mass of chemical sorbed onto the surface of intraparticle pores of the grains per unit mass of the grains (dimensionless).

Biodegradation. The primary microbial redox reactions typically observed in subsurface systems are given in Table 1. The most energetically favorable of these

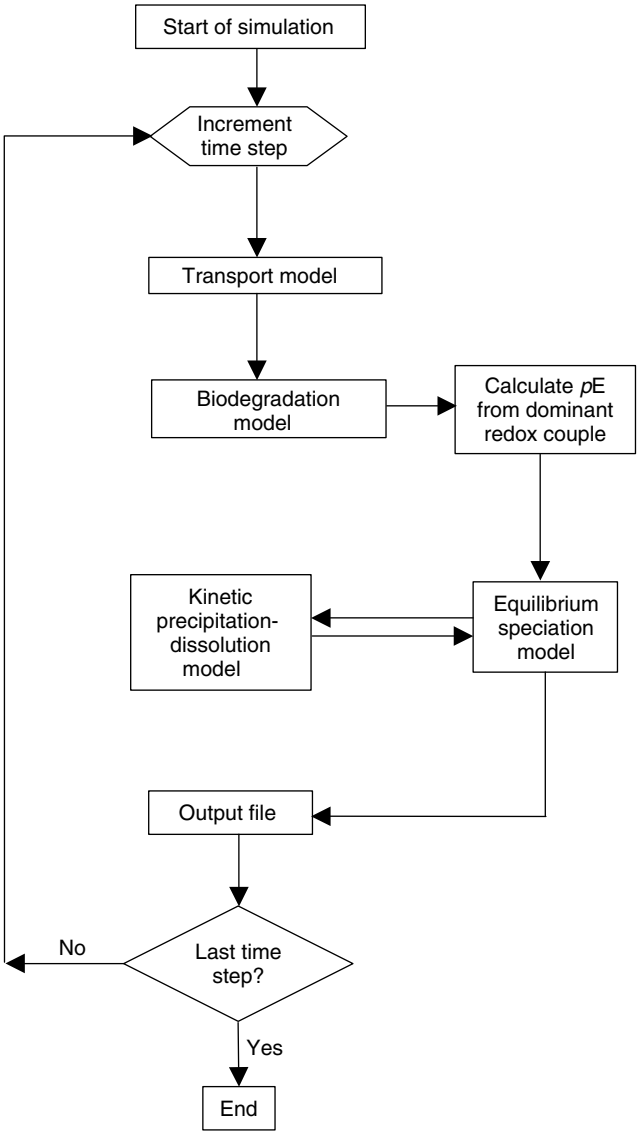


Figure 1. A typical algorithm for kinetic redox modeling in a flow through system.

Table 1. Primary Microbe Mediated Redox Reactions in Subsurface Environments

Redox Reactions	ΔG^o (kcal/mol) (pH = 7)
Aerobic respiration, oxygen reduction $CH_2O + O_2 \rightarrow CO_2 + H_2O$	−120
Denitrification $5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 7H_2O + 2N_2$	−114
Manganese (manganic) reduction $CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O$	−81
Iron (ferric) reduction $CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O$	−28
Sulfate reduction $2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O$	−25
Methanogenic processes $CH_3COOH \rightarrow CH_4 + CO_2$	−22

Table 2. Kinetic Formulations for Ion Precipitation

Model	Rate Equation	Source
Davies and Jones Model	$R = sk\gamma^2\left(\{Ca^{+2}\}^{1/2}\{CO_3^{-2}\}^{1/2} - \frac{K_{sp}^{1/2}}{\gamma}\right)^2$ k = rate constant, s = surface area of the crystal, K_{sp} = solubility product of $CaCO_3$, and γ = divalent ion activity coefficient calculated using the Davies equation.	Inskeep and Bloom (13)
Empirical Model	$R_P = sk_p(\Omega - 1)^n$ $R_D = sk_D(\Omega - 1)^n$ Ω = disequilibrium ratio = $\{Ca^{+2}\}\{CO_3^{-2}\}/K_{sp}$ k_d and k_p = rate constants for dissolution and precipitation, respectively, and n = reaction order.	Inskeep and Bloom (13)
House Model	$R = k((\{Ca^{+2}\}\{CO_3^{-2}\})^{1/2} - K_{sp}^{1/2})^2$	Van Langerak et al. (15)
Nancollas and Reddy Mechanistic Model	$R = sk\gamma^2\left(\{Ca^{+2}\}\{CO_3^{-2}\} - \frac{K_{sp}}{\gamma^2}\right)$	Inskeep and Bloom (13)
Zhang and Dawe Model	$R = k\left(\left(\frac{\{Ca^{+2}\}\{CO_3^{-2}\}}{K_{sp}}\right)^{0.5} - 1\right)^n$	Zhang and Dawe (16)

reactions is aerobic respiration, followed by, in order of decreasing free energy yield, denitrification, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis. The differences in energy yields of these reactions may lead to physical separation (spatial or temporal) of the zones in which each reaction dominates. The rates of reduction of the terminal electron acceptor and the corresponding oxidation of organic substrate are usually represented by zero-order, first-order, and multiple Monod-type expressions. Application of Monod rate expression is justified when the organic compound of interest acts as a primary energy substrate for the microbial community. Assuming an absence of diffusional resistance biodegradation of the substrate and microbial growth in soils can be represented by the following system of equations using the multiple Monod kinetics (12):

$$\frac{\partial S}{\partial t} = -\frac{\mu_{max}}{Y}\frac{S}{K_s + S}\frac{C_{w,ea}}{K_{ea} + C_{w,ea}}\left(X_a + \frac{\rho_b X_s}{\theta}\right) \quad (6)$$

$$\frac{\partial X_w}{\partial t} = \mu_{max}\frac{S}{K_s + S}\frac{C_{w,ea}}{K_{ea} + C_{w,ea}}X_w - K_{dec}X_w - K_{att}X_w + \frac{\rho_b K_{det}X_s}{\theta} \quad (7)$$

$$\frac{\partial X_s}{\partial t} = \mu_{max}\frac{S}{K_s + S}\frac{C_{w,ea}}{K_{ea} + C_{w,ea}}X_s - K_{dec}X_s - K_{det}X_s + \frac{\theta K_{att}X_a}{\rho_b} \quad (8)$$

where S is the substrate concentration in the bulk (mobile) fluid (M/L^3), X_w is the aqueous-phase biomass concentration (M/L^3), X_s is the solid-attached biomass concentration (M/M), $C_{w,ea}$ is the concentration of terminal electron acceptor (M/L^3), K_{dec} is the first-order endogenous decay coefficient (1/T), K_{att} is the biomass attachment coefficient (1/T), K_{det} is the biomass detachment coefficient ($1/T$), μ_{max} is the maximum specific growth rate of the biomass ($1/T$), Y is the yield coefficient for the biomass (cell mass produced per mass of substrate consumed), and K_s and K_{ea} are the saturation constant for substrate and electron acceptor (M/L^3), defined as the concentration for which the specific growth rate is equal to $\mu_{max}/2$.

Precipitation and Dissolution. Precipitation and dissolution processes have often been described by chemical reactions whose rate is proportional to the deviation from equilibrium (13,14). One such kinetic formulation can be written as follows:

$$\frac{dC_j}{dt} = -a_j k\left(\prod_{j=1}^{N}\{u_j\}^{a_j} - K_{sp}\right) \quad (9)$$

where k is the precipitation rate coefficient, N is the number of components forming the solid precipitate, C_j is the dissolved concentration of component j, $\{u_j\}$ is the dissolved free ion activity of component j, a_j is the stoichiometric coefficient of the jth component of the solid, and K_{sp} is the equilibrium solubility product for the solid. Several similar formulations for ion precipitation, using $CaCO_3$ as the precipitating mineral, are presented in Table 2.

MODEL LIMITATIONS AND APPLICABILITY

Geochemical models suffer from inadequacies in two main areas (17):

1. Violation of (local) equilibrium assumption in many environmental systems. Although such processes can be modeled using kinetics, rather than equilibrium, our current knowledge of kinetic rates and mechanisms is primitive.
2. The knowledge of adsorption of solutes on mineral surfaces, an important environmental process, is also at an early stage of understanding.

The "geochemical (and hydrological) models of natural and engineered systems at the present time are, at best, approximations to the real situation. To meet various regulatory requirements, these approximations, and predictions based on these approximations, must be made, and there is no better way to proceed than to construct models based on fundamental science. To this extent, geochemical and hydrological modeling is useful" (17).

BIBLIOGRAPHY

1. Sigg, L. (2000). Redox potential measurements in natural waters: Significance, concepts and problems. In: *Redox—Fundamentals, Processes and Applications*. J. Schüring, H.D. Schulz, W.R. Fischer, J. Böttcher, and W.H.M. Duijnisveld (Eds.). Springer-Verlag, Berlin, pp. 1–12.
2. Liu, C.W. and Narasimhan, T.N. (1989). Redox-controlled multiple-species reactive chemical transport—1. Model development. *Water Resour. Res.* **25**(5): 869–882.
3. Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. (1990). *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. Environ. Res. Lab., USEPA, Athens, GA.
4. Mattigod, S.V. (1995). Chemical equilibrium and reaction models; Applications and future trends. In: *Chemical Equilibrium and Reaction Models*. R.H. Loeppert, A.P. Schwab, and S. Goldberg (Eds.). SSSA Special Publication Number 42, Soil Science Society of America, Madison, WI, pp. 1–5.
5. Waite, T.D. (1989). Mathematical modeling of trace element speciation. In: *Trace Element Speciation: Analytical Methods and Problems*. R.H. Loeppert et al. (Eds.). CRC Press, Boca Raton, FL, pp. 117–184.
6. Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N. (1980). *PHREEQE: A Computer Program for Geochemical Calculations*. U.S. Geol. Surv. Water Resour. Invest., PB81–167801.
7. Walsh, M.P., Bryant, S.L., Schecter, S.R., and Lake, L.W. (1984). Precipitation and dissolution of solids attending flow through porous media. *AICHE J.* **30**(2): 312–328.
8. Carnahan, C.L. (1986). *Simulation of Uranium Transport with Variable Temperature and Oxidation Potential: The Computer Program THCC, Rep. 21639*. Lawrence Berkeley Lab., Berkeley, CA.
9. Wolery, T.J. (1983). *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations, User's Guides and Documentation, Rep. UCRL-53414*. Lawrence Livermore National Lab., Livermore, CA, p. 191.
10. Stumm, W. and Morgan, J.J. (1981). *Aquatic Chemistry*. 2nd Edn. Wiley-Interscience, New York, p. 780.
11. Habbar, A., Kolditz, O., and Zielke, W. (2002). New geochemical simulator rockflow-RTM: development and benchmarking. In: *Geochemical Processes, Conceptual Models for Reactive Transport in Soil and Groundwater*. W-VCH Verlag Gmbh & Co. KGaA, Weinheim, Germany, pp. 95–114.
12. Islam, J. and Singhal, N. (2002). A one-dimensional reactive multi-component landfill leachate transport model. *Environ. Model. Softw.* **17**: 531–543.
13. Inskeep, W.P. and Bloom, P.R. (1985). An evaluation of rate equations for calcite precipitation kinetics at pCO_2 less than 0.01 atm and pH greater than 8. *Geochim. Cosmochim. Acta* **49**: 2165–2180.
14. Smith, S.L. and Jaffé, P.R. (1998). Modeling the transport and reaction of trace metals in water-saturated soils and sediments. *Water Resour. Res.* **34**: 3135–3147.
15. Van Langerak, E.P.A. et al. (2000). Impact of location of CaCO3 precipitation on the development of intact anaerobic sludge. *Water Res.* **34**(2): 437–446.
16. Zhang, Y. and Dawe, R. (1998). The kinetics of calcite precipitation from a high salinity water. *Appl. Geochem.* **13**(2): 177–184.
17. Zhu, C. and Anderson, G. (2002). *Environmental Applications of Geochemical Modeling*. Cambridge University Press, Cambridge, UK, p. 284.

REGIONAL FLOW SYSTEMS

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DEFINITION

A **groundwater flow system** is a three-dimensional entity that has the following components:

—a recharge area where water enters the flow system
—a discharge area where water exits the system
—boundary conditions and physical dimensions

When dealing with flow systems, we often differentiate between **local, intermediate,** and **regional** flow systems. The distinction is primarily a matter of scale; local flow systems cover a much smaller area than intermediate systems, which in turn are smaller than regional systems. **Regional groundwater flow systems** generally involve a large area (10^1–10^2 km), and usually contain several local flow systems, resulting in areas of local recharge as well as springs or other discharge features within the larger system. Often several different aquifers and geologic formations will be connected by a larger regional groundwater system.

Examples of regional flow systems are shown in Fig. 1.

The following is a discussion of each of the three components.

RECHARGE

Recharge refers to the water that is entering a groundwater system. Areas where recharge is occurring are called **recharge areas** or **recharge zones**. There are several different ways that recharge enters a flow system. Recharge can enter a flow system through direct infiltration of precipitation on the outcrop, or by infiltration through the beds of losing streams or reservoirs. In some parts of the world, especially arid regions, infiltration of storm runoff through the beds of intermittent streams is the dominant form of recharge. Water can also enter a flow system through interformational flow, which is usually in the form of flow through leaky confining layers where water is drawn in by drawdowns at wells, or where

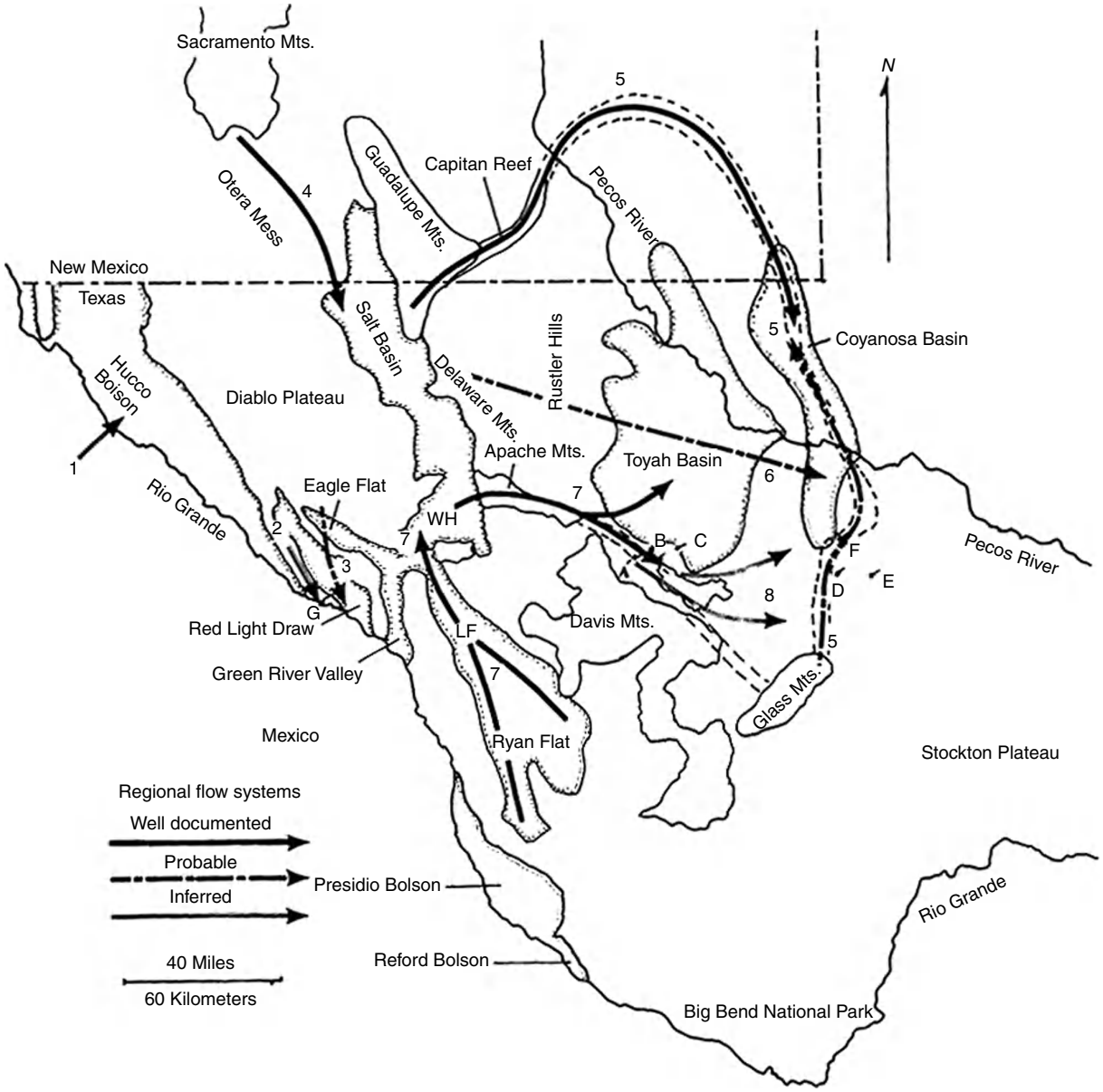


Figure 1. Regional groundwater flow systems of West Texas (after Reference 1).

underlying aquifers have significant overpressuring and are forcing water upwards.

For modeling and other research purposes, recharge is generally considered as some percentage of precipitation. Annual recharge rates in most aquifers are usually between 1–10% of annual precipitation rates. Recharge rates are difficult to quantify; many methods involve measuring precipitation and performing a water balance by quantifying all the other fluxes of water (i.e., surface runoff, evaporation, transpiration) at the surface.

DISCHARGE

There are several ways that water discharges from a flow system. These include discrete discharge to a spring or seep, discharge into a gaining stream or lake, interformational flow, or pumping from a well. In some arid regions, direct evaporation from a shallow water table is the primary mechanism for discharge from the flow system.

Discharge can also be hard to quantify, especially in areas dominated by well pumping or evaporation. Interformational flow is generally small compared to the other mechanisms. Springs and gaining streams can be gauged, and changes in flow across a certain area can be attributed to either recharge or discharge.

BOUNDARY CONDITIONS

Flow systems are three-dimensional bodies that have boundaries. We can consider two basic types of boundaries, or **boundary conditions**, that can characterize the limits of flow systems.

A **no-flow boundary** has a hydraulic gradient of zero ($h/x = 0$), and therefore no flow across the boundary. No-flow boundaries can be actual physical boundaries, such as where permeable aquifer units are in contact with low permeability bedrock at a fault (Fig. 2). A no-flow boundary also exists where flow lines are parallel, creating a **symmetry boundary** (Fig. 3). Modelers often use symmetry boundaries to constrain numerical groundwater models of aquifers. Locally high water levels can create a type of no-flow boundary called a **groundwater divide** (Fig. 4). At a groundwater divide, water flows away from the divide on either side (similar to surface runoff at a drainage divide).

A **constant-head boundary** is one characterized by a set of hydraulic heads that do not change. A nonflowing body of water, such as a lake, pond, or ocean, can create a constant-head boundary (Fig. 5). In this case, the shore of the body of water represents a single **equipotential line** (or line of constant head) in the aquifer, and flow is perpendicular to the shoreline (either into the aquifer from the surface waterbody, or vice versa). A stream can also act as a constant-head boundary (Fig. 6). In a stream boundary, the actual heads will vary along the stream gradient, but each point is considered constant. In this case, each point along the stream gradient represents a point on an equipotential.

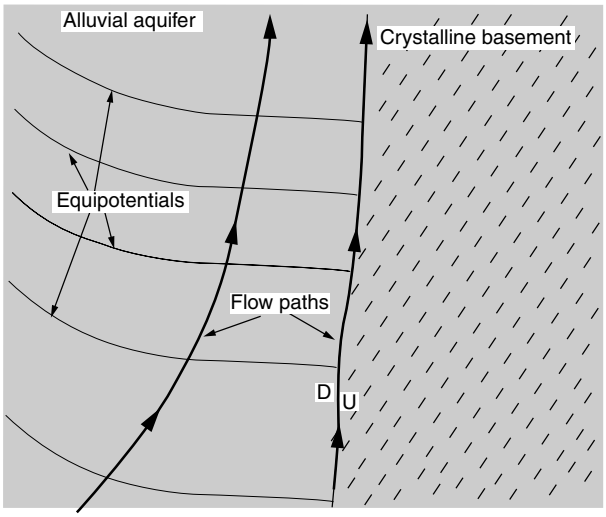


Figure 2. No-flow boundary created by juxtaposition of permeable alluvial sediments and low-permeability crystalline bedrock.

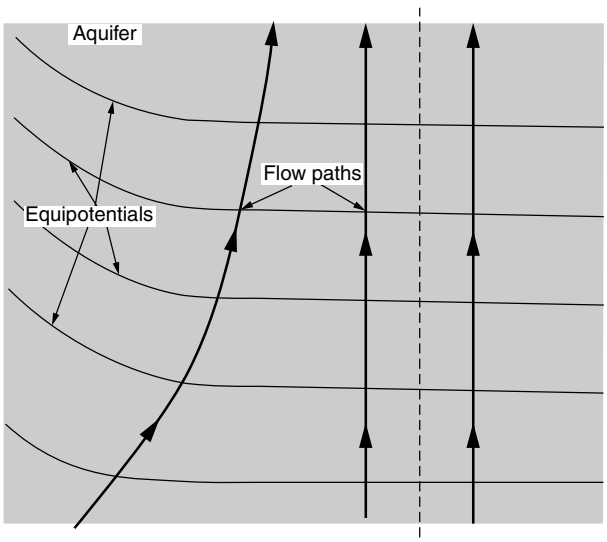


Figure 3. Parallel flow lines create a no-flow symmetry boundary.

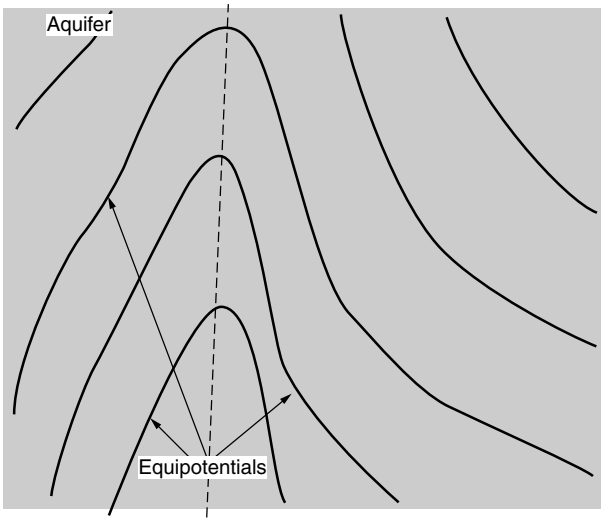


Figure 4. Groundwater divide produced by high water levels.

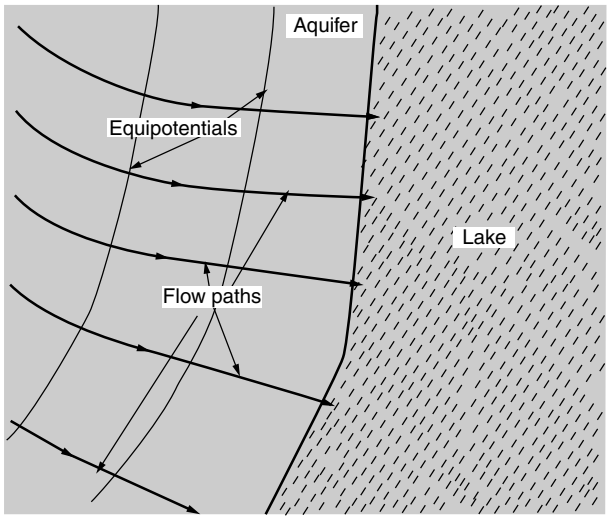


Figure 5. Constant-head boundary at a nonflowing body of water (in this case, a lake).

CHARACTERISTICS OF REGIONAL FLOW SYSTEMS

Water Chemistry

Groundwater in regional flow systems can have residence times ranging from a few decades to 10^4 years. Long residence times usually results in high concentrations of dissolved ions, and regional flow systems frequently

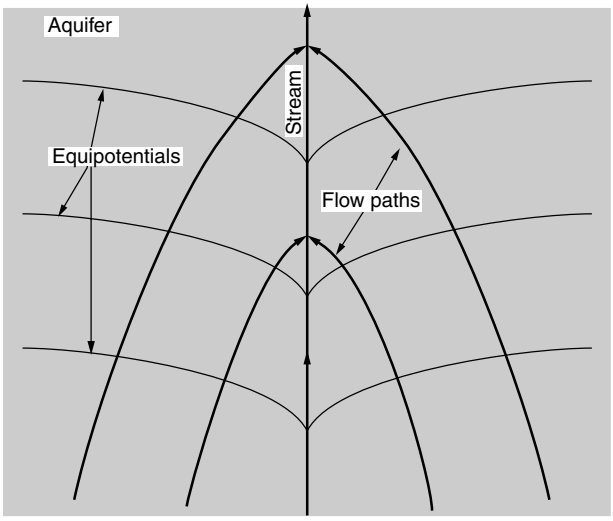


Figure 6. A stream constant-head boundary.

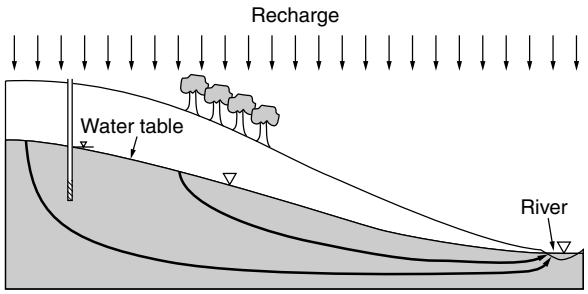


Figure 7. Cross section of water table aquifer showing the relationship between topography and the orientation of the water table.

have total dissolved solids (TDS) concentrations greater than 2000 ppm. The exact distribution of dissolved ions in the water is controlled by the minerals encountered in the subsurface; however, groundwater generally tends to evolve along flow paths toward higher concentrations of sodium and chloride, (2), and groundwater in regional flow systems tends to be dominated by NaCl type waters. Water samples are usually close to saturation with respect to common carbonate (e.g., calcite, dolomite) and sulfate (e.g., gypsum, barite) minerals. Water temperatures are generally higher than average annual air temperatures due to geothermal heating; the difference in temperature is directly related to residence time.

Spring Discharge

Springs in regional flow systems tend to exhibit relatively constant discharge, chemistry, turbidity, and temperature. These springs frequently have both local and regional flow components. These springs respond to local storms with increases in discharge and turbidity and decreases in TDS and temperature but also have a fairly constant baseflow discharge sourced from the regional systems (3). Ecosystems in springs sourced by regional flow systems often have restricted endemic organisms in or near their outlets, and these spring ecosystems often support listed endangered species.

Relationship Between Topography and Flow Systems

King (4) and Hubbert (5) noted the relationship between topography and groundwater flow patterns in unconfined aquifers. Both noticed that the water table tends to be a subdued replica of the topography (Fig. 7), and Hubbert (5) suggested that topography can control flow patterns so that high elevations are recharge areas and low elevations are discharge areas (Fig. 8).

Toth (6) and Freeze and Witherspoon (7) developed computer models that simulated the effects of topography on flow systems. Both of their models supported the conclusions of King and Hubbert. These models also indicated that sinusoidal topography can result in the formation of smaller local flow systems with local recharge and discharge areas within larger regional systems.

BIBLIOGRAPHY

1. Sharp, J.M., Jr. (2001). *Regional Groundwater Flow Systems in Trans-Pecos Texas in Aquifers of West Texas*. R.E. Mace, W.F. Mullican III, and E.S. Angle (Eds.). Texas Water Development Board, Austin, TX, Report 356, Ch. 4, pp. 41–55.
2. Back, W. (1960). Origin of hydrochemical facies of groundwater in the Atlantic Coastal Plain. *Proc. Int. Geol. Congr.*, Copenhagen, pp. 87–95.
3. Uliana, M.M. and Sharp, J.M., Jr. (2001). Tracing regional flow paths to major springs in Trans-Pecos Texas using geochemical data and geochemical models. *Chem. Geol.* **179** (1–4): 53–72.
4. King, F.H. (1899). *Principles and Conditions of the Movements of Groundwater*. U.S. Geological Survey 19th Annual Report, pt. 2, pp. 59–294.

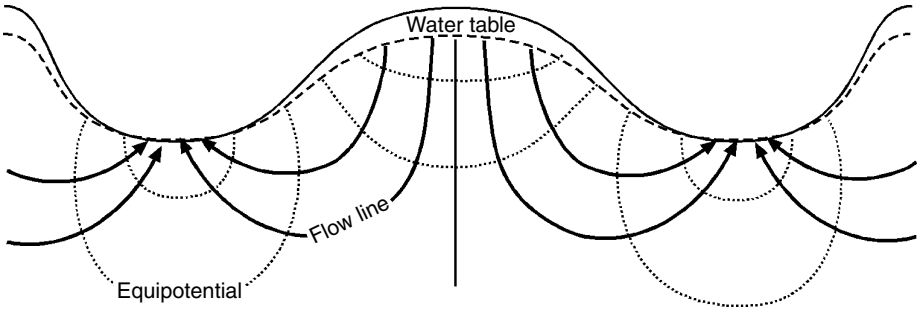


Figure 8. Flow pattern controlled by topography (after Reference 5).

5. Hubbert, M.K. (1940). The theory of groundwater motion. *J. Geol.* **48**: 785–944.
6. Toth, J. (1963). A theoretical analysis of groundwater flow in small drainage basins. *J. Geophys. Res.* **67**: 4375–4387.
7. Freeze, R.A. and Witherspoon, P.A. (1967). Theoretical analysis of regional groundwater flow. II: Effect of water table configuration and subsurface permeability variations. *Water Resour. Res.* **2**: 641–656.

GROUNDWATER REMEDIATION BY INJECTION AND PROBLEM PREVENTION

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A variety of interesting problems can occur in the subsurface as the result of efforts to remediate groundwater. With few exceptions, groundwater remediation requires either an *in situ* injection of reactive chemicals or groundwater recovery, treatment, and disposal. The reinjection of treated water or the placement of chemicals in the subsurface used to treat contaminants can cause unintended subsurface geochemical conditions that may create new contamination issues or impact *in situ* transport properties.

Storm drains, sanitary sewers, and surface streams have been and will continue to be receptors for treated water. However, permit requirements and volume based user fees often contribute significantly to the cost of groundwater remediation systems.

In rural settings, storm or sanitary drains may not be available, and increasingly in urban settings publicly owned treatment works (POTWs) are reluctant (or unable) to accept recovered groundwater. In urban settings, water quality is not the issue; rather, it is stress on the hydraulic capacity of the POTW system. In these instances, the most viable option for water discharge is reinjection.

REINJECTION ISSUES

Treated water may meet the standards for reinjection based on the chemicals analyzed. It is becoming more apparent, however, that there could be contaminants in treated water that are not analyzed. Methyl tertiary butyl ether (MTBE) is a fuel oxygenate used in gasoline. In some pump and treat systems, the MTBE is removed and the MTBE is below the laboratory reporting level. If tertiarty butyl ether (TBA), a breakdown product of MTBE, is not analyzed, it could be present in the treated water and discharged to a stream, storm drain, or into a reinjection well, spreading an otherwise unanalyzed contaminant into the environment. Overlapping plumes of gasoline and undetected perchlorate could also create a new problem if the pumped water is treated for gasoline and then discharged to the storm drain or into the subsurface, with the undetected perchlorate. Lastly, another example is 1,4-dioxane, an extremely soluble hydrocarbon similar in transport properties to MTBE that was used as a stabilizer in percent concentrations for some chlorinated solvents.

Reinjection can be less expensive (at least to set up) than permit fees and flow based discharge fees. As such, it is sometimes implemented even when other options are available. Lastly, an injection regime may be part of a program to obtain hydraulic control of a site.

The most common source of problems for groundwater recharge systems is plugging. Any recharge system will eventually foul, and the design of the system should provide for that eventuality. The goal is to minimize the rate at which the fouling occurs. The purpose here is to examine some of the pitfalls that can occur when the recharge option is selected. Without exception, it is much easier to prevent damage from occurring than it is to remedy a damaged condition.

SUSPENDED SOLIDS

Suspended solids are a major cause of plugging. In most instances, solids will collect within the first 0.5 in. of a well pack. At a flow rate of 10 GPM and total suspended solids (TSS) at 5 mg/L, approximately 0.66 lb of solids will be introduced per day. In a year, this would total 240 lb, or about 2 ft^3 of solids, which would be capable of fouling about 100 ft^2 of injection face (30 linear feet of a 1-ft diameter well). Generally, infiltrated water must have a TSS level <2 mg/L in order to maintain adequate infiltration rates over a long period.

AIR

Entrained air can impact recharge capacity through simple physical blockage or through what is termed the "Jamin effect." The Jamin effect results when capillary forces act on small advective channels that contain alternating air bubbles and water. These channels are then capable of responding to finite pressure gradients without allowing fluid flow, meaning that surging an impacted well will not displace the entrained air. Once in a formation, air can be extremely difficult to remove.

The problem is particularly exacerbated by allowing injected water to fall into a well (rather than piping below the groundwater surface), thus mixing with air that can be transported into the adjacent formation. Saturated zone *in situ* bioremediation systems using injected air or hydrogen peroxide can also be susceptible to air entrainment problems.

Injection of water that is cooler than the receiving aquifer will cause degassing as the two waters mix. The solubility limit of oxygen in pure water at 40 °F is 13.1 mg/L; at 50 °F it is 11.3 mg/L. Over a 24-h period, at a flow rate of 10 GPM, approximately 0.20 lb of oxygen would degas upon contact with the formation water, which represents about 2.5 ft^3 of gas entrained in the pore spaces directly adjacent to the injection zone (as depth increases the gas volume would decrease). Assuming a 1-ft diameter

well, and that entrainment of air through a 1-ft section of the formation would decrease injection efficiency through the Jamin effect, a well with a 30-ft screened interval would have flow inhibited within 10 d.

MICROBIAL FOULING

To prevent microbial growth, care must be taken to ensure there is no source of carbon or nutrients (nitrogen and phosphorus) in the injected water. The carbon content of water should be evaluated through a total organic carbon (TOC) analysis, not just contaminants of concern (such as BTEX). Bacteria will exploit any carbon resource, not just those under regulatory discharge limits. TOC must be <10 mg/L to ensure that reasonable infiltration rates can be maintained over cost effective durations.

In instances where the groundwater is iron or sulfate rich, iron or sulfate reducing bacteria may also create problems.

CHEMICAL INCOMPATIBILITY

Chemical reactions between the injected and formation water are common. Typical reactions result in the formation of precipitants in the mixing zone. These reactions are complex and temperature sensitive. Differences in redox potential (usually due to dissolved oxygen levels) and carbonate chemistry are most often responsible for problems.

When injecting into clay-rich soils, ionic reactions can also come into effect. Clay particles can be dispersed (to cause plugging deeper in the formation) or swell when exposed to recharge water with ionic character different from the formation water. These reactions can be induced through exposure to water of different ionic concentration or through exposure to water with different types of cations present at any concentration (e.g., water discharged from a caustic or lime precipitation system).

Iron precipitation can be a serious problem in groundwater systems that are high in soluble ferrous iron. Iron present in recovered water may precipitate forming TSS that must be removed before reinjection. However, iron precipitation is also possible in the mix zone if the redox conditions of the recharge water are significantly different from the formation water.

OVERDEVELOPMENT

Lastly, injection efficiency has been observed to be reduced by as much as 50% from compaction of the gravel/sand pack around a well through overzealous surging during well development, pumping tests, or redevelopment performed to alleviate some of the problems described above, which is a common problem. In this instance, more is *not* better; well development should be judiciously applied based on the composition of the pack around the casing.

Impact from all of the above can be minimized in an injection system during the design stage of a project. It requires a thorough evaluation of the chemistry of the discharge that includes determination of ionic character, redox condition, chemical composition, and temperature. The same must be done for the formation water. Potential reactions and problems should be evaluated by a competent geochemist. It may be determined that a different method of water treatment would be more cost effective (i.e., eliminating air stripping to prevent precipitation reactions driven by elevated dissolved oxygen).

EH/PH CHANGES

A variety of *in situ* injection processes change Eh/pH conditions. Chemical oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2) release oxygen as part of the reaction. Enhanced bioremediation using oxygen (O_2) diffusion, air sparging, or magnesium peroxide (MgO_2) also are designed to take an anaerobic reducing environment and convert it into an aerobic environment. For example, a petroleum hydrocarbon being treated using ozone in the anaerobic core of a plume would change Eh/pH conditions in the treatment area.

These changes have the effect of changing the valence states of certain metals, such as chromium. If high concentrations of chromium are present naturally or from a release, and there are manganese containing minerals present in the mineral matrix, the formerly reduced chromium compound can be oxidized and converted from chromium (3+) [Cr(III)] to chromium (6+) [Cr(VI)], a toxic and mobile form of chromium. Normally, the oxidized chromium would move with the groundwater downgradient to naturally reducing conditions, which should restore the original Eh/pH. However, when a water supply well or vulnerable surface water is located close to the *in situ* treatment area, there may not be enough of a distance and retention time for the reconversion of Cr(VI) back to Cr(III). One option is to create an Eh/pH restoration treatment wall immediately downgradient from the initial treatment zone. The Eh/pH restoration wall should be constructed to place the liquids (molasses, corn syrup), gases (propane), or solids (nanoscale iron particles) into the aquifer through trenches, wells, ports, or other delivery means that could be supplied on a constant basis to restore the Eh/pH of the environment. After all the petroleum hydrocarbon treatment is performed in the center of the hydrocarbon plume treatment area, the Eh/pH restoration wall could be shut down after the last of the remaining oxidized water has passed the Eh/pH restoration wall. Changing Eh/pH requires redox reaction kinetics that may favor certain reactions. For example, it is much easier to convert Cr(VI) to Cr(III) than the reverse.

An oxidizing Eh/pH treatment wall would be required if originally oxidizing conditions were present and reducing chemicals (carbon sources) were used for anaerobic treatments of chlorinated solvents such as perchloroethene (PCE) or trichloroethene (TCE), for example. In this case the reduced conditions might convert the more stable and less toxic arsenic (5+) to the toxic arsenic (3+) that is soluble under normal pH conditions. A further exacerbation of potential arsenic problems occurs under reducing conditions when some portion of the ferric iron in the mineral matrix is converted to ferrous iron. The ferrous iron is soluble and the process will release any arsenic

that had previously adsorbed to the iron oxides, which act as a major redardation sink for arsenic in groundwater systems. An oxidizing Eh/pH treatment wall in an area of high arsenic would supply oxygen to restore arsenic to As(V) and oxidize ferrous iron to the arsenic removing ferric oxide species, lowering the potential of creating a new subsurface problem.

Proper bench testing, chemical evaluations, and rigorous planning to prevent future treatment problems is less costly and time consuming than encountering the mistakes after developing a poorly designed project.

GROUNDWATER REMEDIATION: *IN SITU* PASSIVE METHODS

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Passive *in situ* remediation technologies (PIRT) use a variety of physical, chemical, or biological processes that act without significant human intervention in the subsurface to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. Passive remediation uses the natural movement of water to disperse treatment chemicals or to move contaminated groundwater through a treatment zone.

In many early EPA Superfund site remediations, slurry walls were used. Slurry cutoff walls are a simple passive treatment method to isolate contaminants or prevent migration. Frequently, a pump and treat system is used with a slurry cutoff wall to to maintain groundwater pressure on the wall and to prevent groundwater from rising above and around the wall. Slurry walls are generally constructed of bentonite, polyethylene, or sheet piling. Project depths rarely exceed 15 meters.

PERMEABLE REACTIVE BARRIERS

Early examples of passive remediation are permeable reactive barriers (PRB) (Fig. 1). Within these passive treatment zones are included funnel and gate treatment technologies. The funnel and gate system is a hybrid of both low permeability barriers and a permeable treatment system. Originally proposed by the University of Waterloo, it is most widely used with zero-valent iron to degrade chlorinated volatile organic compounds (VOCs) such as trichloroethylene (TCE) and daughter products. These types of treatment systems are generally less than 15 meters deep.

Deeper treatment methods using drilling rigs and directional high-pressure fracturing technologies developed for depths exceeding 100 meters to inject treatment chemicals have been pioneered by GeoSierra. These deeper PRBs are generally used with zero-valent iron as the treatment material, which is injected under high pressure to form a fracture wall between closely spaced deep boreholes. The passive treatment wall is designed to be perpendicular to groundwater flow.

BIOREMEDIATION

Phytoremediation, another passive method, uses specific plants and trees to extract specific contaminants from soil and groundwater. Some of the targeted contaminants include heavy metals and radionuclides. Common plants used in phytoremediation include mustard plants as well as poplar trees. Phytoremediation has great promise and will increase in acceptance as more case studies are completed. An overview article documents some of the potential of phytoremediation (2).

For passive and semipassive methods of remediation, aerobic and anaerobic bioremediation offer options for a variety of contaminants. For low permeability sediments (clay and silts), the molecules of the dissolved gases (oxygen, propane, and others) and the microbes are much smaller than the pore throat sizes of the sediments, which allows enhanced bioremediation to be considered in geologic settings where other more active technologies such as dual-phase extraction would not be feasible.

Aerobic *in situ* enhanced bioremediation is a cost-effective way to treat residual contamination in groundwater from surface spills or leaking underground tanks of hydrocarbon fuels such as gasoline, diesel, kerosene, motor oil, jet fuels, and used oil. Hydrocarbon degrading microbes will break hydrocarbons down to carbon dioxide and water if the right amounts of oxygen and nutrients are available.

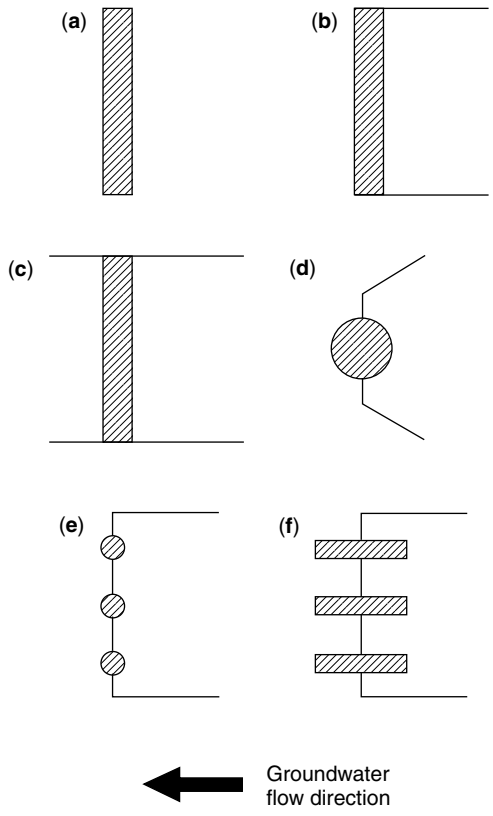


Figure 1. Possible geometries of passive treatment walls: (**a**) continuous trench, (**b**) with lateral hydraulic control, (**c**) with lateral hydraulic control and downgradient lateral barriers, (**d**) with a single treatment caisson, (**e**) with multiple treatment caissons, (**f**) with parallel alleys (1).

Typically, the aerobic microbial degradation of hydrocarbons is limited by the amount of oxygen present. Oxygen can be added in a variety of ways: from peroxygens such as magnesium peroxide, sodium peroxide, calcium peroxide, potassium permanganate, and hydrogen peroxide (H_2O_2). Oxygen sources as gases include oxygen (O_2) and ozone (O_3). Higher concentrations of oxidizers such as hydrogen peroxide and ozone would temporarily destroy microbial colonies, creating a barren zone that might last for a few weeks. Ultimately, the aerobic microbial colonies would move back into barren zones from adjacent areas and reestablish themselves with the benefit of significantly higher oxygen levels.

Anaerobic *in situ* enhanced bioremediation is used for chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE). The same process can be used to reduce heavy metals, nitrates, and perchlorate. Nitrates are generated by agricultural processes and runoff from fertilizers. Perchlorate is an ingredient in rocket fuels and flares. For anaerobic processes, remediation requires carbon sources. Molasses, cheese whey, corn syrup, milk, glucose, as well as hydrogen, methane, and propane have been used. Reductive bioprocesses have been well documented (3).

REMEDIAL CRITERIA FOR DEVELOPING NATIONS

One of the main challenges in assessing and remediating petroleum hydrocarbon contaminated sites is developing an appropriate cost-effective remediation strategy, especially for nonindustrialized countries. For developing nations, technologies would have to match local geologic conditions, use readily available materials and resources, be performed *in situ*, require a minimal amount of equipment and little or no power, have no time constraints, and meet local and national regulatory guidelines. In addition, the technologies would require training that would allow local contractors to perform the work proficiently.

ENHANCED BIOREMEDIATION

Natural attenuation consists of unenhanced physical, chemical and biological processes that limit the migration and reduce the concentration of contaminants in the subsurface (4). The most important process in petroleum hydrocarbon degradation is aerobic bioremediation because it can destroy a large percentage of the hydrocarbon contaminant mass. Destruction occurs because of aerobic bacteria that use oxygen to oxidize hydrocarbons (reduced materials) to obtain energy. Aerobic biological degradation of hydrocarbon fuels and selected other organic compounds have been well documented (3,5–7). Enhanced bioremediation is the process of supplying an appropriate amount of oxygen, nutrients, and other amendments, if needed, to the subsurface to enhance the biodegradation process, significantly increase remediation effectiveness, and decrease treatment time.

Gasoline is a mixture of numerous compounds, including benzene, toluene, ethylbenzene, and xylenes (BTEX). Gasoline sometimes also contains additives, such as methyl tertiary-butyl ether (MTBE). Contaminant concentrations below saturation are degradable. Gasoline floating on the top of the groundwater table, also called free-product, is toxic to hydrocarbon degrading microbes.

Gasoline, MTBE, a gasoline additive, and BTEX compounds degrade aerobically in the presence of dissolved oxygen. Natural attenuation of gasoline constituents has been growing as a remediation technology since the mid 1990s. Presently, a variety of technologies are available that create low to high concentrations (10–60 ppm) of stable dissolved oxygen in groundwater. Once this elevated dissolved oxygen mixes with gasoline-contaminated ground water, natural biodegradation processes occur (3,8).

BENCH TESTS AND OXYGEN DEMAND THRESHOLD

Bioremediation enhanced by the addition of dissolved oxygen has been proven an effective technology to reduce both BTEX and MTBE. However, many groundwater environments contain numerous materials that cause competing reactions for the oxygen from solid and dissolved compounds high in ferrous iron and other metals in the reduced state, and organic and inorganic compounds that have high biological and chemical oxygen demand. These compounds, also called "oxygen sinks," consume large volumes of injected dissolved oxygen before aerobic bacteria can use the oxygen as part of the process of consuming gasoline and associated compounds.

The oxygen demand parameters significantly affect both enhanced bioremediation and chemical oxidation technologies. Oxygen demand includes the solid and dissolved substances that compete with microbes for oxygen. The parameters include solid oxygen demand (SOD) in saturated soil and biological oxygen demand (BOD) and chemical oxygen demand (COD) in groundwater. By better understanding nonmicrobial oxygen demand, the amount of oxygen required by microbes at a specific site that has specific geologic conditions during enhanced bioremediation can be predicted. Laboratory work generally includes measuring specific variables in the soil and groundwater such as alkalinity, pH, dissolved oxygen, contaminant concentration, macronutrients, heterotrophic plate count, specific degraders, chemical oxygen demand, biological oxygen demand sulfate, nitrate, total iron, ferrous iron, total dissolved solids, total inorganic carbon, and total organic carbon. The oxygen demand threshold must be overcome before significant petroleum hydrocarbon degradation will occur under aerobic conditions.

OXYGEN DELIVERY

For aerobic bioremediation, an efficient oxygen mass transfer method is needed to place high levels of dissolved oxygen in the groundwater. There are many methods of delivering oxygen to groundwater. A spargeless delivery of supersaturated levels of dissolved oxygen into groundwater is one method to ensure an abundance of oxygen to get over the oxygen demand threshold quickly. Use of chemical oxidants such as hydrogen

peroxide or ozone can be used to reduce oxygen-competing reactions rapidly.

To deliver dissolved oxygen into the aquifer, a spargeless gas emitter tool that infuses 100% oxygen into groundwater via 50.8-mm diameter (2-inch) monitor wells has been developed (8) by inVentures Technologies, Inc (Fig. 2). There are no power sources or moving parts. The oxygen is released by pressure from an industrial-grade oxygen cylinder. The proprietary structured polymer inside the oxygen diffusion tool provides a large surface area for gas transfer into the gas infusion tool, which is placed into an existing monitor well. The system can be reinstalled and reused on other sites.

The gas infusion tool is connected to a regulated supply of industrial compressed oxygen (100% concentration). Field experience has shown that dissolved oxygen levels of 30–60 mg/L have been achieved in each monitor well where a gas infusion tool is installed. The dissolved oxygen is infused into the monitoring well at a typical rate of 5 to 20 cc/minute, depending on the head pressure in the well. The effective radius of influence is typically 3 to 5 meters, even in low permeability soil such as clay (Mapleshade, New Jersey, U.S. site) or in fractured bedrock (Englewood, Colorado, U.S. site).

Field performance data for a pilot test site in Mapleshade, New Jersey, with MtBE, tert-butyl alcohol (TBA), and BTEX bioremediation illustrates the gas infusion technology (8). Depth to water is 2 to 4 meters below grade. Groundwater velocity is 0.09 to 0.12 meters/day at a gradient of 0.028. Recovery wells yield up to 4 liters per minute. The existing on-site air stripper-GAC system had iron clogging problems from ferrous iron at 30 to 80 mg/L. Dissolved oxygen (DO) concentrations in deep piezometers have increased from low baseline levels to more than 1 mg/L at a minimum of 5 meters downgradient of the infusion point. Shallow piezometers showed little DO change from baseline.

After 6 months of using gas infusion devices at the Mapleshade, New Jersey, U.S. site, an effective barrier of dissolved oxygen was established. Data indicate significant reductions in MtBE (up to 99%), TBA (50%), and benzene (85%) concentrations downgradient of the gas infusion tools.

THE IMPORTANCE OF ADEQUATE HYDROGEOLOGIC CHARACTERIZATION FOR *IN SITU* REMEDIATION

Understanding the subsurface environment is essential to developing a practical, efficient, cost-effective and timely *in situ* remediation strategy. System design is optimized when important geologic factors such as lithology, permeability, porosity, soil and groundwater chemistry, and contaminant type and concentration and their anticipated fate and transport, are fully evaluated with respect to the design and installation of oxygen injection ports or wells and rates of injection. Geologic factors control the movement, distribution, and quality of

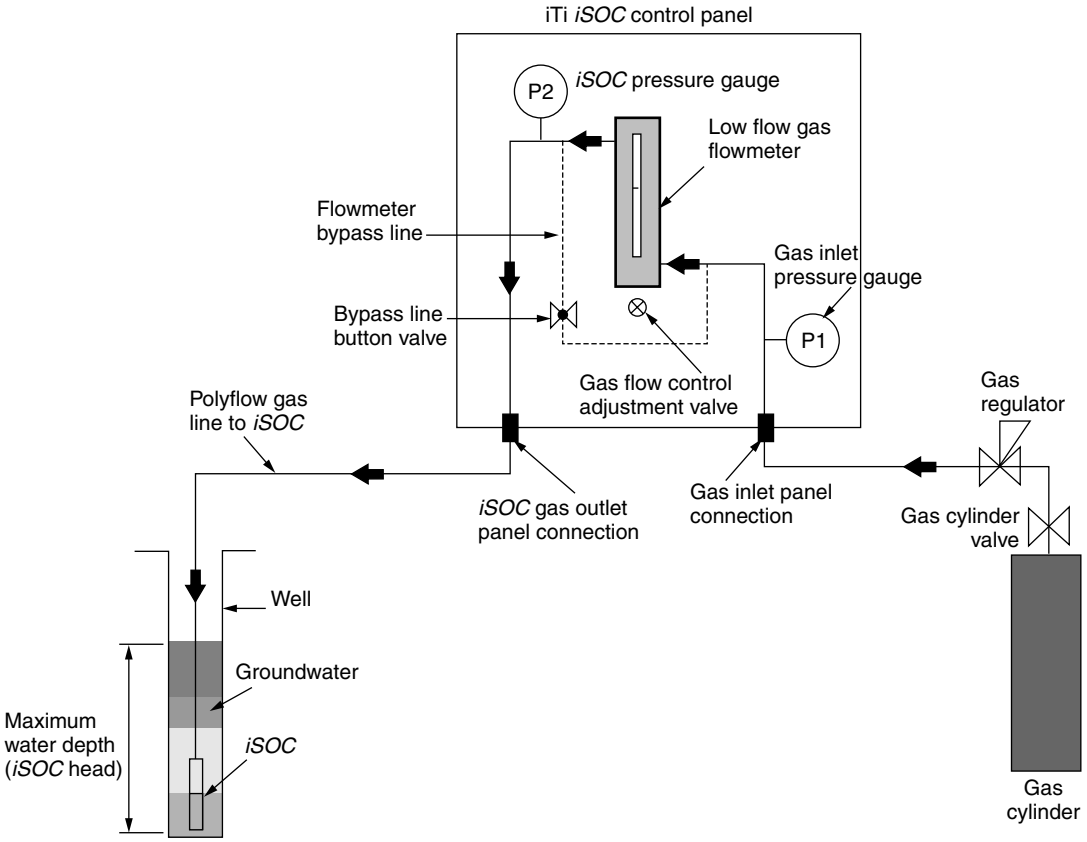


Figure 2. Diagram of semipassive gas diffusion device (iSOC).

groundwater as well as contaminants via a combination of several physical, chemical, and biological processes (9,10).

Shallow groundwater contamination by petroleum hydrocarbons results from surface or near-surface activities, including releases from underground and aboveground storage tanks and pipelines and accidental spills. The largest percentage of environmentally contaminated sites in the world lies on alluvial and coastal plains consisting of complex interstratified sediments. Lithologic contacts, some abrupt and some gradational, significantly influence permeability, porosity, and preferred flow pathways of contaminants in soil and groundwater.

Geology is the prime controlling agent for the movement of groundwater contaminants. A comprehensive understanding of the three-dimensional framework of geologic materials provides data for study of groundwater vulnerability to contamination and the lateral and vertical extent of hazardous and toxic constituents in the subsurface. Effective design and monitoring of subsurface remedial systems requires hydrogeologic characterization.

Lithology and stratigraphy are the most important factors affecting contaminant movement in soils and unconsolidated sediments. Stratigraphic features, including geometry and age relations between lenses, beds, and formations and the lithologic characteristics of sedimentary rocks, such as physical composition, soil type and chemistry, grain size, grain packing, and cementation, are among the most important factors affecting groundwater and contaminant flow in sedimentary rocks. Igneous–metamorphic rocks are geologic systems produced by deformation after deposition or crystallization. Groundwater and contaminant flow in igneous–metamorphic rocks are most affected by structural features such as cleavages, fractures, folds, and faults.

In summary, passive and semipassive remedial methods use minimal or no power, have few or no movin g parts, have few or no time constraints, and meet local and national regulatory guidelines. As for all forms of *in situ* remediation, proper assessment and hydrogeological characterization are the keys to success.

BIBLIOGRAPHY

1. Warner, S.D., Szerdy, F.S., and Yamane, C.L. (1998). *Permeable Reactive Treatment Zones: A Technology Update, Contaminated Soils*. Vol. 3. Amherst Scientific, Amherst, MA, Chap. 27, pp. 315–327.
2. Lehr, J. (2000). Phytoremediation: A promising path to the elimination of heavy metals and radionuclides in groundwater and soil. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.26–14.29.
3. Suthersan, S.S. (2002). *Natural and Enhanced Remediation Systems*. CRC Press/Lewis, Boca Raton, FL.
4. Testa, S.M. (1996). *Groundwater restoration and site closure: Society of Petroleum Engineers*. Paper 35885, pp. 1–11.
5. Rice, D. et al. (1995). *Recommendations to improve the cleanup process for California's leaking underground fuel tanks*. Submitted to the California State Water Resources Control Board and the Senate Bill 1764 Leaking Fuel Tank Advisory Committee, Lawrence Livermore National Laboratory Report, Livermore, CA.
6. Mace, R.E., Fisher, R.S., Welch, D.M., and Parra, R.A. (1997). *Extent of Mass and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Sites in Texas*. Texas Bureau of Economic Geology, Geological Circular 97-1.
7. U.S. EPA. (1985). *Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites*. EPA/540-2-85/001, Washington, DC.
8. Kolhatkar, R., Kuder, T., Philp, P., and Wilson, J.T. (2002). Stable Carbon Isotope Analyses to Demonstrate MTBE Biodegradation in Ground Water. *Groundwater Resour. Assoc. (GRA) MTBE Symp.*, October 17, 2002, San Jose, CA.
9. Testa, S.M. (1994). *Geological Aspects of Hazardous Waste Management*. CRC Press/Lewis, Boca Raton, FL.
10. Testa, S.M., and Winegardner, D.L. (2000). *Restoration of Contaminated Aquifers*, 2nd Edn. CRC Press/Lewis, Boca Raton, FL.

READING LIST

Jacobs, J.A. (2000). Passive *in situ* remediation technologies. In: *Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.12–14.25.

Jacobs, J. and von Wedel, R. (1997). Enhanced *in situ* biodegradation via high pressure injection of oxygenating agents and nutrients. *Am. Inst. Prof. Geol., 34th Annu. Meet.*, Houston, TX, Abstracts, p. 27.

GROUNDWATER REMEDIATION BY *IN SITU* AERATION AND VOLATILIZATION

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INTRODUCTION

There are a variety of groundwater remediation processes that use *in situ* aeration and volatilization as a part of their technology. Some of these technologies have a bioremediation component to them as well. These technologies include soil venting, soil vapor extraction, air sparging, bioventing, and biosparging.

Soil venting is a term used for an *in situ* aeration process that is a powerful remediation technology for the treatment of soils exposed to a variety of hydrocarbons. The practice of soil venting includes the following variations in application:

- Soil vapor extraction (SVE) systems are designed to exploit hydrocarbons potential for volatilization.
- Air sparging is an aeration process in which volatilizing air is injected into the saturated zone beneath the water table. Soil venting is used to recover the vapor laden air as it exits the water table.

- Bioventing is an aeration process designed to deliver oxygen to the subsurface for use by indigenous bacteria to degrade hydrocarbons; the focus is on minimizing hydrocarbon volatilization.
- Biosparging is a variant of air sparging in which oxygen stimulated biodegradation is the aim rather than volatilization. As with air sparging, soil venting is used to recover gas discharged through the water table.

Figure 1 illustrates and compares the potential effectiveness of soil vapor extraction and bioventing.

The data illustrated in Fig. 1 was calculated using the following premises:

- The air flow rate is 10 SCFM (Standard Cubic Feet per Minute). For the vapor transport calculations, it is assumed that the 10 SCFM air stream becomes saturated with hydrocarbon vapor. Volatilization driving vapor pressures were calculated at 8 °C.
- For the biodegradation calculations, it is assumed that the oxygen provided by the 10 SCFM air flow is completely used for hydrocarbon biooxidation.
- Biodegradation of each of the hydrocarbons proceeded to carbon dioxide and water.

This data was derived from theoretical calculations predicated on the fundamental principals governing the action of each of the processes (i.e., volatilization or biooxidation). In actuality, these processes and other subsurface interactions (with soil moisture, for example) are more complex. However, the base principals do apply and are, in the overall process, upheld. Although based on a simplified system, the data serves to illustrate the fundamental principals of, and differences between, soil vapor extraction and bioventing.

Following is a more detailed explanation of these processes and a case history that illustrates the use of biosparging technology at a site contaminated with volatile and nonvolatile hydrocarbons.

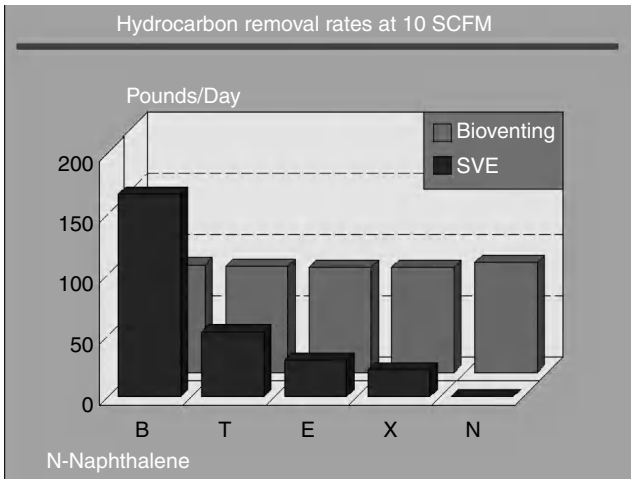


Figure 1. Hydrocarbon removal by SVE and biooxidation.

SOIL VAPOR EXTRACTION

By stimulating an advective air flow through soil venting, adsorbed hydrocarbons are exposed to air that does not carry an existing vapor load. Upon this exposure, equilibrium driven mechanisms will force the hydrocarbons to volatilize into the induced air flow. Every hydrocarbon has a specific temperature-dependent vapor pressure that determines the maximum (saturated) vapor concentration that can be obtained in the air flow. This vapor-saturated air is directed to the surface where it may be discharged to the atmosphere, or more commonly, treated to remove the hydrocarbon vapors before discharge.

The key element in this vapor extraction process is the fact that the mass transport rates are determined by a physical property (the vapor pressure) of the hydrocarbon. Not all hydrocarbons have the same vapor pressure, and the lower the vapor pressure, the lower the overall mass transport rate will be for that compound, thus the dramatic trend seen in Fig. 1 for the SVE portion of the graph. Table 1 presents the basic data used to prepare the soil vapor extraction part of Fig. 1.

Benzene is extremely volatile and offers an excellent mass transport potential of 166 pounds per day. However, naphthalene is at the other extreme; with a vapor pressure less than 1 mm Hg, it is at the lower end of hydrocarbons considered amenable to removal by soil vapor extraction. In this instance, only 0.13 pounds per day would be removed. The other petroleum hydrocarbons fall somewhere between the two.

The dependence of soil vapor extraction on the varying physical property of vapor pressure places serious constraints on the rate of SVE remediation at sites

Table 1. Vapor Pressure and Volatilization Driven Mass Transport Rate

Hydrocarbon	Vapor Pressure*	Molecular Weight	Saturated Vapor Concentration	Lbs Removed in One Day at 10 SCFM
Benzene	41.0	78.1	11.5×10^{-3} lbs/ft^3	166
Toluene	11.1	92.1	3.67×10^{-3} lbs/ft^3	52.8
Ethylbenzene	5.5	106.2	2.10×10^{-3} lbs/ft^3	30.2
Xylene	4.0	106.2	1.53×10^{-3} lbs/ft^3	22.0
Naphthalene	0.02	128.2	9.2×10^{-6} lbs/ft^3	0.13

*mm Hg at 8° Centigrade

impacted with petroleum hydrocarbons. Even gasoline has significant concentrations of hydrocarbons with relatively low vapor pressures. Heavier petroleum products, such as jet fuel, kerosene, diesel fuel, and lubricating oil, are thought to be nonresponsive to soil vapor extraction technology. Based on soil vapor extraction alone, that thought is an accurate one.

Air Sparging

Air sparging is the process of hydrocarbon volatilization stimulated by the injection of air beneath the water table. With air sparging, the volatilization process takes place under saturated conditions, emulating the action of an air stripping surface treatment system. The governing physical parameter that relates a hydrocarbon's volatilization potential from water is Henry's constant. According to Haarhoff and Cleasby (1), Henry's constant is directly related to a hydrocarbon's vapor pressure, water solubility, and temperature of the air/water/hydrocarbon system, which is a more complex physical/chemical system than volatilization of free phase or adsorbed hydrocarbons from soil in a vapor extraction system. In an air sparging system, the injected air and entrained volatilized hydrocarbons are captured above the water table with a conventional soil venting system.

$$P_a = H_a X_a$$

where P_a is the partial pressure of constituent a in air, H_a is the Henry's law constant (atm), and X_a is the solution concentration of the chemical a (mole fraction).

Some Henry's law constants for gasoline compounds include tetraethyl lead (4,700 atm), ethylbenzene (359 atm), xylenes (9266 atm), benzene (230 atm), toluene (217 atm), naphthalene (72 atm), and MTBE (27 atm) (2). Henry's law constants of greater than 100 atmospheres are generally considered volatile, and consequently more likely to be volatilized rather than biodegraded.

BIOVENTING

Bioventing is the term for aerobic biodegradation stimulated by oxygen provided to a hydrocarbon impacted subsurface zone by an air flow induced through soil venting. Many factors exist that affect the outcome and success of bioventing projects.

Intrinsic permeability (k), in cm^2/sec, and product composition are important aspects for biosparging projects. Ineffective permeability for bioventing includes k values of 10^{-16} to 10^{-12}. This range corresponds to lithologies of clay and the lower permeability ranges of glacial till. Moderate to minimal effectiveness for bioventing includes sediments with k values of 10^{-10} to 10^{-5}, including silt, loess, silty sand, and the lower permeability ranges of clean sand. The most effective permeability for bioventing includes k values of 10^{-4} to 10^{-2}, which includes the upper permeability range of clean sand and all gravels. In some generally low-permeability settings, heterogenetic prefererential pathways may exist that can offer influence beyond what would be initially expected.

Petroleum hydrocarbons are generally biodegradable, regardless of their molecular weight, as long as the indigenous microbes have an adequate supply of oxygen and nutrients. The most volatile and most soluble to least volatile and least soluble petroleum products include gasoline, kerosene, diesel, fuel oils, and lube oils. Bioventing is more effective with the more volatile components (2).

Site characteristics that must be evaluated include intrinsic permeability of the sediments, soil structure and stratification, temperature, (10 °C or higher), pH (6 to 8), microbial population density (generally greater than 1,000 colony-forming units per gram of dry soil), nutrient concentrations (ammonia as nitrogen and orthophosphate; carbon-nitrogen-phosphorous ratios are best at 100:10:1), and dissolved ferrous iron concentrations (Fe^{+2} is less than 10 mg/L). The contaminant characteristics also need to be evaluated, which include chemical structure of compounds, concentrations and toxicity, vapor pressure, product composition and boiling point, and Henry's law constant. Approximately 3 to 3.5 pounds of oxygen are needed to degrade one pound of petroleum hydrocarbons. This amount of oxygen does not take into account the oxygen demand in the sediments (sediment oxygen demand) or in dissolved in the groundwater (chemical oxygen demand with the subset of biological oxygen demand).

The power of bioventing lies in the underlying process responsible for it, the biologically mediated oxidation of hydrocarbons to carbon dioxide and water. The data calculated for the bioventing portion of Fig. 1 is based on the stoichiometric consumption of oxygen; that is, each mole of carbon present will require one mole of oxygen (O_2) to be converted to carbon dioxide (CO_2):

$$O_2 + C = CO_2$$

Each mole of hydrogen requires 1/4 mole of oxygen (as an O_2 molecule) to produce one mole of water. It can be more conveniently expressed as follows:

$$O_2 + 4\ H_2 = 2\ H_2O$$

The exact stoichiometry for each of the hydrocarbons illustrated in Fig. 1 is shown in Table 2.

A flow rate of 10 SCFM can deliver 270 pounds of oxygen to a treatment zone in a period of 24 hours. Based on the above stoichiometry, the potential biodegradation rates in pounds per day are indicated in Table 3.

This entire process is independent of any other physical property of these hydrocarbons. The prime issue with regard to *in situ* remediation by bioventing is how much

Table 2. Biooxidation Stoichiometry

Compound	Chemical Formula		Moles O_2 Required		Oxidation Products
Benzene	C_6H_6	+	7.5 O_2	=	6 CO_2 + 3 H_2O
Toluene	$C_5H_5(CH_3)$	+	9 O_2	=	7 CO_2 + 4 H_2O
Ethylbenzene	$C_6H_5(C_2H_5)$	+	10.5 O_2	=	8 CO_2 + 5 H_2O
3-Xylene	$C_6H_4(CH_3)_2$	+	10.5 O_2	=	8 CO_2 + 5 H_2O
Naphthalene	$C_{10}H_8$	+	12 O_2	=	10 CO_2 + 4 H_2O

Table 3. Biooxidation Rate

Compound	Biooxidation Potential—Lbs/Day
Benzene	88
Toluene	87
Ethylbenzene	86
3-Xylene	86
Naphthalene	90

oxygen can effectively be transported to the reaction (contaminated) zone. However, practical limits exist to the effectiveness of biodegradation and the linear effect of the stoichiometric biooxidation reaction with oxygen. The potential problem lies with compounds that are recalcitrant to biodegradation. With respect to petroleum hydrocarbons, these recalcitrant compounds are typically polynuclear aromatic (PNA) compounds having high ring counts. In many products, however, high ring count PNAs are not a significant amount of the total hydrocarbon makeup. In addition, these compounds are most often still biodegradable, but at a slower rate than that observed for the less refractory hydrocarbons.

Indigenous Bacteria

A key concern over the viability of the bioventing approach is the presence of indigenous bacteria capable of being stimulated to degrade hydrocarbons. Figure 2 illustrates soil gas data from a site impacted with petroleum hydrocarbons.

These samples were collected under static conditions, no remediation activity has taken place. This soil gas is representative of equilibrium conditions existing at the impacted site. Although volatilized hydrocarbon vapors (from the contaminant impact) are also present in the soil gas, Fig. 2 only shows the three dominant soil gases: carbon dioxide, oxygen, and methane. Under normal atmospheric conditions oxygen concentration is 21% and carbon dioxide is approximately 300 ppm (0.03%). As a result of the presence of carbonate minerals and natural organic materials, CO_2 in uncontaminated soils is typically found at concentrations from 1.5–3% (3). Methane is present in the atmosphere in trace amounts (1.5 ppm). As Fig. 2 illustrates, the soil gas concentrations at this contaminated site are significantly skewed from those levels. Carbon dioxide is elevated at 11–12%, oxygen is depressed to around 5%, and methane is elevated at 3–5%. Following is an outline of the process responsible for the generation of this soil gas blend:

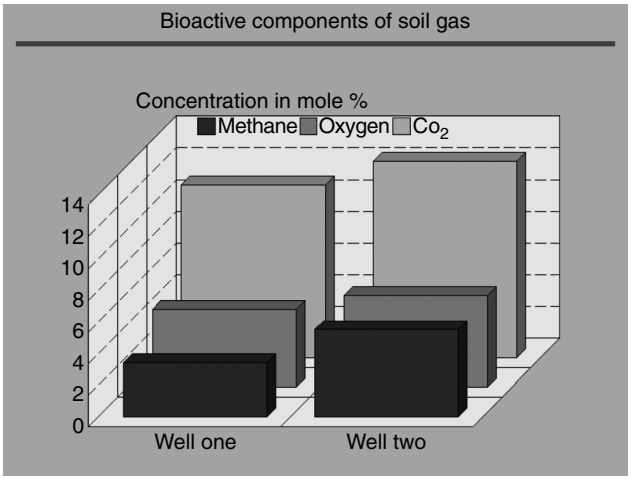


Figure 2. Bioactive soil gases in the vadose zone.

On release of hydrocarbons into the subsurface, the indigenous bacteria began an aerobically driven biooxidization process. The endproduct of this aerobic microbial degradation was carbon dioxide and water (see Table 2).

After the aerobic microbial activity had consumed oxygen in the soil gas to near the observed 5% level, facultative anaerobes became active. These bacteria have the ability to support metabolic activity under full aerobic or oxygen depressed conditions (the transition has been observed in the field and laboratories to normally occur at oxygen levels near 5%). The degradation products (seen in the gas phase) of the anaerobic activity are methane and additional carbon dioxide. The methane is a result of the fact that, in microscale isolated zones within the geologic matrix, deeply methanogenic conditions may be reached under these circumstances.

The fundamentally important point of the data illustrated in Fig. 2 is that this aerobic/anaerobic activity occurred naturally. No bacteria were added to the soil; the existing indigenous bacteria generated these gases. No nutrients were added. The indigenous bacteria were able to become active under natural subsurface conditions, using available oxygen, nitrogen, phosphorous, and trace nutrients. With depletion of the oxygen levels, the facultative anaerobic activity became dominant at the expense of the aerobic biooxidation. This anaerobic degradation occurs at a rate several orders of magnitude slower than that observed for aerobic degradation (4). If this were not the case, it would be cost effective to let the anaerobic degradation occur at its own pace with no other intervention.

What is required for timely bioremediation is the installation of a soil venting system to displace this soil gas (equilibrated to the existing chemical and microbiological conditions) with fresh, fully oxygenated air, thus restimulating the natural aerobic biodegradation of the impacting hydrocarbons, which is the essence of the bioventing process.

Biosparging

The governing processes engaged in a biosparging system are identical to those in bioventing. The biosparging stimulated biooxidation follows the same stoichiometry presented in Table 2. The injected air, biooxidation products (CO_2), and some fraction of volatilized hydrocarbons are collected above the water table with a soil venting system, just as described for air sparging. The last sentence contained a key statement, that "some fraction of volatilize hydrocarbons" are generated by a biosparging (and bioventing) system. The next section analyzes this statement in more detail.

SOIL VAPOR EXTRACTION VERSUS BIOVENTING A SIMULTANEOUS PROCESS

When a soil venting system is operated at a site impacted by petroleum hydrocarbons, both of the discussed mechanisms are engaged. The determination of which process is dominant lies in how the soil venting system is operated.

A soil venting system can be operated such that 60–90% of the impacting hydrocarbons are volatilized and 10–40% are biodegraded, i.e., soil vapor extraction. Bioventing reverses those numbers, 60–90% of the hydrocarbons are biodegraded and 10–40% are volatilized (5). Note that some degree of biodegradation is unavoidable even in a system that is designed and operated as a pure soil vapor extraction system. The site soils would have to be sterilized to prevent it. Conversely, some level of volatilization is equally unavoidable in a bioventing system.

The value of the bioventing approach lies in three areas:

First, every pound of hydrocarbon that is degraded *in situ* is a pound that will not require subsequent treatment on the surface, resulting in significant cost savings.

Second, equipment costs and operational costs (primarily energy) are less using the lower air flow rates capable of supporting the bioventing approach. Oxygen does not need to be brought to the subsurface at a rate faster than the ability of the bacteria to consume it.

Third, as Fig. 1 illustrates, soil vapor extraction does not work well with hydrocarbons that have low vapor pressures.

Remediation by soil vapor extraction is very rapid when applied to hydrocarbons with high vapor pressures. For example, a release of pure benzene could theoretically be cleaned up faster using a straight soil vapor extraction approach rather than bioventing. Although surface treatment expenses must still be taken into account in the overall project costs.

Soil vapor extraction is definitely the preferred approach when remediating biological recalcitrant compounds that have high vapor pressures such as chlorinated solvents. However, in instances where the released materials are petroleum hydrocarbons, such as fuels or lubricants, bioventing is likely to be the most cost and time effective remediation approach.

BIOSPARGING—A CASE HISTORY

Following is a field example of the biosparging process discussed above. This project is ongoing at a facility that was closing an RCRA hazardous waste drum storage area (DSA). The wastes stored in the DSA were "Spent Non-Halogenated Solvents" (F003/F005). Figure 3 shows a plan view of the site, the DSA, and the installed remediation system.

The geology beneath the site consists of:

- approximately 30 feet of sand interbedded with a peat layer 1 to 3 feet thick at a depth of 16 feet; silt and clay underlies the sand.
- depth to groundwater is 6 feet below grade (see Fig. 4).

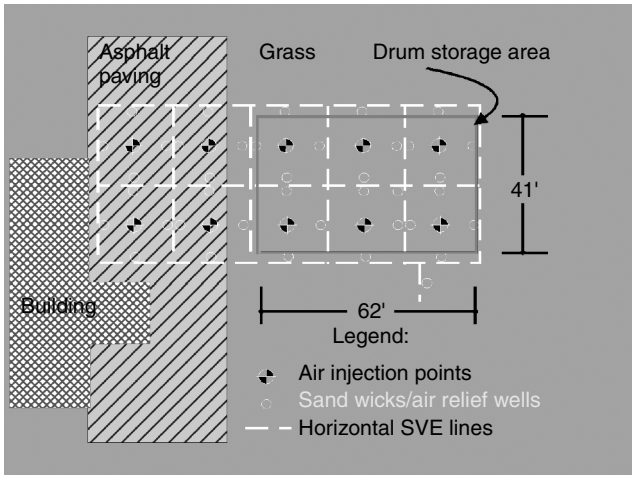


Figure 3. Plan view of biosparging site.

- soil and groundwater contamination was limited to the sand/peat unit above the clay.

Soil contamination included ethylbenzene (160 mg/Kg), toluene (110 mg/Kg), total xylenes (620 mg/Kg), naphthalene (440 mg/Kg), and other polycyclic aromatics at low mg/Kg levels.

Groundwater contained 2 mg/L ethylbenzene and 16 mg/L total xylenes.

The remediation system put into place was an *in situ* saturated zone treatment using biosparging, the details (Fig. 4) of which are as follows:

- A series of sparge points were installed to a depth of 30 feet just above the surface of the lower clay layer, which placed them about 14 feet beneath the peat layer.
- A series of 4-inch borings, filled with graded sand to act as air relief wells (sand wicks), were installed to a depth of 30 feet. The sand wicks act as a conduit for injected air bubbles through the peat

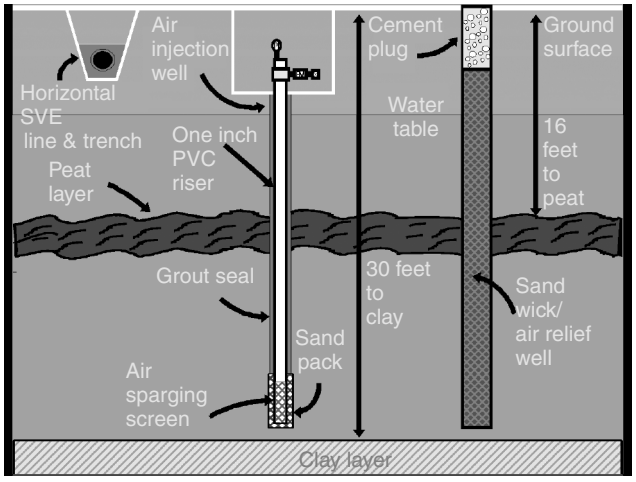


Figure 4. Cross-sectional view of biosparging site with sand wicks.

layer, preventing unacceptable horizontal migration of the injected air and any entrained vapor, which is a common and critical problem for the application of air sparging/biosparging in heterogeneous soils.

- A soil venting recovery system was installed in horizontal trenches above the water table to capture the injected air and hydrocarbon vapors generated from the biosparging system. The area was then covered with a plastic liner and soil to prevent short circuits in the soil venting system.

The discharge of the soil venting system was treated with vapor phase activated carbon.

An important point with regards to this system was the biosparging aspect of the design. Although vapor phase activated carbon was installed as a necessary treatment of coproduced hydrocarbon vapors, the intent of the remedial design was to minimize the actual volatilization and concentrate on oxygen-stimulated biodegradation of the hydrocarbons *in situ*. This approach minimized the carbon usage and also had the potential to remove the nonvolatile constituents of the impacting hydrocarbons. To this end, air injection was only at 12 SCFM, a rate estimated to match the kinetics of the microbiological biooxidation. The horizontal soil venting system was operated at 60 SCFM to ensure that all the injected air (and minimal hydrocarbon vapor load) were adequately recovered.

Although provisions were made for the addition of nutrients (nitrogen, phosphorus, and trace minerals), nutrients were not actually used in this phase of the project. Under many conditions, existing nutrient levels are often adequate to support microbial activity at an acceptable level. Under most circumstances, oxygen supplementation is the dominant factor required for microbial stimulation. Nutrient addition to the vadose and saturated zones (although possible) is a complication that should be avoided unless required. Figures 5 and 6 illustrate the results after system startup. Figure 5 illustrates the trend of the vaporized hydrocarbon and carbon dioxide observed in the recovered soil gas, and Fig. 6 illustrates the trend of dissolved oxygen (DO) in the groundwater and carbon dioxide in the soil gas.

The hydrocarbon versus carbon dioxide in soil gas above the biosparging system shows a sharp increase in the concentration in the VOCs recovered in the soil gas by day ten of system operation (Fig. 5). Initial carbon dioxide levels are quite low. In a manner very typical of microbiological systems, carbon dioxide concentrations steadily increased to a maximum level over a 30-day period.

This period is termed the "lag phase," as the indigenous microorganisms adapt to the sudden introduction of oxygen into their environment and the use of the impacting hydrocarbons as a carbon source.

In turn, the VOC concentrations continue a steady decline as degradation begins to become more dominant. The most striking feature is the continuous generation of significant amounts of carbon dioxide after day 30, with very low concurrent levels of VOC emission, which is primarily because of the biooxidation of nonvolatile hydrocarbon components (such as lighter PNAs), which

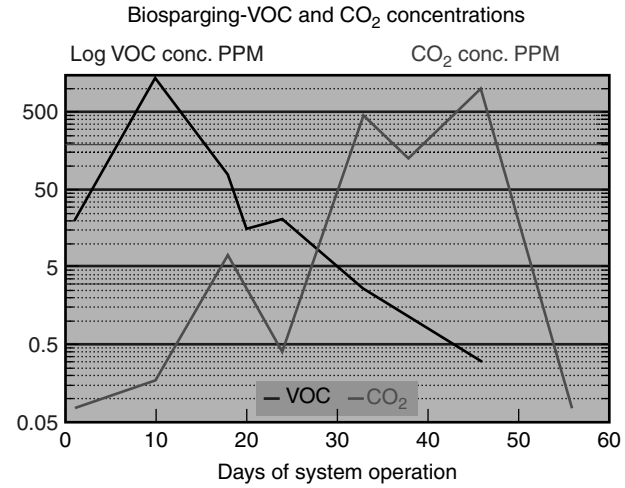


Figure 5. Hydrocarbon vs. carbon dioxide in soil gas above biosparging.

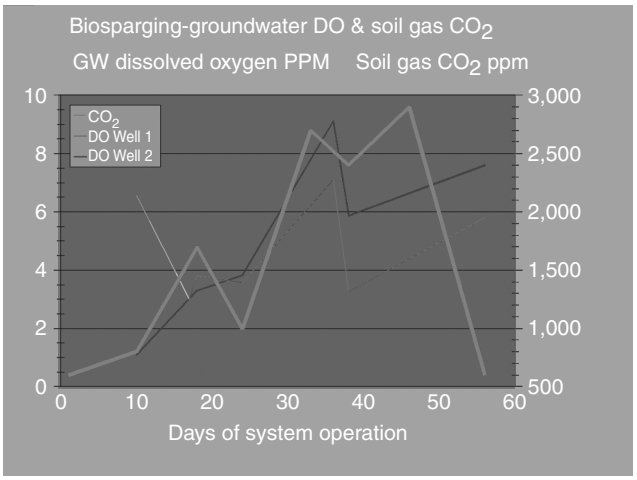


Figure 6. CO_2 in soil gas vs. dissolved oxygen in groundwater.

are not responsive to removal through volatilization. Last, after 50 days of operation, the carbon dioxide levels precipitously decline in conjunction with VOCs becoming almost undetectable, which indicates that the hydrocarbons have been consumed and the stimulated bacteria have ran out of the hydrocarbons serving as their carbon source.

Figure 6 serves to further illustrate the biological activity in the saturated zone of the impacted soils. The initial low levels of the dissolved oxygen may have been because of chemical oxygen demand within the aquifer matrix (primarily dissolved iron). After meeting that COD, the DO increased in tandem with carbon dioxide production.

Of particular interest is the marked drop in DO between day 35 and day 40, which coincides with the peak biological activity. When the carbon dioxide levels began to drop, the DO increased once again. At the peak level of activity, the microbes were able to consume most of the oxygen provided by the injected air, as planned. With depletion

of the food source, more oxygen is free to appear as DO. This site data has been presented to provide a topical field example of biosparging. It is from the early stages of the remediation. The hydrocarbon attenuation indicated by Figs. 5 and 6 is occurring in the advective zone of the impacted saturated zone soils and groundwater.

In conclusion, aeration is a powerful remediation tool in the vadose and saturated zones. The manner in which an aeration system is operated will determine the dominant process stimulated by that aeration: volatilization or biooxidation. Biooxidation has distinct advantages with regard to the range of nonvolatile hydrocarbons that can be remediated and offers lower potential off-gas treatment costs. The core issue is to understand the underlying mechanisms responsible for both processes and apply that knowledge accordingly.

BIBLIOGRAPHY

1. Haarhoff, J. and Cleasby, J.L. (1990). Evaluation of air stripping for the removal of organic drinking-water contaminants. *Water SA.* **16**(1): 13–22.
2. United States Environmental Protection Agency (USEPA). (2004). Biosparging. In: *How to Evaluate Alternate Cleanup Technologies for Underground Storage Tank Sites; A Guide for Corrective Action Plan for Regulators*. EPA 510-R-04-002, Washington, DC.
3. Suchomel, K.H., Kreamer, D.K., and Long, A. (1990). Production and transport of carbon dioxide in a contaminated vadose zone: a stable and radioactive carbon isotope study. *Environ. Sci. Technol.* **24**: 1824–1831.
4. Atlas, R.M. (1981). Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiolog. Rev.* **45**(1): 180–209.
5. Miller, R.N., Hinchee, R.E., Vogel, C.M., Dupount, R.R., and Downey, D.D. (1990). A field scale investigation of enhanced petroleum hydrocarbon biodegradation in the vadose zone at Tyndall AFB, Florida. *Proc. NWWA Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference*, Houston, TX, pp. 339–351.

READING LIST

Vance, D.B. (1993). Groundwater remediation—first principals. *National Environment. J.* **3**(2): 18–20.

Vance, D.B. (1993). Hydrophobic organic chemicals and total organic carbon—the ideal and reality of site clean-up. *National Environment. J.* **3**(3).

REMEDIATION OF CONTAMINATED SOILS

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Soil contamination is caused by a variety of industrial, agricultural, and domestic activities, and poses a major threat to the environment. Although soil contamination can result from a variety of organic and inorganic chemicals, this article focuses on remediation of metal-contaminated soils. Heavy metals such as Pb, Cr, Cd, Zn, Cu, and Hg can cause significant damage to environmental and human health, particularly because of their indefinite persistence in the environment. In the United States alone, 1200 sites are on the National Priority List (NPL) for remediation of contaminated soils, of which 63% are contaminated with toxic heavy metals. A plethora of remediation techniques are now available for the cleanup of such contaminated sites. The selection of the most appropriate site remediation technique depends on various factors such as site characteristics, concentration, types of pollutants to be removed, and end use of the contaminated medium. The major technologies available to date can be grouped under the following categories: isolation, immobilization, toxicity reduction, physical separation, and extraction. This article provides an overview of the various sources of heavy metal pollution in soils, the common remediation technologies available for soil cleanup, and the various factors that influence the type of remediation method that would be most appropriate for effectively remediating metal-contaminated soils.

INTRODUCTION

Environmental contamination due to human activities is an ancient problem that has been further aggravated by growing urbanization and increasing affluence. Dramatic accumulation of pollutants from chemical manufacturing, wastewater treatment, agriculture, mining and smelting, food processing, energy production, and pulp and paper production has led to deterioration of soil and water quality (1). Recent research is increasingly focused on the ecological and human health effects of the contaminants, and guidelines or standards on soil, drinking water, irrigation water, crop tissues, foodstuff, biosolids, and fertilizers are now becoming available (1). Heavy metals released by a variety of industrial, agricultural, and domestic activities are a potential risk to both human population and wildlife. In contrast to many organic pollutants, which are often degraded in the soil, the danger of heavy metals is aggravated by their indefinite persistence in the environment (2). Exposure to heavy metals has been linked to developmental retardation; various cancers; kidney damage; and development of autoimmunity leading to diseases of the joints, kidneys, circulatory and nervous systems. In addition, heavy metals can cause reduction in growth, inhibition in photosynthesis and respiration, and degradation of cell organelles in plants and microorganisms (3).

Remediation of contaminated soils involves reduction, extraction, removal, stabilization and/or containment of contaminants in the subsurface to a level acceptable for site closure. Site closure can be brought about by the reduction of risk posed by the presence of contaminants in the subsurface to an acceptable level. General approaches to remediating metal contamination include isolation, immobilization, toxicity reduction, physical separation, and extraction. Contaminated soil can be remediated by

chemical, physical, or biological techniques. The available techniques can be grouped into two categories: (1) *ex situ* techniques that require removing the contaminated soil on- or off-site and (2) *in situ* methods that remediate without excavating the contaminated soil (4). The selection of the most appropriate soil and sediment remediation method depends on the site characteristics, concentration, types of pollutants to be removed, and the end use of the contaminated medium. The United States Environmental Protection Agency (USEPA) included 13 metals in its priority pollution list: Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn (1). This review discusses the various sources of heavy metal pollution, evaluates the remediation methods available for soil cleanup, and the various factors that influence the type of remediation method that would be most appropriate for effective remediation.

SOURCES OF CONTAMINANTS

Major contributors to the metal burden in soils include discarded manufactured products in scrap heaps/landfills (As, Cr, Cu, Pb, Mn, and Zn), coal ashes (As, Cd, Pb, Mn, Hg, Mo, Ni, Se, V, and Zn), and agricultural and livestock wastes (As, Cu, and Zn) (1). Pollution sources can be broadly categorized into two sources: point sources and nonpoint sources. Point sources refer to discrete and localized contamination processes. Local accumulation of pollutants can arise from landfilling, mining, and smelter processes. Nonpoint sources are related to diffuse processes or human activities that cover large areas, for example, agricultural practices resulting in pesticide contamination (1). The major sources of soil metal contamination can be summarized as follows.

Airborne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals convert to oxides and condense as particulates, unless a reducing atmosphere is maintained (5).

Process Solid Waste

Process solid wastes result from a variety of industrial processes. These metal-bearing solid wastes are disposed above ground in waste piles, below ground, or under cover in landfills. Examples of process solid wastes include slag, fly ash, mold sand, abrasive waste, ion exchange resins, spent catalysts, spent activated carbon, and refractory bricks (6). Waste piles are exposed to weathering, which can lead to dispersal of the contamination to the surrounding soil, water, or air (7).

Sludge(Biosolids)

The composition of biosolids depends on the original waste stream and the process from which it was derived. Biosolids resulting from a uniform waste stream (such as wastewater treatment) are typically more homogeneous and have more uniform matrix characteristics. Sludge pits, on the other hand, often contain a mixture of wastes that have been aged and weathered, causing a variety of reactions to occur (5).

Soils

Soils can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials. The solubility of metals in soil is influenced by the chemistry of the soil and groundwater (1). Factors such as pH, pE, ion exchange capacity, and complexation/chelating with organic matter affect metal solubility directly.

CHEMICAL FATE AND MOBILITY OF METALS IN SOILS

The fate and transport of metals in soils depends significantly on the chemical form and speciation of metals (8). The term speciation means the distribution of elements among chemical forms or species. Heavy metals can occur in various forms in soils and water. For an accurate health risk assessment, not just the total metal concentration, but understanding its speciation is of paramount importance (9). In soils, speciation of metals depends on the physical and chemical characteristics of the soil, such as pH, redox, organic, carbonate, clay, and oxide content (10). A potential method for determining if heavy metals can be removed by a particular remediation technique or for predicting removal efficiencies is to determine speciation by selective extraction techniques. For example, it is believed that exchangeable carbonate and reducible oxide fractions may be amenable to soil washing techniques (11). Removal of the organically and residually bound fractions may not be economical or necessary to recover, as these fractions are generally not considered bioavailable (9).

REMEDIAL APPROACHES FOR METAL CONTAMINATED SOILS

Several technologies exist for the remediating metal contaminated soils (7), that can be broadly classified into five general categories; isolation, immobilization, toxicity reduction, physical separation, and extraction.

Isolation

Isolation technologies attempt to prevent the transport of contaminants by containing them within a designated area. Contaminated sites may also be isolated temporarily to limit transport during site assessment and site remediation (7). Isolation can be accomplished via these methods.

Capping. Capping systems provide an impermeable barrier to surface water infiltration into contaminated soil to prevent further release of contaminants into the surrounding surface water or groundwater (7). Other advantages of capping are control of odor emissions, improving aesthetics, and elimination of risks associated with human contact. Caps can be simple, single layered or complex multilayered systems (12). The selection of capping materials depends on site characteristics,

remedial objectives, and risk factors associated with the site (12).

Subsurface Barriers. Subsurface barriers may be used to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site. Vertical barriers are commonly used to restrict the lateral flow of groundwater. For effective isolation of the contaminated matrix, the barrier should extend and key into a continuous, low-permeability layer, such as clay or competent bedrock, below the contaminated area (12,13). Slurry walls, sheet curtains, and grout piles are some of the widely used vertical barriers. Technologies for constructing horizontal barriers, such as grout injection by vertical boring and horizontal drilling, are also under investigation. Horizontal barriers would enable control of downward migration of contaminants by lining the site without requiring excavation of the contaminated matrix (7).

Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. Mobility is usually decreased either by physically restricting contact between the contaminated matrix and surrounding groundwater or by chemically altering the contaminant to make it more stable with respect to dissolution (7). Immobilization techniques can be performed *ex situ* or *in situ* via these methods.

Solidification/Stabilization. Solidification and stabilization (S/S) immobilization technologies are the most commonly selected treatment options for metal contaminated sites (14). Solidification involves forming a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as fixation, usually uses a chemical reaction to convert the waste to a less mobile form. Inorganic binders such as cement, fly ash, or blast furnace slag, or organic binders such as bitumen are used to form a barrier around the waste. The most important method used to immobilize metals is by precipitation of hydroxides within the solid matrix (15).

Vitrification. The mobility of metals can also be decreased by high-temperature treatment of the contaminated area that results in the formation of vitreous materials, usually a solid oxide. Most soils can be treated by vitrification, and a wide variety of inorganic and organic contaminants can be targeted (16). *Ex situ* vitrification includes steps such as excavation, pretreatment, mixing, feeding, and melting. The vitrified material can be recycled for use as clean fill, aggregate, or other reusable materials (5). *In situ* vitrification involves passing electric current through the soil using an array of electrodes inserted vertically into the soil (17).

Toxicity and/or Mobility Reduction

Chemical and/or biological processes can be used to alter the form of metal contaminants to decrease their toxicity and/or mobility.

Chemical Treatment. Chemical reactions can be initiated that are designed to reduce the toxicity or mobility of metal contaminants (7). The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization. Changing oxidation states of metals by oxidation or reduction can detoxify, precipitate, or solubilize metals (18). The most commonly used oxidizing agents are potassium permanganate, hydrogen peroxide, hypochlorite, and chlorine gas; some of the common reducing agents used are alkali metals, sulfur dioxide, sulfite salts, and ferrous sulfate. Chemical neutralization is used to adjust the pH of extremely acidic or basic soils. This process can be used to precipitate insoluble metal salts from contaminated water or to prepare for chemical oxidation or reduction. Chemical treatments can be performed both *in situ* or *ex situ*. Chemical agents are non specific, so they target all reactive metals, which might make them more toxic or mobile (18).

Biological Treatment. Until recently, biological techniques were more commonly used for remediating organic contaminants, but they are beginning to be applied for metal remediation. However, until now, most biological treatment applications have been at the bench and pilot scale; very few have been tested on a field scale. Biological treatment exploits natural biological processes that allow certain plants and microorganisms to aid in remediating metals through processes such as adsorption, oxidation/reduction reactions, and methylation (19). Biological treatment technology can be broadly classified.

Phytoremediation. Phytoremediation refers to the specific ability of plants to aid in metal remediation. Some plants have developed the ability to remove ions selectively from the soil to regulate uptake and distribution of metals in their tissues. Potentially useful techniques for metal remediation at contaminated sites include these (20).

Phytoextraction. Phytoextraction employs hyperaccumulating plants to remove metals from the soil by uptake into the roots and shoots of the plants. The aboveground shoots can be harvested to remove metals from the site and subsequently disposed of as hazardous waste or treated for the recovery of metals.

Phytostabilization. Phytostabilization involves using plants to limit the mobility and bioavailability of metals in soil. Phytostabilizing plants are characterized by high tolerance of metals in surrounding soils but low accumulation of metals in the plants.

Bioleaching. Bioleaching uses microorganisms to solubilize metal contaminants in the soil. This process has been adapted from the mining industry for metal remediation (7). Certain microorganisms can oxidize/reduce metal contaminants directly; others produce oxidizing/reducing agents that interact with metals to change their oxidation states, thereby decreasing their mobility and/or toxicity. Methylation by microorganisms involves attaching methyl groups to inorganic metal ions to form organometallic compounds, which can then be removed by volatilization (7).

Physical Separation

Physical separation is an ex-situ process that attempts to separate contaminated material from the rest of the soil matrix by exploiting certain physical characteristics of the metal and soil. Physical separation techniques operate on the basis of particle size, particle density, surface, and magnetic properties of the contaminated soil. These techniques are most effective when the metal is either in the form of discrete particles in the soil or if the metal is sorbed to soil particles that occur in a particular size fraction (21). Screening, classification, gravity concentration, and magnetic separation are some of the most important physical separation techniques used for soil remediation. *Screening* separates soils according to particle size when the soil passes through sieves with particular size openings. *Classification* involves separation of particles based on the velocity with which they fall through water (hydroclassification) or air (air classification) (21). *Gravity concentration* separates particles on the basis of gravity differences (21). *Magnetic separation* subjects particles to a strong magnetic field using electromagnets or magnetic filters and relies on the magnetic properties of minerals for separation (8).

Extraction

Heavy metals can be extracted from soil either by treating the soil with a solution containing chemical extractants or via electrokinetic processes.

Soil Washing. Washing can be used to remove metals from soil by chemical or physical treatment methods in aqueous suspension. Soil washing is an ex-situ process that requires soil excavation prior to treatment. Chemical treatment involves adding extraction agents that react with the contaminant and leach it from the soil (22,23). The type of extractant used depends on the contaminants present and the characteristics of the soil matrix. Many processes manipulate the acid/base chemistry of the slurry to leach contaminants from the soil. Chelating agents such as EDTA selectively bind some metals and can be used to solubilize metals from the soil matrix (22). Oxidizing and reducing agents, such as hydrogen peroxide or sodium borohydride, provide yet another option to aid in solubilizing metal because chemical oxidation/reduction can convert metals to more soluble forms (24). Surfactants can also be used to extract metals from soil (7).

Pyrometallurgical Extraction. Pyrometallurgical technologies use elevated temperature extraction and processing to remove metals from contaminated soils. Soils are treated in a high-temperature furnace to remove volatile metals from the solid phase. Subsequent treatment steps may include metal recovery or immobilization. This process usually produces a metal-bearing slag, from which the metals can be recovered for reuse (25).

In-situ Soil Flushing. This method is used to mobilize metals by leaching contaminants from soils so that they can be extracted without excavating the contaminated materials. An aqueous extracting solution is injected or sprayed onto the contaminated area to mobilize the contaminants, usually by solubilization. The extractant can be applied *via* surface flooding, sprinklers, leach fields, vertical/horizontal injection wells, basin infiltration systems, or trench infiltration systems (26). Similar extracting agents are used for in-situ soil flushing and soil washing, including acids/bases, chelating agents, and oxidizing/reducing agents (18). The liquid containing the contaminants is subjected to pump-and-treat methods. Once the water is pumped from the soil, the heavy metals are removed by sodium hydroxide or sodium sulfide precipitation, ion-exchange, activated carbon adsorption, ultrafiltration, reverse osmosis, electrolysis/electrodialysis, or biological means (9).

Electrokinetic Treatment. Electrokinetic remediation technologies apply a low density current to contaminated soil to mobilize contaminants in the form of charged species. The current is applied by inserting electrodes into the subsurface. This method relies on the natural conductivity of soils (due to the presence of water and salts) to influence movement of water, ions, and particulates through the soil profile. The contaminant metals are concentrated in the solution around the electrodes (5), and are removed by a variety of processes, including electroplating at the electrodes, precipitation/coprecipitation at the electrodes, complexation with ion exchange resins, or by pumping the water from the subsurface and treating it to recover the extracted metals (5).

SUMMARY AND FUTURE DIRECTIONS

Containment technologies, the least expensive, are widely used to control the transport of hazardous materials and to prevent the spread of contamination (9). Containment is the preferred remedial method for sites that have low levels of wastes of low toxicity and low mobility or wastes that have been pretreated to obtain these characteristics. The advantages of containment technologies include relatively simple and rapid implementation, often at a much lower cost than alternatives that require excavation, ability to treat large areas and volumes of waste, and the potential for successful containment as the final action at the site (7). Among the major disadvantages of containment technologies are the high level of uncertainties regarding the long-term effectiveness of the containment process and the need for long-term inspection because untreated contaminants remain on-site.

Metals are considered relatively immobile, so the remediation approaches generally used involve solid-phase processes such as solidification/stabilization and vitrification (9). These techniques are mostly done ex-situ, but they can be also used for in-situ remediation. They are useful at sites that are large, but the contamination is relatively shallow. The benefits of *in situ* remediation systems over conventional methods are the lower final cost for remediation, minimum cost for operations and maintenance, no moving parts that could break, and no discharge permits or waste disposal of liquids for in-situ groundwater treatment. Vitrification is expensive but can be used to remediate mixed wastes, where few technologies are currently available. Electrokinetics and soil flushing methods are also promising, and have been used successfully at a few sites (9). At present,

phytoremediation and bioleaching are areas of primary focus of remediation research, because these techniques are environmentally friendly and relatively cheap. These techniques are useful for areas of low contamination, but longer treatment times are generally necessary. Some of the areas where research is still needed to use these technologies commercially are enhancing the metal accumulation capacity of plants by biotechnology, determining the correlation between soil properties and bioavailability, and developing methods to extract metals from plants (27).

BIBLIOGRAPHY

1. Adriano, D.C. (1986). *Trace Elements in Terrestrial Environments*, 2nd Edn. Springer-Verlag, New York.
2. Garbisu, C. and Alkorta, I. (2001). Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. *Biores. Technol.* **77**: 229–236.
3. Vangronsveld, J. and Clijsters, H. (1994). Toxic effect of metals. In: *Plant and Chemical Elements*. M.G. Farago and V.C.H. Weinheim (Eds.). VCH Verlags Gesell Shaft, New York, pp. 149–177.
4. Khan, A.G. et al. (2000). Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere* **41**: 197–207.
5. Smith, L.A. et al. (1995). *Remedial Options for Metals Contaminated Sites*. Lewis, Boca Raton, FL.
6. Zimmerman, L. and Coles, C. (1992). Cement industry solutions to waste management-the utilization of processed waste by-products for cement manufacturing. In: *Cement Industry Solutions to Waste Management: Proc. 1st Int. Conf. Canadian Portland Cement Association*, Toronto, Canada, pp. 533–545.
7. Evanko, C.R. and Dzombak, D.A. (1997). *Remediation of Metal Contaminated Soils and Groundwater*. Technology Evaluation Report, TE-97-01. Groundwater Remediation Technologies Analysis Center, Pittsburgh, PA.
8. Allen, J.P. and Torres, I.G. (1991). Physical separation techniques for contaminated sediment. In: *Recent Developments in Separation Science*. N.N. Li (Ed.). Vol. V, CRC Press, Boca Raton, FL.
9. Mulligan, C.N., Yong, R.N., and Gibbs, B.F. (2001). Remediation technologies for metal-contaminated soils and groundwater: An evaluation. *Eng. Geol.* **60**: 193–207.
10. Kabata-Pendias, A. (1992). Trace metals in soils in Poland—occurrence and behavior. *Trace Substance Environ. Health* **25**: 53–70.
11. Li, W., Peters, R.W., Brewster, M.D., and Miller, G.A. (1995). Sequential extract evaluation of heavy metals-contaminated soils. How clean is clean? In: *Proc. Waste Manage. Assoc., 88th Annu. Meet. Exhibition*. San Antonio, TX., June 18–23.
12. Rumer, R.R. and Ryan, M.E. (1995). *Barrier Containment Technologies for Environmental Remediation Applications*. John Wiley & Sons, New York.
13. USEPA. (1985). *Handbook: Remedial Action at Waste Disposal Sites*. EPA/525/6-85/006, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
14. Conner, J.R. (1990). *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York.
15. Bishop, P., Gress, D., and Olafsson, J. (1982). Cement stabilization of heavy metals: Leaching rate assessment. In: *Ind Wastes-Proc. 14th Mid-Atlantic Ind. Waste Conf.* C.A. Cole and D.A. Long (Eds.). Technomics, Lancaster, PA.
16. USEPA. (1992). *Vitrification Technologies for Treatment of Hazardous and Radioactive Waste*. Handbook EPA/625/R-92/002, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.
17. Buelt, J.L. and Thompson, L.E. (1992). *The In-situ Vitrification Integrated Program: Focusing on an Innovative Solution on Environmental Restoration Needs*. Battelle Pacific Northwest Laboratory, Richland, WA.
18. NRC. (1994). *Alternatives for Groundwater Cleanup*. National Academy Press, Washington, DC.
19. Means, J.L. and Hinchee, R.E. (1994). *Emerging Technologies for Bioremediation of Metals*. Lewis, Boca Raton, FL.
20. Salt, D.E., Smith, R.D., and Raskin, I. (1998). Phytoremediation. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **49**: 643–668.
21. Rosetti, P.K. (1993). *Possible Methods of Washing Fine Soil Particles Contaminated with Heavy Metals and Radionuclides*. M.S. Thesis, Carnegie Mellon University, Pittsburgh, PA.
22. Elliot, H.A. and Brown, G.A. (1989). Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils. *Water Air Soil Pollut.* **45**: 361–369.
23. Ellis, W.D. and Fogg, T. (1985). *Interim Report: Treatment of Soils Contaminated by Heavy Metals*. Hazardous Waste Engineering Research Laboratory, Office of Research and Development, USEPA, Cincinnati, OH.
24. Tuin, B.J.W. and Tels, M. (1990). Extraction kinetics of six heavy metals from contaminated clay soils. *Environ. Technol.* **11**: 541–554.
25. USEPA. (1996). *Engineering Bulletin: Technology Alternatives for the Remediation of Soils Contaminated with Arsenic, Cadmium, Chromium, Mercury and Lead*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Cincinnati, OH.
26. USEPA. (1996). *Report: Recent Developments for In-situ Treatments of Metals-contaminated Soils*. PB96-153135, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
27. Datta, R. and Sarkar, D. (2004). Effective integration of soil chemistry and plant molecular biology in phytoremediation of metals: an overview. *Environ. GeoSci.* (in press).

GROUNDWATER REMEDIATION PROJECT LIFE CYCLE

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During the past decade, the groundwater remediation project life cycle has been used to characterize the status of an environmental project. If groundwater or soil contamination is suspected, a general process from assessment to closure occurs. In some cases, the project may involve many stakeholders, including landowners, responsible parties, bankers, operators/tenants, consultants, and regulators. In addition, others in the process might include environmental attorneys, realtors, developers, and interested parties such as neighbors and the community.

Although the timing and specific activities may vary from site to site, a general phased process occurs. Environmental evaluations of potential leakage or spillage of hazardous substances into the subsurface generally consist of four phases (Phase I through Phase IV). The generalized four-phase approach reflects the realistic process required to take a potentially impacted property from assessment phase (Phase I) through to the final monitoring and site closure phase (Phase IV). The phases generally proceed in order starting with Phase I. Some sites where soil or groundwater contamination is already suspected or documented might start with Phase II when a site has an underground tank or even Phase III, in the case of visually stained surface soils.

PHASE I

A Phase I Environmental Assessment is a set of noninvasive techniques to acquire information from site inspection and to obtain data supplied by others, including owners, operators, employees, and regulators. Sometimes, the Phase I Environmental Assessment is performed as part of a due diligence activity for a property transfer, as required by a financial institution on industrial, agricultural, and commercial properties. The transfer of ownership could occur during a corporate merger or acquisition or a routine sale. Other times, a Phase I Environmental Assessment is performed for financing or refinancing a loan on a commercial, industrial, or agricultural property. Other times, these activities might be required by regulatory agencies on properties when contamination is found, but no clear source of contamination is evident.

Phase I Environmental Assessments involve a site inspection, the development of the history of the property, and a review of data supplied by regulators, environmental lists and building permit databases, owners, tenants, and others.

A broad-based facility audit inspection focuses on the utilities, industrial processes, any signs of contamination, and all current and past permits and manifests (1). During the site facility inspection, the sources of all utilities (water, sewage, electrical, natural gas, electrical backup systems) are documented. Aboveground or underground storage tanks are frequently located at facilities that have backup power generators. The processes of the industrial facility from the input of the raw materials to the outflow of the finished products and associated liquid, solid and vapor wastes is reviewed. Recycling systems are documented. Visual clues of process activities such as staining, spillage, or leakage of liquids; and release of vapors or solid residues are documented and photographed. An investigator must also examine the permits for the facility, including any hazardous materials business plans, operating permits, hazardous material storage permits, building permits, waste generator permits, OSHA safety and training files, material safety data sheets (MSDS), environmental fines or compliance memos from regulatory agencies, and manifests for transportation and disposal of any hazardous materials generated on site.

Techniques include interviews of knowledgeable persons, review of historical aerial photography, and examination of published and unpublished historic maps. The maps include both historic topographic maps supplied by the USGS and Sanborn Fire Insurance Maps, as well as other local historic maps. Reverse telephone or address directories, chain-of-title reports, and regulatory databases may be reviewed. Noninvasive data may be collected on a property using handheld vapor meters. Other noninvasive techniques that would generate data include surface geophysics such as ground penetrating radar (GPR) and magnetic or induction surveys to locate buried tanks, pipes, or drums.

A passive vapor survey can be used to locate upward migrating volatile organic compounds that may lie within a few centimeters from the surface. This approach consists of placing a natural (carbon) or synthetic (Gore-sorber) adsorbent a few centimeters into the subsurface. The sorbent is usually placed in the upper end of an inverted glass or plastic container or test tube that has an open bottom where migrating vapors enter and collect. The collection device is left for an extended time, from a few days to a few weeks. Subsequently the adsorbent is removed and analyzed using a gas chromatograph. When the vapor data are evaluated, investigators can plot the various VOCs detected and concentration patterns on site maps. This exercise frequently allows an interpretation on the location of a source of detected shallow VOC contamination.

PHASE II

A Phase II Subsurface Investigation is normally invasive and is designed to evaluate the lithologic and hydrogeologic conditions by collecting soil, soil vapor, and groundwater samples. A variety of techniques and equipment are currently available for assessing the subsurface. Environmental subsurface investigation tools range in size, cost, and operating complexity from hand augers and hand-operated drive samplers to direct push technology (DPT) rigs to hollow stem auger rotary rigs. Samples are collected for field screening and physical testing. Selected soil, vapor, or groundwater samples are submitted under chain-of-custody procedures in a refrigerated environment (for volatile and semivolatile compounds) to a certified laboratory for chemical testing.

As part of Phase II, groundwater monitoring wells may be installed. Several Phase II Subsurface Investigations might be required prior to completing the Phase II process and fully characterizing the vertical and lateral extent of the soil and groundwater contamination.

PHASE III

A Phase III Corrective Action is the remediation portion of an environmental project. This phase involves designing and implementing the corrective action plan for remediation of soil and/or groundwater. A corrective action plan, evaluating remedial options and feasibility, is typically submitted to the regulator for approval prior to

commencing the field work. A laboratory bench test might be designed to optimize biological or chemical conditions using soil and groundwater derived on site. This phase may also have a pilot test where the various technologies selected are field tested to verify the successes and failures prior to performing the full-scale remediation. After the bench tests and pilot scale tests, a final remedial action plan is usually prepared with the final selection of the remedial option.

Remediation might include extractive technologies (soil vapor extraction, groundwater pump and treat, dual phase extraction). These technologies remove liquids and vapors and treat the contaminants using a variety of above-ground technologies. Other technologies include bioremediation (*in situ*), chemical oxidation (*in situ*), monitored natural attenuation (*in situ*), soil excavation and removal to a landfill (dig and haul), or other technologies that are first evaluated in the corrective action plan.

Drilling techniques might be used during the remediation phase in designing and constructing vapor or groundwater extraction wells. In Phase III, it is unlikely that all contamination is removed, and therefore some residual amount of contamination will be left in place. A well-planned soil and groundwater confirmation sampling program is key to evaluating the success of a Phase III Remediation Project. As part of a Phase III Remediation Project, additional soil and groundwater sampling (a Remedial Investigation) might be planned if additional new source areas of impacted soil or groundwater are detected that were previously unknown.

Once the technology is selected and approved, the full-scale remediation is performed. Upon completing the full-scale remediation activities, equipment such as free-product pumping systems, soil vapor extraction, and aboveground air and water treatment units are demobilized and removed from the site. All drilling and remediation derived wastes are removed from the property. Site restoration may include replanting or resurfacing in disturbed areas.

PHASE IV

After remediation, the regulatory agencies generally require at least a minimum of 1 year quarterly groundwater monitoring verifying that the majority of the source of the contamination has been removed. This phase includes the proper abandonment of existing groundwater monitoring wells after site closure has been obtained. Phase IV might include a sensitive receptor survey to evaluate human health risks or sensitive environments that might be impacted if residual contamination is left in place. A risk based corrective action (RBCA) is a computer model that evaluates residual contamination as to the type of contamination, contamination levels in soil, vapor and groundwater, possible receptors, depth to the contamination, types of soils, and other factors. As part of the site closure process, deed restrictions may be required and notifications to any future contractors performing subsurface work that certain areas of the site might be impacted.

The Phase I to Phase IV project life cycle is an engineering approach that has been used on tens of thousands of sites. Every site is different, so the logical and stepwise approach is a generally accepted model for moving a project from initial discovery toward site closure.

BIBLIOGRAPHY

1. Wadge, L. (2000). Site evaluation, auditing and assessment. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 11.1–11.6.

READING LIST

Jacobs, J. (2000). Monitoring well construction and sampling techniques. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 11.46–11.68.

INNOVATIVE CONTAMINATED GROUNDWATER REMEDIATION TECHNOLOGIES

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INTRODUCTION

Contamination of groundwater is a problem of global proportions. Ever increasing demand for clean water for human, industrial, and agricultural uses, forces society to protect groundwater resources from further pollution and also to restore already polluted aquifers. Groundwater contamination originates from numerous sources, such as accidental spills, illegal dumping, leaking landfills, industrial wastewater discharge, and leakage of underground storage tanks. A major problem is that once toxic compounds have entered the subsurface, they are very difficult and costly to remove using conventional remediation strategies. Conventional remediation methods, such as flushing-out the contamination with water (known as the pump-and-treat method), generally have been proven inefficient. The National Research Council indicated that large sums of money are wasted by implementing these conventional methods (4).

The development of improved methods for remediating of contaminated aquifers has become a major environmental priority (1,2). Many innovative remediation technologies have emerged that promise fast and cost-effective cleanup of contaminated ground water. According to Cherry et al. (3), there are two general types of new technologies, those that destroy or immobilize contaminants *in situ* (e.g., chemical oxidation, chemical reductive dehalogenation, cometabolic and other bioremediation processes) and those that bring the contaminant mass to the surface for treatment or disposal (e.g., enhanced-flushing technologies, thermal treatment).

The following is a discussion of innovative remediation methods. The description of these new technologies is selective and by no means complete. It focuses on the *in situ* remediation of contaminated aquifers and cleanup technologies for vadose zone contamination but neglects *ex situ* treatment technologies (e.g., soil washing, thermal desorption). This is not an attempt to describe the theoretical and technical details involved but rather a summary of the concepts and challenges inherent in subsurface remediation. For a more detailed discussion of innovative remediation technologies, refer to a number of excellent publications (1–5) or good Internet sources (e.g., Ground-Water Remediation Technologies Analysis Center at www.gwrtac.org/html/techs.html, USEPA Technology Innovation Office at www.epa.gov/swertio1/remed.htm, or clu-in.org).

ANATOMY OF A SPILL

The area where a spill occurred and where most of the contaminant mass is concentrated is called the source zone. Sometimes the extent of the source zone is known, but more often it is not—especially in case of older spills and illegal dumping. The source zone can be limited to the vadose (i.e., unsaturated) zone or, if a sufficient volume of liquid contaminant has been spilled, can include the saturated zone. Once in the subsurface, a contaminant can partition into the vapor or aqueous phase, can remain stationary at residual concentration, or can continue to migrate as a free phase. Diffusive vapor phase transport is an important contaminant-spreading mechanism in the vadose zone (6). Dissolved contaminants in the saturated zone are transported away from the source zone by advection and dispersion. The contaminated water emanating from the source zone is called the plume. The general shape of the plume is that of an elongated teardrop; it tends to be much longer than wide. Contaminant concentrations are highest near the source zone and decrease toward the plume's outer edges. Even if the source zone is removed, the plume's center of mass (mean position of solute mass) can continue to move downgradient and spread, causing the plume to become larger. The plume continues spreading until it is intercepted by a natural or man-made hydrologic boundary, such as a river, drain, or well. In absence of a hydrologic boundary, the plume may eventually slow down or stop spreading entirely, which is the case when the contaminant degradation rate is in equilibrium with the contaminant-spreading rate. This equilibrium has been observed in some cases where petroleum products were released from underground storage tanks. Conversely, the degradation rates of many synthetic contaminants (especially those of halogenated compounds) are extremely slow. Thus, there are examples where a plume can grow across large distances, often for many miles.

INNOVATIVE REMEDIATION TECHNOLOGIES

A large variety of toxic compounds have entered the environment, including organic and inorganic compounds, heavy metals, radioactive substances, and biological contaminants. Realizing that each of these compound classes has distinct chemical and physical properties, quite different remediation approaches are required. For instance, a method that works well for removing heavy metals will most likely not work for a gasoline spill and vice versa. Thus, there are as many different remediation strategies as there are classes of toxic compounds. The hydrogeologic setting of a contaminated site may also elude or favor a specific remediation method, and, in some cases, a combination of two or more remediation technologies may be advantageous. The following is a description of innovative remediation techniques that remove or immobilize contaminants and methods that destroy contaminants *in situ*.

Removal and Immobilization Technologies

Removal and immobilization of contaminants are popular subsurface remediation strategies. Immobilization is a technique often used for heavy metal stabilization or fixation. This technology relies on injecting agents that form stable and insoluble metal precipitates with metals such as mercury or radioactive nuclides. Recently, the role of biogenic metal fixation processes has also been investigated. One of the greatest obstacles to *in situ* metal immobilization is delivery of the precipitant to the contaminant because it requires careful control of the subsurface conditions, such as pH. Therefore, immobilization has been most successfully used for treating excavated sediments, such as dredged materials.

Although applicable to many contaminant classes, contaminant removal is most often used to eliminate organic contaminants—especially nonaqueous phase liquids (NAPL). NAPLs have been identified as one of the most important groups of environmental contaminants (4,7). Examples include chlorinated solvents, gasoline, polychlorinated biphenyls, creosote, and coal tar.

NAPL's have distinct physicochemical properties and can exist in different compartments in subsurface environments, occupying the pore spaces as separate liquids or gaseous phases, dissolved in water, or attached to soil particles (8). Fluids whose densities are less than that of water are known as light nonaqueous phase liquids (LNAPL). Examples include gasoline and crude oil. LNAPLs accumulate on the water table and in the capillary fringe zone. They may also migrate downgradient away from the source zone, dissolve into the ground water, or may smear throughout the upper part of the aquifer due to water table fluctuations. In contrast, a DNAPL is a nonaqueous phase liquid that is denser than water. Examples include trichloroethene (TCE) and 1,1,1-trichloroethane. A DNAPL, therefore, can sink below the water table into deeper parts of the aquifer. Due to interfacial forces, a fraction of the contaminant may be retained in pores as immobile globules or ganglia, which tend to dissolve very slowly (9). If a DNAPL encounters less permeable geologic strata (such as fine silt or clay horizons), it may form pools. DNAPL pools, ganglia, and globules are a major problem for site remediation because they tend to be relatively small and dispersed and thus difficult to locate. With an unfavorably low surface area to mass ratio, these DNAPL bodies serve as long-term sources of groundwater contamination (3).

Conventional pump-and-treat systems may work well for plume containment, but it is widely recognized that this method is neither an effective nor economical means of complete remediation of sites contaminated with NAPLs (10). Pump-and-treat methods remove contaminants from the subsurface by forced displacement of the immiscible liquid due to artificially increased pore water velocities and by dissolution into the groundwater. Because most field sites require unrealistically high hydraulic gradients to displace residual NAPLs, dissolution is the primary removal mechanism. Thus, the inefficiency of the pump-and-treat approach is attributed to the low aqueous solubility of most NAPLs and the relatively large interfacial tensions between the groundwater and the NAPL. Overcoming low solubility and large interfacial tension is one major strategy for removing NAPLs from the subsurface. Methods that modify the contaminant solubility and interfacial tension are known as chemically enhanced flushing technologies. Based on the removal mechanism, chemically enhanced flushing technologies can be grouped loosely into two categories: (1) mobilization and removal of NAPL through immiscible displacement and (2) increase of the apparent solubility of a NAPL in the aqueous phase and removal by enhanced dissolution. Chemical agents that have been used for enhanced flushing include cosolvents (5,11), surfactants (5,12), dissolved organic matter (13), and complexing agents, such as cyclodextrin (14,15,18) (see Table 1).

Enhanced flushing of contaminated aquifers generally requires injecting an aqueous solution containing a solubility-enhancing agent. This solution is flushed through the contaminated aquifer and then extracted. Enhanced flushing works best in permeable sediments, such as sand and gravel. Conventional injection and extraction wells can be used to control the flow field of the flushing solution. This application scheme is, in principle, similar to conventional pump-and-treat systems. But due to the solubility enhancing properties of the agent in solution, mass removal rates are much higher, and consequently remediation times are much shorter. Many solubility-enhancing agents, such as most surfactants, also decrease the interfacial tension between the NAPL and the aqueous phase, which can result in mobilization of the NAPL. In some cases, mobilization is desirable because it increases the overall mass removal rate. However, if mobilized NAPL escapes hydraulic control and migrates off-site or into deeper aquifer horizons (as can be expected of DNAPLs), previously uncontaminated areas can become contaminated. Some surfactants are also sorbed to the sediment, which increases the amount of surfactant required to remove the NAPL. In addition, many cosolvents and surfactants are somewhat toxic, and there is concern about residuals left behind in the subsurface after primary remediation has been implemented. Thus, careful selection of appropriate enhancing agents and well-designed injection/extraction systems are crucial for successful application of chemically enhanced flushing technologies.

Thermal *in situ* treatment is a second approach for removing contaminants—especially volatile compounds and NAPL—from the subsurface. This method is based on heating polluted sediment and groundwater by hot air, water, steam, or energetic waves to move or mobilize contaminants toward extraction wells. The extraction wells capture the contaminants and deliver them to the surface for further treatment. In addition, heating can destroy contaminants that are unstable at elevated temperatures. Depending on the heat source, there are several thermal treatment methods available (Table 2). A special case of thermal treatment is *in situ* vitrification, which has been used to destroy or immobilize pesticides, heavy metals, and dioxins. This method requires heating the contaminated sediment by applying strong electrical currents until the contaminated sediment melts. After cooling, the vitrified material bears little resemblance to the original sediment, and it can no longer be considered an aquifer.

Air sparging and soil vapor extraction (SVE) are methods commonly used for removing volatile contaminants from groundwater and the vadose zone, respectively. Air sparging requires installing air injection and vacuum extraction wells. The injection wells are placed in the

Table 1. Chemically Enhanced Flushing Methods for Contaminant Removal from the Subsurface

Method	Removal Mechanism
Cyclodextrin flushing	Hydrophobic contaminant can form a complex within the hydrophobic interior of the cyclodextrin molecule. Because the cyclodextrin's exterior is hydrophilic, the contaminant/cyclodextrin complex has a higher solubility compared to the contaminant in aqueous solution. It can then be flushed out of the ground and treated on the surface.
Surfactant flushing	Above the critical micelle concentration, surfactant molecules cluster together to form micelles. The micelles have a hydrophobic interior into which hydrophobic contaminants can partition. Like cyclodextrin, the micelle's exterior is hydrophilic and therefore water-soluble. The contaminant bound within the micelle can then be flushed out of the ground and brought to the surface for further treatment. In addition, surfactant can lower the interfacial tension between a NAPL and the aqueous solution. This can result in NAPL mobilization.
Cosolvent flushing	The addition of cosolvents, e.g., ethyl or methyl alcohol, decreases the polarity of the aqueous phase. This enhances the dissolution of hydrophobic contaminants, which can then be flushed out of the ground. Sometimes, cosolvents and surfactants are applied together.
Dissolved organic matter flushing	Dissolved organic matter is usually applied as humic acid solution. The humic acid attracts hydrophobic contaminants and facilitates their transport. The humic acid/contaminant solution is then extracted from the ground and treated on the surface.

Table 2. Thermal Treatment Methods for Contaminant Removal from the Subsurface. Based on the Mechanism of Delivering Heat to the Contaminated Zone, Several Approaches are being Used

Method	Source of Heat and Removal Mechanism
Hot air injection	Hot air is injected through injection wells. Volatile contaminants evaporate or mobilize. The contaminant phase is captured by extraction wells. Some instable contaminants may break down when heated.
Steam injection	Similar to hot air injection, but steam is the source of heat.
Hot water injection	Injection of hot water into the source zone. Contaminants are mobilized and can be extracted from the subsurface.
Thermal conduction	Heat is transferred to the contaminated zone from heated steel wells or by using thermo blankets (shallow aquifers). Removal mechanisms are evaporation and destruction.
Radio-frequency heating	Contaminants evaporate when sediment is heated by radio waves. Wells function as antennas from which the radio waves are emitted.
Electrical resistance heating	Steel wells deliver an electrical current that heats up the sediment and groundwater. Contaminants evaporate or break down.

contaminated zone and screened below the water table. Air is pumped into the wells and forced to bubble through the contaminated aquifer. Volatile contaminants, such as gasoline and most solvents, move from the aqueous phase into the air phase. The vapors rise to the water table and into the vadose zone where they can be pulled out of the ground by vacuum extraction wells. SVE works similarly to air sparging, but vapors are removed only from the vadose zone. The vapors are pulled out of the unsaturated sediment using vacuum extraction wells. Additional air vents or air injection wells can aid SVE. In contrast to air injection wells, air vents passively allow fresh atmospheric air to enter the vadose zone. In most cases, injecting oxygen-rich atmospheric air into the subsurface enhances the bioactivity, which, in return, can result in faster breakdown of many contaminants. An extraction well can be converted into an injection well, which allows minimizing dead zones (parts of the contaminated zone that are bypassed). Depending on the size of the contaminated area, the number of wells can range from a few to more than a hundred. SVE and air sparging technologies are widely used because they are comparably inexpensive and require little engineering.

Phytoremediation is another innovative contaminant removal method. This method involves using plants to remediate contaminated water and sediments. The principal processes involved are phytostabilization, phytodegradation, phytoextraction, and phytovolatilization (Table 3). The contaminants are usually taken up in dissolved form. The efficiency of phytoremediation depends on a variety of factors, such as pH, soil properties, climate, and plant physiology. Phytoremediation, for example, has been used for remediating nitroaromatic explosives and heavy metals (19). A shortcoming of this method is that it is inefficient during winter months and it is confined to relatively shallow zones of contamination.

In Situ Destruction Technologies

The innovative remediation technologies that have been discussed so far were mostly aimed at immobilizing or removing the contaminant form the subsurface. A second strategy is based on *in situ* destruction of contaminants. Biotic and abiotic methods are available. Both approaches are discussed in the following sections.

Oxidation Processes. Many organic contaminants, such as petroleum hydrocarbons, solvents, and pesticides, can be destroyed or converted into harmless compounds when exposed to chemical oxidizers. Oxidation is a process by which an oxidant provides the chemical energy (e.g., as free oxygen radicals) to change the chemical composition of the target molecule into an oxidized and less harmful state. A simple example is the oxidation of methanol to carbon dioxide and water.

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

Potassium or sodium permanganate ($KMnO_4$, $NaMnO_4$) and hydrogen peroxide (H_2O_2) are commonly used oxidants for site remediation. When dissolved in water and injected into the contaminated zone, the oxidant comes in contact with the contaminant and destroys it. Because not all of the oxidant is consumed in most cases, it may be necessary to extract the remaining solution. The success of *in situ* oxidation is determined by the oxidant's ability to reach the contamination, which is relatively unproblematic in sand and gravel deposits but can be a challenge in dense silt and clay. Because permanganate converts into much less soluble manganese dioxide (MnO_2), precipitation and subsequent reduction in the aquifer's permeability may be problematic.

Another *in situ* oxidation technology is based on Fenton's reaction. Fenton's reagent is a mix of H_2O_2 and iron salts that are injected into the contaminated zone. The presence of the iron salt creates hydroxyl radicals that readily oxidize chlorinated solvents and other contaminants, such as fuel oils and BTEX. The Fenton's reagent reaction is much more efficient than H_2O_2 alone, but a disadvantage is that Fenton's reagent is toxic to microbes, making it incompatible with bioremediation.

Table 3. Phytoremediation Methods for Contaminant Removal from the Subsurface

Method	Removal and Remediation Mechanism
Phytostabilization	Contaminants are bound in the plant tissue.
Phytodegradation	Plant-assisted microbial or enzymatic breakdown of contaminants.
Phytoextraction	Bioconcentration of contaminants within harvestable zone of the plant.
Phytovolatilization	Plant takes up and volatilizes contaminants via its leaves.

The injection of ozone (O_3) has been used to remediate sites contaminated with polycyclic aromatic hydrocarbons (PAHs), fuels, chlorinated solvents, and other contaminants. Ozone is a strong oxidant and, compared to oxygen, is 12 times more soluble. Therefore, it can be delivered to the contaminant much more efficiently. However, the half-life of O_3 limits its ability to migrate through soil across large distances. Ozone is a gas and must be generated on-site, for example, by using ultraviolet light. *In situ* ultraviolet (UV) oxidation is a special case of ozone treatment. This technique exposes the contaminated groundwater to ozone and H_2O_2 generated by intense UV radiation. UV radiation is provided by UV light bulbs that are installed inside a well. The target contaminants are destroyed by direct reaction with the oxidizers and through the interaction with UV light.

Each oxidizing agent has its own special treatment application, and the selection of the oxidizing agent is based not only on the contaminant type but also on sediment and groundwater properties. Some oxidizing agents are corrosive or can cause explosions if not handled adequately. However, when designed properly, chemical oxidation is safe and has been used at hundreds of sites.

Reduction Processes. Environmental hydrogeologists have realized that zero-valent iron effectively reduces many halogenated contaminants if placed within the flow path of contaminated groundwater (16). This revelation resulted in the development of a new remediation technology, permeable reactive barriers (PRB). A PRB requires installing a permeable barrier ("wall") across the flow path of a contaminant plume. The plume moves passively through the wall, and the dissolved contaminants come in contact with reactive materials that either degrade or retain the contaminants. The earliest PRBs were iron walls that consisted of a narrow trench filled with zero-valent iron granules mixed with sand and gravel. These iron walls were first tested for passive treatment of dissolved chlorinated contaminants such as TCE. As the TCE comes in contact with the iron, its chlorine atoms are removed by one or more reductive dechlorination mechanisms. The necessary electrons are supplied by the oxidation of iron. Given sufficient residence time, the TCE degrades to harmless compounds (chloride, water, etc.), and clean groundwater flows out the other side of the PRB. Since then, other active agents such as a palladium-enhanced metal catalyst, chelators, sorbents (e.g., carbon), precipitators (e.g., limestone), and microbes were added to the PRB system to retain or destroy those compounds that the iron walls could not degrade sufficiently. By including a funnel-and-gate system the PRB's efficiency is further enhanced. The funnel-and-gate system for *in situ* treatment of contaminated plumes consists of barriers of low hydraulic conductivity (e.g., slurry walls or sheet piles). Like a funnel, the barriers channel the contaminated water to a gate that contains the *in situ* reactor (17).

PRBs are widely used to control organic contamination in ground water; but they have been applied to metals (e.g., chromium VI) and radionuclide contaminants too. Passive treatment walls are generally intended for long-term control of the migration of contaminants in groundwater. An important advantage of this technology is that no pumping and no moving parts are required. Thus, this technology may be more cost-effective than pump-and-treat methods. In the United States, several dozens PRBs have been installed, but this technology is currently limited to sites with relatively shallow plumes (less than 50 ft). The installation of a PRB requires a comparatively high initial investment and a commitment to long-term monitoring, which is because the treatment approach is limited to the contaminant plume and does not target the source zone itself.

Bioremediation. Microorganisms can use many contaminants as food and energy sources and, in the processes, break down these compounds. *In situ* groundwater bioremediation, also called enhanced biodegradation, is a remediation technology that encourages growth and reproduction of indigenous microorganisms (yeast, fungi, or bacteria) that enhance the biodegradation of toxic organic constituents. Creating a favorable environment for the microorganisms can stimulate the activity of microbes. Generally, this means providing some combination of electron acceptors (oxygen, nitrate), nutrients (nitrogen, phosphorous), moisture, and controlling the temperature and pH. In most cases, electron acceptors and nutrients are the two most critical components of a bioremediation system. These compounds are delivered by pumping air and nutrient solutions into the contaminated zone. Sometimes, microorganisms adapted to degradation of the specific contaminants or additional food sources (e.g., molasses) are added to enhance the biodegradation process.

Bioremediation can take place under anaerobic and aerobic conditions. In anaerobic conditions, no oxygen is present. The microorganisms break down chemical compounds and release the energy they need. Aerobic conditions support biological activity in which microorganisms use available atmospheric oxygen to function. Anoxic conditions exist when nitrate is the base of microorganism respiration. With sufficient oxygen, microorganisms will convert many organic contaminants to carbon dioxide and water. Degradation pathways can be very complex. Sometimes intermediate products that are less, equally, or even more toxic than the original contaminants are produced. Some contaminants are also degraded by enzymes produced by microbiological metabolism. These enzymes aid the degradation of contaminants that are difficult or impossible to treat otherwise (e.g., cometabolic biodegradation of TCE).

In situ groundwater bioremediation is a widely used technology because it can effectively degrade dissolved and adsorbed organic constituents. As a general rule of thumb, short-chain, low molecular weight, and more water-soluble compounds are biodegraded more rapidly and to lower residual levels compared to long-chain, high molecular weight, less soluble compounds. The effectiveness of bioremediation systems is controlled by how well electron acceptors and nutrients can be delivered to the contaminated zone and how bioavailable and biodegradable the target contaminants are. Aerobic degradation has been proven most effective for treating aliphatic and aromatic petroleum hydrocarbons (e.g., gasoline and diesel fuel). Anoxic, anaerobic, and cometabolic approaches are

sometimes used for remediating chlorinated solvents, but remediation rates are generally slower compared to aerobic respiration of petroleum hydrocarbons.

Natural Attenuation. Dilution, dispersion, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials are processes that occur naturally and help to reduce the concentration, toxicity, and mobility of chemical or radioactive contaminants. Natural attenuation relies on these processes. Therefore, natural attenuation is not a technology as such, but rather is a cleanup strategy that uses nature's own decontamination capabilities. Nonetheless, natural attenuation is not a "do nothing" solution because it requires careful monitoring and testing of the processes that take place in the subsurface. For example, long-term contaminant degradation rates have to be sufficient to ensure public health and compliance with regulatory criteria. Therefore, monitoring of plume spreading or changes in hydrogeological, geochemical, or microbiological conditions that might reduce the effectiveness of natural attenuation is required.

Because natural attenuation does not require direct human intervention, it has become a very popular remediation strategy at many contaminated sites. However, natural attenuation may not be a viable method for removing the source of the pollution, because many of the natural attenuation mechanisms may be inactive in the presence of high contaminant concentrations. In these instances, other remediation methods must be used to remove the bulk contamination first.

CONCLUSION

Innovative remediation technologies have greatly improved the effectiveness of subsurface cleanup operations. Some technologies have already progressed into full-scale commercial applications; others remain in the developmental stage or have just emerged from research labs. However, remediation costs can be extremely high, and there is an ongoing debate about the economical cost of remediation versus the gains to public health. Against this background, improved risk assessment methods and concepts are necessary to ensure optimum remediation effectiveness—regardless of the remediation technology used.

BIBLIOGRAPHY

1. Grubb, D.G. and Sitar, N. (1994). *Evolution of technologies for in-situ cleanup of DNAPL contaminated sites*. EPA Report 600/R-94/120.
2. National Research Council (NRC) (U.S.). (1997). *Innovation in Ground Water and Soil Cleanup*. National Academy Press, Washington, DC.
3. Cherry, J.A. and Pankow, J.F. (1996). *Dense Chlorinated Solvents and other DNAPLs in Groundwater*. Waterloo Press, Portland, OR, P. 522.
4. National Research Council (NRC) (U.S.). (1994). *Alternatives for Ground Water Cleanup*. National Academy Press, Washington, DC.
5. Lowe, D.F., Oubre, C.L., and Ward, C.H. (1999). *Surfactants and Cosolvents for NAPL Remediation: A Technology Practices Manual*. Lewis Publishers, Boca Raton, FL, p. 412.
6. Conant, B.H., Gillham, R.W., and Mendoza, C.A. (1996). Vapor transport of trichloroethylene in the unsaturated zone; field and numerical modeling investigations. *Water Resources Research* **32**(1): 9–22.
7. Mercer, J.W. and Cohen, R.M. (1990). A review of immiscible fluids in the subsurface. *J. Contam. Hydrol.* **17**(6): 106–163.
8. Knox, R.C. and Sabatini, D.A. (1992). Transport and remediation of subsurface contaminants, colloidal, interfacial, and surfactant phenomena. *American Chemical Society Symposium Series* 491, American Chemical Society, Washington, DC.
9. Schwille, F. (1984). Pollutants in porous media: the unsaturated zone between soul surface and ground water. *Ecology Studies*. Springer-Verlag, New York, Vol. 47, pp. 27–48.
10. Mackay, D.M., Roberts, P.V., and Cherry, J.A. (1985). Transport of organic contaminants in ground water. *Environ. Sci. Technol.* **19**(5): 384–392.
11. Imhoff, P.T., Gleyzer, S.N., Mcbride, J.F., Vancho, L.A., Okuda, I., and Miller, C.T. (1995). Cosolvent-enhanced remediation of residual dense nonaqueous phase liquids; Experimental investigation. *Environ. Sci. Technol.* **29**(8): 1966–1976.
12. Fountain, J.C., Klimek, A., Beirkirch, M.G., and Middelton, T.M. (1991). The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer. *J. Hazardous Mater.* **28**: 295–311.
13. Johnson, W.P. and John, W.W. (1999). PCE solubilization and mobilization by commercial humic acid. *J. Contam. Hydrol.* **35**: 343–362.
14. Wang, X. and Brusseau, M.L. (1993). Solubilization of some low-polarity organic compounds by hydroxypropyl-β-cyclodextrin. *Environ. Sci. Technol.* **27**: 2821–2825.
15. Boving, T.B. and McCray, J.E. (2000). Cyclodextrin-enhanced remediation of organic and metal contaminants in porous media and ground water. *Remediation* **10**(2): 59–83.
16. Burris, D. and Cherry, J.A. (1992). Emerging plume managing technologies: In situ treatment zones. In: *Proceeding of the Air and Waste Management Association*. Annual Meeting, Kansas City, MO, June 21–26, 1992.
17. Star, R.C. and Cherry, J.A. (1994). In situ remediation of contaminated ground water: The funnel-and-gate-system. *Ground Water* **32**: 465–476.
18. Boving, T.B., Wang, X., and Brusseau, M.L. (1999). Cyclodextrin-enhanced solubilization and removal of residual chlorinated solvents from porous media. *Environmental Science and Technology* **33**(5): 764–770.
19. Rodgers, J.D. and Bunce, N.J. (2001). Treatment methods for the remediation of nitroaromatic explosives. Review paper. *Wat. Res.* **35**(9): 2101–2111.

RESISTIVITY METHODS

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INTRODUCTION

Many problems connected with groundwater can be investigated by geophysical methods. Of these, situation of water table, thickness of aquifer, delineation of weathered

or fracture zone, fresh–salt water interfaces, groundwater quality, and groundwater pollutant flow direction are the most important.

Among all surface geophysical techniques for groundwater prospecting, geoelectrical methods are the most widely applied methods for both alluvial plains and karstic terrains all over the world because of their high capability in detecting water-bearing layers and because they are simple and inexpensive in carrying out field investigation.

The rock matrix of most geological formations is basically highly resistive and does not conduct electricity. There are, however, exceptions such as clay and shale, which are conducting minerals. These formations have low electrical resistivities when compared with other rock formations. Normally, the resistivity of a rock formation reduces only when it contains moisture. This reduction in resistivity depends on the relative quantity and quality of the water it contains.

In nature, groundwater is stored in geologically formed pore spaces. When these pores are interconnected, the groundwater moves from a high potential to a low potential zone. The rock layers at different depths have different "porosities" and, consequently, different water content. The more water in a formation, the lower the electrical resistivity, provided there is no other conducting layer such as clay or shale. If the contained water is brackish or saline, the resistivity of that layer drops even further (1).

The conductivity of an underground formation also varies as its homogeneity varies. The variation in conductivity affects the flow density, which, in turn, affects the distribution of the potential difference under the ground. The size of this effect depends on the size, shape, position, and resistivity of the heterogeneity.

If we suppose that heterogeneity is a spherical void in a karstic limestone filled with water or clay (a good example of a highly conductive material inside one of low conductivity), the concentration of the flow inside the void would be much more than that out of the void and, to the same extent, the variation in potential difference would be different (Fig. 1). This variation can be detected at the ground surface (2).

Thus, by measuring or determining the resistivities of earth layers at different depths, it is possible to infer indirectly the hydrogeologic character of a particular subsurface layer and also the quality of water it contains. The most applicable geoelectrical methods are resistivity methods in which an electrical current is passed into the ground so that the current distributes itself according to the conductivities of the geologic materials coming under the influence of the current.

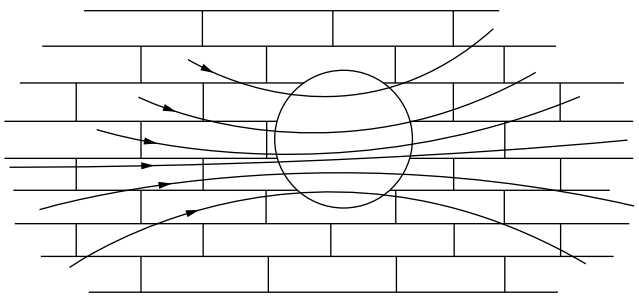


Figure 1. Concentration of electrical current in a spherical void filled with water or clay in a limestone formation (1).

RESISTIVITIES OF GEOLOGICAL FORMATIONS

The resistivity of rocks and minerals has a wide range (Fig. 2). For example, fresh igneous and metamorphic rocks have resistivities up to 10^5 to 10^6 ohm-m (ohm-meters), whereas shale and clay have resistivities less than 10 ohm-m. No other physical property found in geophysical prospecting varies so widely (3) and this is one of the best reasons for applying resistivity methods.

RESISTIVITY METHODS: THEORY AND APPLICATION

Resistivity (ρ) is a physical property of a substance. It is defined as the resistance to the flow of electric current by a unit cube of the substance when voltage is applied across the opposite faces. It is expressed in ohm-l (l is meters, feet, . . .). The resistance of a substance is a function of the resistivity, size, and shape. If the substance has a regular shape, then

$$R\rho L/A \tag{1}$$

where R = resistance, ohm;
ρ = resistivity of the substance, ohm-m;
L = length of the substance, m; and
A = cross-sectional area, m^2.

The inverse of resistivity is called conductivity.

We usually deal with heterogeneous media in geologic formations, so the term "apparent resistivity" is used instead of resistivity.

Measurement of Resistivity

In general, at least four electrodes are required for measuring the resistivities of subsurface formations. An electric current is introduced between one pair of electrodes, called current electrodes. The potential difference produced by current flow is measured by another pair of electrodes, called potential electrodes or probes. The apparent resistivity measured is (1):

$$\rho_a = K(\Delta V)/I$$

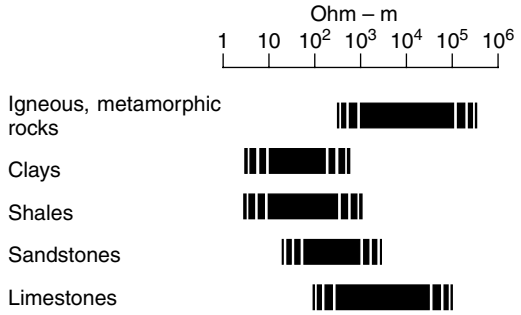


Figure 2. Ranges of resistivity in ohm-meters for some geologic formations (3).

where ρ_a = apparent resistivity, ohm-m;
K = geometric factor, which depends on the type of electrode configuration selected; and
I = electric current, (A).

Electrode Configurations. There are several electrode arrangements for geoelectrical operations (4):

Wenner Array. In this configuration, the four electrodes A, M, N, and B are placed along a straight line (Fig. 3), and $AM = MN = NB = a$.

Schlumberger Array. Schlumberger array is the most widely used method in electrical prospecting. In this configuration, the four electrodes are placed along a straight line in the same order as the Wenner array, but $AB > 5MN$ (Fig. 4).

Lee Partitioning Array. Lee partitioning array is the same as the Wenner array except that an additional potential electrode O is placed at the center of the array between the potential electrodes M and N (Fig. 5).

Dipole–Dipole Array. In this array, the distance between the current electrodes A and B (current dipole) and the distance between the potential electrodes M and N (measuring dipole) are significantly smaller than the distance r between the centers of the two dipoles (Fig. 6).

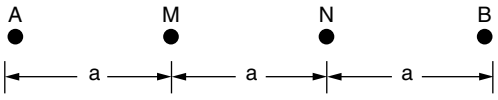


Figure 3. Wenner array (5).

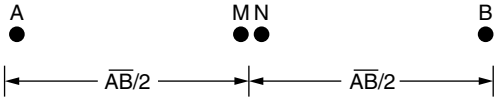


Figure 4. Schlumberger array (5).

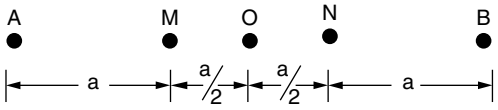


Figure 5. Lee partitioning array (5).

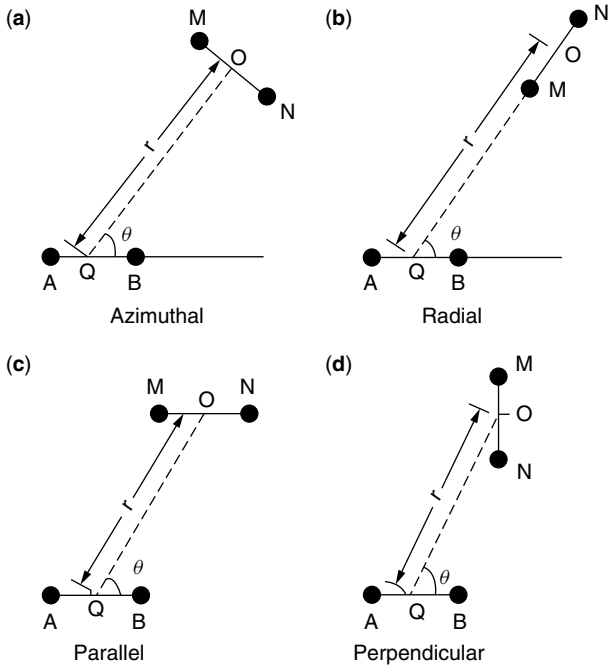


Figure 6. Dipole–dipole arrays (5).

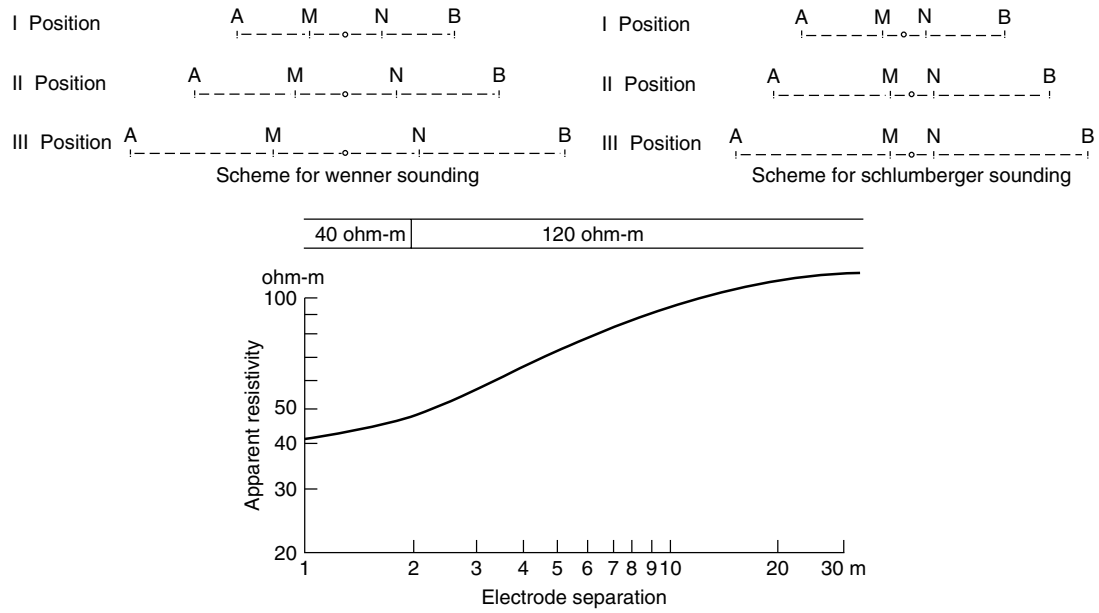


Figure 7. Scheme of array expansion for electrical sounding in Wenner and Schlumberger arrays (up). Variation of apparent resistivity with electrode separation for a two-layer earth where $\rho_{layer2} > \rho_{layer1}$ (down) (1,3).

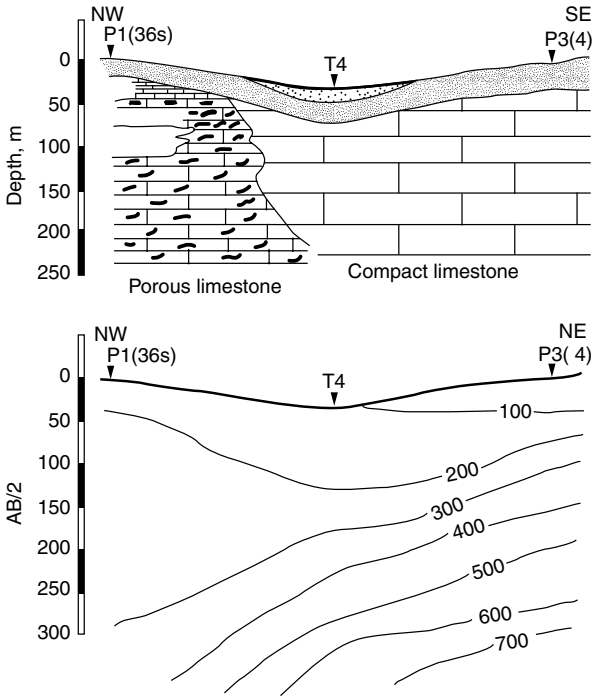


Figure 8. A geologic cross section along a karstic formation (up) and the apparent resistivity section for the same place (down) at Oshnavieh area, western Azerbaijan, Iran (6).

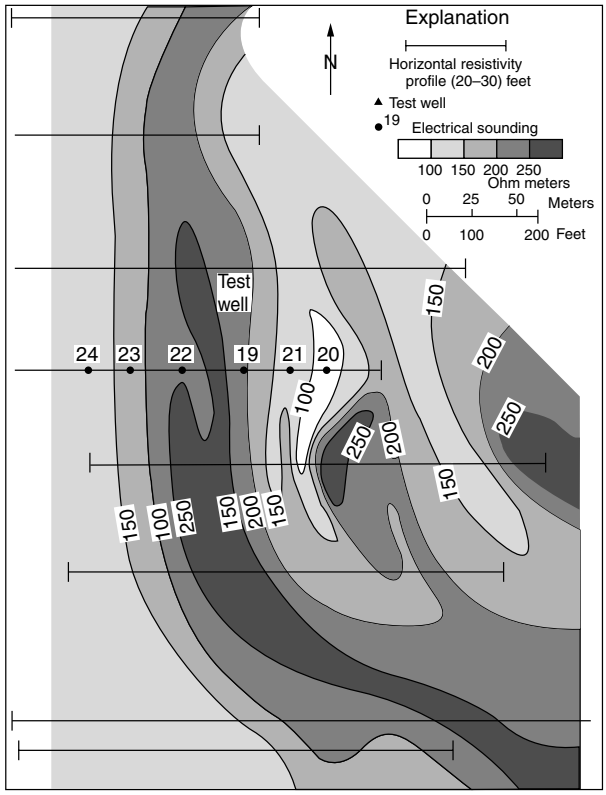


Figure 9. An apparent resistivity map for a site at Campbel, California. The low resistivity zone delineates a buried stream channel (5).

Electrical Sounding and Horizontal Profiling

Electrical sounding is a process for depth investigations, and horizontal profiling is a process for detecting lateral variations in resistivity. The basis for an electrical sounding, regardless of the electrode array selected, is that the farther away from a current source the measurement of the potential is made, the deeper the probing will be. So a curve of electrode spacing against apparent resistivity is made (Fig. 7).

In horizontal profiling, a fixed electrode spacing is chosen (preferably based on the results from a previous

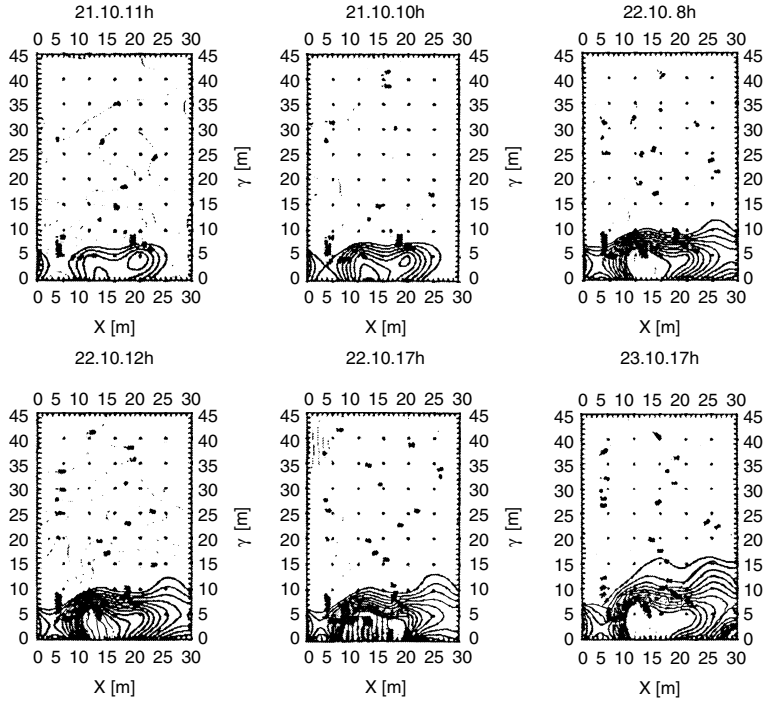


Figure 10. Determining pollution flow direction and velocity by the resistivity method (9).

electrical sounding), and the whole electrode array is moved along a profile horizontally. So a curve shows the variation of apparent resistivity for different points along the profile. Maximum apparent resistivity anomalies are obtained by orienting the profiles normal to the strike of the geologic structures.

Usually, the result of electrical sounding and horizontal profiling are apparent resistivity sections and maps. These plots indicate the variations in geoelectrical properties of the study area in vertical and planar surfaces, respectively. These plots can help in understanding the underground structure and lithology of different geoelectrical behaviors known for different geologic formations (Figs. 8 and 9).

RESISTIVITY METHODS AND GROUNDWATER POLLUTION STUDIES

Geoelectrical methods can be used easily to investigate groundwater contamination because pollution or any dissolved solid in groundwater directly affects its electrical conductivity and resistivity. So this method can be used to detect pollution plumes provided that the pollution has changed the resistivity of the groundwater enough to be detected.

Two case studies will be presented here to show the capability of the technique. In the first, a "tracer" has been intentionally introduced into the groundwater system, and the changes in groundwater resistivity have been investigated to find the velocity and direction of the tracer movement. In the second case, the resistivity method has been used to map the extent of the pollution zone in groundwater beneath a waste disposal site.

Case Study 1

This case is actually a single well technique in which a tracer is injected into the aquifer through a borehole. The tracer is NaCl, which is cheap and also has good electric properties. It is important to remember that this substance is selected to increase the conductivity of the water. If the study site is composed of saline soil and saline groundwater, injection of fresh water would again result in a suitable resistivity contrast. Before injection, geoelectrical sounding and horizontal profiling should be performed so that the base geoelectrical condition of the formation can be understood.

The study case is an unconfined shallow aquifer consisting of coarse gravel in Germany. A network for resistivity measurements is considered along the south–north direction, which, it is thought, is the direction of groundwater flow. After injecting 250 kg of salt, resistivity was measured every 5–6 hours at all points. The result is shown as isoresistivity maps in Fig. 10. The movement of the salt plume is clearly shown on the maps, and its velocity has been calculated as 7 meters per day. Contrary to what was supposed before, the direction of the movement of the plume was almost from west to east (7).

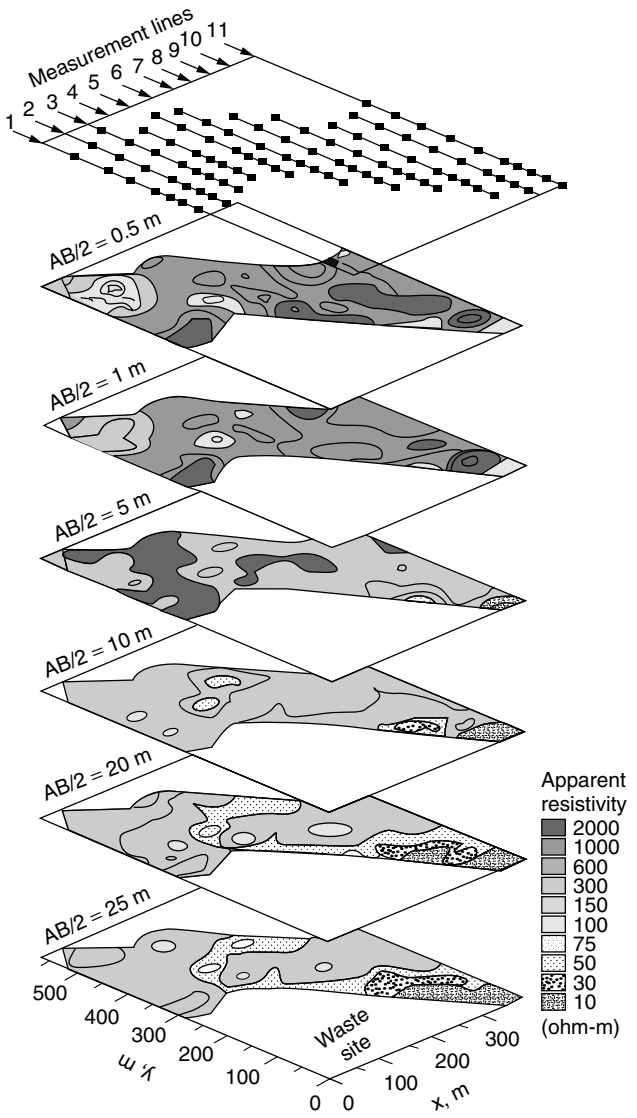


Figure 11. Geoelectrical measurement lines and apparent resistivity maps for different electrode spacings (8).

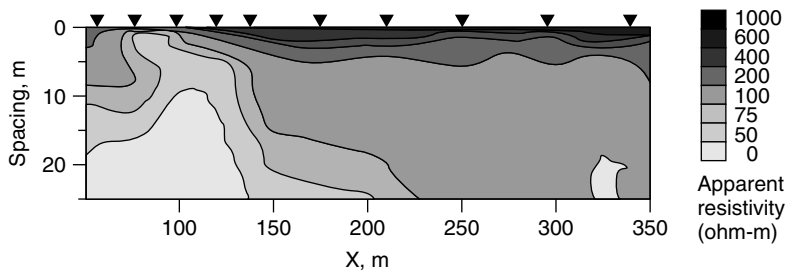


Figure 12. Resistivity pseudosection from south–north along measurement line 9 (8).

Case Study 2

In this case, the resistivity method has been used to map the extent of contamination induced by an open waste disposal site and to determine where to locate future monitoring wells. The site is located SE of the city Isparta, Turkey, on a nearly 100 m thick Quaternary alluvial deposit of gravel, sand, and clay. The Schlumberger sounding resistivity method was used to map resistivities from 0.5 down to 25 meters in depth. Figure 11 shows the apparent resistivity maps for different electrode spacings. As expected, leachate from the waste disposal site has decreased groundwater resistivity. The deeper layers are characterized by low resistivities, and the shallower ones by high resistivities.

A resistivity pseudosection along measurement line 9 is performed, and the result is shown in Fig. 12. As can be seen, the low resistivity front from the waste disposal site base is characterized by its low resistivity and is developing northward. So, the extent of groundwater pollution can easily be manifested using geoelectrical mapping (8).

BIBLIOGRAPHY

1. Rao, T.G. (Ed.). (1992). *Groundwater Exploration Techniques*. National Geophysical Research Institute, Hyderabad, India.
2. Jahani, H.R. (2005). *Applied Geophysical Methods for Groundwater Investigations*. Iranian Hydraulic Association, Tehran, Iran.
3. Griffiths, D.H. and King, R.F. (1988). *Applied Geophysics for Geologists and Engineers*. Pergamon Press, Oxford.
4. U.S. Soil Conservation Service. (1971). *Seismic and Resistivity Methods of Geophysical Exploration*. Water Resources Publications, United States Soil Conservation Service, Washington, DC.
5. Zohdy, A.A.R. et al. (1990). *Application of Surface Geophysics to Groundwater Investigations*. U.S. Geological Survey, Denver, CO.
6. Iranian National Karst Research Center. (1997). *Resistivity Methods of Geophysical Explorations in Karstic Areas in West Azerbaijan Province*. Shiraz.
7. Hotzl, H. and Werner, A. (Eds.). (1992). *Tracer Hydrology*. A.A. Balkema, Rotterdam, The Netherlands.
8. Karlýk, G. and Ali Kaya, M. (2001). Investigation of groundwater contamination using electric and electromagnetic methods at an open waste-disposal site: A case study from Isparta, Turkey. *Environ. Geol.* **40**(6): 725–731.

RISK ANALYSIS OF BURIED WASTES FROM ELECTRICITY GENERATION

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An important aspect of generating electricity from nuclear power is the disposal of the high level radioactive waste. The most widely anticipated plan is to convert it into a rock-like material and bury it deep underground, typically 600 meters below the surface. In evaluating the safety of this procedure, a key element is to estimate the probability per year, P, for an atom of this buried waste to be dissolved by groundwater and eventually enter a human stomach. Obviously, this probability is site dependent and depends on present underground characteristics and future events in the region, many of them unpredictable, including climate changes, geological land uplifting causing rivers to change their courses, volcanoes, earthquakes, and human intrusion.

INTRODUCTION

A first estimate of P can be obtained by considering that all properties of the region are the U.S. average (lower 48 states); the purpose of this article is to obtain such an estimate. Most relevant characteristics and future changes in them are occurring somewhere in the United States and are hence taken into account with or including some estimate of their probability of occurrence. The value of P we obtain can be interpreted as the average value of P for a large number of randomly chosen sites. It seems reasonable to assume that the very elaborate site selection efforts by geological and hydrologic experts should choose a site at least as secure as a randomly chosen site.

We assume that the waste converted to a rock-like material behaves like average rock—differences between them will be considered later—and calculate P for average rock. P can be calculated as the dissolution rate, R, the probability per year for an atom of the rock to be dissolved in groundwater, times the probability, p, for an atom once dissolved into groundwater to enter a human stomach:

$$P = R \times p \tag{1}$$

Dissolution Rate for Rock, *R*

We begin by calculating R. From the rate at which rivers carry dissolved and suspended material into the oceans, it is estimated (1) that the surface of the continent is eroding at an average rate of 5×10^{-5} (hereafter, we use the notation 5 E−5) meters per year (hereafter, m/y). About 28% of this material is in solution, corresponding to 1.4 E−5 m/y removed by chemical dissolution. It is estimated (2,3) that 15% of the water flow in rivers is derived from groundwater (aquifers), and the rest comes from surface runoff. If the concentrations of dissolved materials were the same in rivers as in aquifers, this would mean that the latter dissolve $(0.15 \times 1.4\ \text{E}{-5}) = 2.1\ \text{E}{-6}$ m/y of rock thickness. The average concentrations of a few dissolved materials in aquifers (4) and in river water (5) are listed in Table 1. Silica and calcium are such important

Table 1. Average Concentrations in mg/kg of Dissolved Materials in Aquifers[a] and in River Water[b]

Material	Silica	Calcium	Magnesium	Potassium	Iron	Uranium
Aquifers	20	30	3	2	0.3	3 E−4
Rivers	7	15	4	2.2	0.5	4 E−4

[a] Ref. 4.
[b] Ref. 5.

components of rock that we interpret these data to indicate that aquifers carry about twice the concentration of dissolved material in rivers, which leads to the conclusion that $[30/(30 + 85)] = 26\%$ of the dissolved material in rivers, $(0.26 \times 1.4\ \text{E}{-5}) = 3.6\ \text{E}{-6}$ m/y of rock depth, is contributed by aquifer dissolution of rock.

The next problem is to estimate what fraction of this material, f, is removed per meter of depth at 600 m; let us say from between 599 m and 600 m. As a crude gross overestimate, we might assume that rock erosion is constant with depth down to 600 m and zero below 600 m, in which case $f = 1/600 = 16\ \text{E}{-4}$. A more reasonable approach is as follows: The annual circulation of groundwater, defined as the quantity per year entering or leaving aquifers at the stated depth, has been given (2,3) as

shallow (<800 m) : 310 E9 cubic meters per year

deep (>800 m) : 6.2 E9 cubic meters per year

If we assume that the flow decreases exponentially with depth and that the rate of rock dissolution is proportional to this groundwater flow, determining the constants in the relationship from these data, we find (6) that $f = 2.6\ \text{E}{-4}$, one-sixth of our crude gross overestimate.

Using this gives the quantity of rock eroded per year per meter of depth at 600 m below the surface as $(3.6\ \text{E}{-6} \times 2.6\ \text{E}{-4}) = 1.0\ \text{E}{-9}$ m/y. If 1.0 E−9 m/y of depth is dissolved from one meter of rock depth, the probability per year for an atom of that rock to be dissolved must be 1.0 E−9. Thus,

$$R = 1.0\ \text{E}{-9} \tag{2}$$

This result plays a key role in our risk analysis, so it is interesting to seek alternative approaches to calculating it. One such approach follows: A typical aquifer reaching to the waste burial depth of 600 m may be about 100 km long and have a flow velocity of 100 m/y through rock of 10% porosity, discharging into a river The water discharged from it annually per square meter of cross-sectional area is then 10% of the volume of a column of water 100 m long and one square meter in cross section, which is 10 cubic meters, or 10,000 liters (L).

Chemical analyses of groundwater (4) indicate that it typically contains 30 mg/L or 30 E−6 kg/L (milligrams per liter, or kilograms per liter) of Calcium (Ca), so it discharges (30 E−6 kg/L × 10,000L =) 0.3 kg of Ca into the river each year. This is the first entry in Column (2) of Table 2. This calcium was derived by dissolution from the rock through which the aquifer had passed, 100 km, or 1E 5 m, long, one square meter in cross section, and a specific gravity of about 3.0, which gives it a mass of $(3000 \times 1\ \text{E}5) = 3\ \text{E}8$ Kg. Typical rock contains 5% Ca (1), so the Ca contained in this source rock is $(0.05 \times 3\ \text{E}8) =$ 15 E6 kg; this is the first entry in Column (3) of Table 2. If 0.3 kg of Ca per year is dissolved from 15 E6 kg of Ca in the rock, the probability for a Ca atom to be dissolved must be $(0.3/15\ \text{E}6) = 2\ \text{E}{-8}$ per year; this is the first entry in Column (4) of Table 2. Table 2 includes data for other materials, obtained analogously to that for Ca.

Table 2. Calculation of Fractional Removal per year of Rock Materials by a Typical Aquifer. Columns (2) and (3) refer to a 1 Square Meter Cross Section of the Aquifer. See Discussion in Text

(1) Material	(2) Kg/y into River	(3) Kg in Rock (× 1 E6)	(4) Fraction Removed (× 1 E−8)
Ca	0.3	15	2
Mg	0.03	3	1
K	0.02	3	0.7
Fe	0.003	9	0.03
U	3 E−6	8 E−4	0.3
Silica	0.2	150	0.13
Carbonate	1.3	18	8

Of the materials listed in Table 2, the materials in the radioactive waste are most similar to Fe and U and not at all similar to carbonate ions. Thus, the numbers in Column (4) of Table 2 might give an estimate of about $R = 7\ \text{E}{-9}$, seven times higher than Eq. 2. But the aquifer we have assumed in this calculation is substantially more robust than the groundwater encountered by average rock at 600 m depth, so it seems reasonable to conclude that Eq. 2 is roughly verified.

Probability of Transport from Groundwater to Human Stomachs, *p*

Next we turn to the problem of estimating the probability of transferring an atom of material dissolved in groundwater into human stomachs, p in Eq. 1. We assume that once the material is dissolved in groundwater, it moves with groundwater, eventually reaching shallow aquifers that feed into rivers. Contributions to p derive from our use of rivers and wells drilled into aquifers for potable water, from fish removed from rivers and used for food, and from use of well and river water for irrigating food crops. The potable water path is the simplest to calculate and, it turns out, the most important. The average person ingests 2 L/day of potable water which corresponds to ingestion by the U.S. population of $2 \times 365 \times 2.8\ \text{E}8 = 2.0\ \text{E}11$ L/y (liters per year). Of this, 45% is derived from wells, and 55% comes from rivers (7), corresponding to 9 E10 and 1.1 E11 L/y respectively entering human stomachs. The estimated water flow in U.S. rivers is 1.7 E15 L/y (1) and 1.9 E15 L/y (2,3); we use 1.8 E15 L/y. The estimated water flow in aquifers is 16% of the flow in rivers (3), or 2.9 E14 L/y The contributions to p from the use of rivers and wells for potable water are then

$$p(\text{rivers}) = (1.1\ \text{E}11/1.8\ \text{E}15) = 6.1\ \text{E}{-5}$$

$$p(\text{well water}) = (9\ \text{E}10/2.9\ \text{E}14) = 3.1\ \text{E}{-4}$$

Note that we have ignored removal of material by filtration processes, making these conservative estimates, that is, more likely to be high than low.

Analyses of the fish and irrigation contributions to p will be sketched below. They give results that

vary considerably from element to element because of variations in bioaccumulative factors (8). For the fish pathway, p(fish) is rarely larger than 1 E−5, and for most important elements in the waste, it is much smaller. For the irrigation pathway, p(irrigation) is rarely more than 1 E−4 and somewhat less for the most important elements in the waste. We therefore take as conservative estimates

$$p(\text{fish}) = 1\ \text{E}{-5}$$

$$p(\text{irrigation}) = 1\ \text{E}{-4}$$

Summing these four contributions gives $p = 5\ \text{E}{-4}$. Using this and Eq. 2 in Eq. 1 then gives the result we are seeking for P:

$$P = (1\ \text{E}{-9} \times 5\ \text{E}{-4}) = 5\ \text{E}{-13} \qquad (3)$$

Alternative Approach for Transfer from Rock to Human Stomachs

We now present an essentially independent method (9) for calculating P, based on our knowledge of quantities of elements entering human stomachs each year (10,11) and the quantities of these materials in rock (5), supplemented by an estimation of the fraction of these that derive from soil rather than from rock.

We begin with the very crude assumption that all material entering human stomachs derives from the top 600 m of rock. We know how much of each chemical element is contained in this rock (5), and we know how much of each chemical element enters human stomachs each year (10,11), so the ratio of these gives a crude estimate of P for each element. An average of these, weighting for the importance of each element in the waste, gives

$$P(\text{very crude}) = 1\ \text{E}{-11}$$

Some of the crudeness of this estimate may be reduced by dropping the implication that all depths of rock down to 600 m are equally likely to contribute and assuming that the contribution from various depths is proportional to the groundwater flow at that depth. Using the exponential decrease in this flow alluded to before, it turns out that the flow at 600 m depth is 16% of the average for the top 600 m, giving an improved, but still rough estimate:

$$P(\text{rough}) = (0.16 \times 1\ \text{E}{-11}) = 1.6\ \text{E}{-12}$$

This result is still an overestimate because most of the material entering human stomachs derives from the top layers of soil rather than from the underlying rock. To analyze this problem, a pathway analysis was developed (9) as shown in Fig. 1. The numbers attached to the arrows are the fraction of the input into the compartment derived from that arrow. For example, 90% of human oral intake is from food, and 10% is from drinking water; 2% of the minerals in food comes from seafood (derived from rivers), 88% comes directly from soil, and 10% comes from soil via irrigation water (which is derived 63% from rivers and 37% from wells). Using Fig. 1, the various pathways from rock to human stomachs and

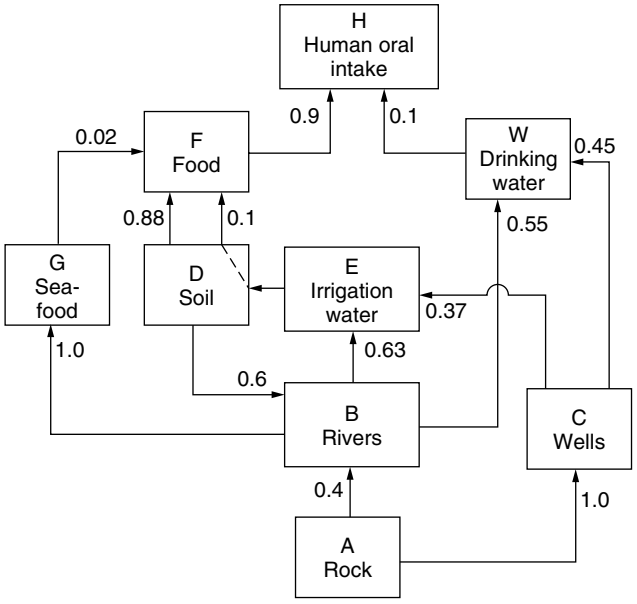


Figure 1. Pathway diagram for transmission of materials from rock and soil into food and water ingested by people. Numbers attached to each line show the fraction of the input to the target box that is derived from that line.

their fractional contributions to human intake are then calculated as

$$\begin{aligned}
\text{ABWH} \quad & 0.4 \times 0.55 \times 0.1 = 0.022; \\
\text{ACWH} \quad & 1.0 \times 0.45 \times 0.1 = 0.045; \\
\text{ABEFH} \quad & 0.4 \times 0.63 \times 0.1 \times 0.9 = 0.023; \\
\text{ACEFH} \quad & 1.0 \times 0.37 \times 0.1 \times 0.9 = 0.033; \\
\text{ABGFH} \quad & 0.4 \times 1.0 \times 0.02 \times 0.9 = 0.007; \\
& \text{TOTAL} \quad = 0.13
\end{aligned}$$

Our final value for P is then

$$P(\text{final}) = (0.13 \times 1.6\ \text{E}{-12}) = 2\ \text{E}{-13} \qquad (4)$$

This result, Eq. 4, is in substantial agreement with the estimate from Equation 3 derived from essentially independent approaches.

HIGH LEVEL WASTE VERSUS AVERAGE ROCK

This result applies to average rock, but our interest is in applying it to the rock-like material, probably a borosilicate glass, into which the waste has been converted. The principal difference is in leachability by groundwater. Leach rates by distilled water for various rocks and glasses have been measured, and the results were correlated with the Gibbs free energy of hydration (12). It was concluded that the leach rate for borosilicate glass is similar to that for basalt and about three times more rapid than the leach rate for average rock. Applying this to the results in Eqs. 3 and 4 gives the rate of transfer for an atom of buried high level waste into a human stomach as about 1.0 E−12 per year.

Concerns have been raised that the high level waste glass may be much less secure than average rock because it is not in chemical equilibrium with the local rock–ground water regime. However, chemical equilibrium is a surface phenomenon (13,14). Groundwater is saturated with dissolved silica. If a foreign silica-based material such as glass is emplaced, there is initially rapid dissolution, removing a very thin surface layer. But this brings more silica into the water which then becomes supersaturated with silica, resulting in precipitation of silica from the water onto the surface—this would be the most insoluble component of the silica originally in the water. The result is a buildup of highly insoluble silica on the surface. Waste can then be dissolved only by diffusion through this surface layer, a very slow process. Moreover, this leads to further thickening of the surface layer, which further retards the diffusion process. Consequently, the rate of dissolution decreases exponentially, only a tiny fraction of the waste becomes involved in the process, and dissolution proceeds only as for the surrounding rock.

BIBLIOGRAPHY

1. Garrels, R.M. and MacKenzie, F.T. (1971). *Evolution of Sedimentary Rocks*. W.W. Norton Co., New York.
2. Todd, D.K. (1980). *Groundwater Hydrology*. John Wiley & Sons, New York.
3. Ad Hoc Panel on Hydrology. (1962). *Scientific Hydrology, Federal Council for Science and Technology*. Washington, DC.
4. White, D.E., Hein, J.D., and Waring, G.A. (1963). *Chemical Composition of Sub-Surface Waters, Chap. F in Data of Geochemistry*, 6th Edn. M. Fleischer (Ed.). U.S. Government Printing Office, Washington, DC.
5. Bowen, H.J.M. (1979). *Environmental Chemistry of the Elements*. Academic Press, New York.
6. Cohen, B.L. (1985). A simple probabilistic risk analysis for high level waste repositories. *Nuclear Technology* **68**: 73–76.
7. Byrne, F. (1974). *Earth and Man*. Wm. C. Brown Co., Dubuque, IA.
8. Cohen, B.L. (1984). Probability for human intake of an atom randomly released into ground, rivers, oceans, and air. *Health Physics* **47**: 281–292.
9. Cohen, B.L. (1986). A generic probabilistic risk analysis for a high level waste repository. *Health Physics* **51**: 519–528.
10. International Commission on Radiological Protection. (1975). *Report of the Task Group on Reference Man*. ICRP Publication 23, Pergamon Press, New York.
11. Pennington, J.A.T. et al. (1984). Selected minerals in food survey, 1974–1982. *Jour. Am. Dietetic Assn*. **84**: 771ff.
12. Plodinek, M.J., Jantzen, C.M., and Wicks, G.C.. (1983). *Stability of Radioactive Waste Glasses Assessed from Hydration Thermodynamics*. Savannah River Laboratory Reports DP-MS-83-61, DP-MS-83-21, and DP-MS-83-66.
13. Cohen, B.L. (1980). Analysis, critique, and evaluation of high level waste water intrusion scenario studies. *Nuclear Technology* **48**: 63ff.
14. Cohen, B.L. (1985). Critique of the National Academy of Sciences study of the isolation system for geologic disposal of radioactive waste. *Nuclear Technology* **20**: 433ff.

GROUNDWATER CONTAMINATION FROM RUNOFF

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INTRODUCTION

Groundwater is water that lies below the soil surface and fills the pore spaces in and around rock, sand, gravel, and other materials. Groundwater, under most conditions, is safer and more reliable for use than surface water because surface water is more readily exposed to pollutants from factories, for example, than groundwater. This by no means says that groundwater is invulnerable to contamination. Once groundwater is contaminated, it is extremely costly to remove the contaminant. Any chemicals that are easily soluble and penetrate the soil are prime candidates as groundwater pollutants.

HOW MUCH DO WE DEPEND ON GROUNDWATER?

According to 1985 U.S. figures, groundwater provides an estimated

- 22% of all freshwater withdrawals
- 53% of drinking water for the total population and 97% of drinking water for the rural population
- 40% of public water supply withdrawals
- 46% of domestic and commercial use
- 24% of industrial and mining use
- 34% of agricultural use (mostly for irrigation)

CAUSES OF URBAN RUNOFF

Urban runoff can be attributed to many things, including the amount of rainfall, the soil conditions, and the degree of urbanization. Rainwater can go in many directions once it has reached the earth's surface. Rainwater can be absorbed by the soil on the land surface; absorbed by surrounding vegetation; directly deposited into oceans, streams, and rivers; and infiltrate through the surface and subsurface soils into the groundwater.

Urban runoff can happen anytime of the year when excessive water use from irrigation, car washing, and other sources carries litter, lawn clippings, and other urban pollutants into storm drains.

The majority of people live in cities that are becoming larger and larger and are sprawling into vast suburban neighborhoods. Roofs, parking lots, streets, and other impervious surfaces of an urban environment cause rainwater to collect and be forced out through a storm drain system. If the drainage system does not connect to a wastewater treatment facility, then the rainwater and everything that is carried with it travels into groundwater, local streams, and rivers.

GROUNDWATER CONTAMINATION FROM URBAN RUNOFF

Not too long ago, urban runoff was considered an insignificant contributor to groundwater contamination. Urban runoff is now recognized as a significant source of contamination in water. Effluents from urban areas contain large concentration of oils, greases, nutrients, heavy metals, and detergents. Detergents that are soluble can pass through the soil and pollute groundwater. Raw sewage dumped in shallow soakpits and seepage from polluted lakes, ponds, and streams also pollute groundwater. Rainfall could pick up substantial contaminants from dust and air and join the aquifer below. The infiltration of liquids containing toxic pollutants may cause pollution in sandy soils and well waters.

Some of the contaminants expected in urban runoff are shown in Table 1. Groundwater moves through rocks and subsurface soil, so it has lots of opportunity to dissolve substances as it moves. For that reason, groundwater often has more dissolved substances than surface water. Even though the ground is an excellent mechanism for filtering out particulate matter, such as leaves, soil, and bugs, dissolved chemicals and gases can still occur in large enough concentrations in groundwater to cause problems. Underground water can be contaminated through urban runoff containing industrial, domestic, and agricultural chemical wastes, which includes chemicals such as pesticides and herbicides that many homeowners apply to their lawns. Contamination of groundwater by road salt is of major concern in northern areas of the United States. Salt is spread on the roads to melt ice, and salt is so soluble in water that excess sodium and chloride is transported through runoff after ice melts and finally contaminates subsurface groundwater.

In the United States today, there may be more than 20,000 known abandoned and uncontrolled hazardous waste sites, and numbers grow every year. If there is a leak, these contaminants may be carried away with runoff and finally make their way down through the soil and into the groundwater.

Landfills are another major source of contamination. Landfills are the places where our garbage is taken to be buried. Landfills are supposed to have a protective bottom layer to prevent contaminants from getting into the water. After rainfall, contaminants from the landfill (car battery acid, paint, household cleaners, etc.) are washed away with surface runoff and make their way down into the groundwater. The problem of pollution from landfills is greatest where high rainfall and shallow water tables occur. Important pollutants frequently found in leachate include BOD, COD, iron, manganese, chloride, nitrate, hardness, and trace elements. Hardness, alkalinity, and total dissolved solids are often increased.

Chemicals include products used on lawns and farm fields to fertilize plants. The primary fertilizers are compounds of nitrogen, phosphorus, and potassium. Phosphate and potassium fertilizers are readily adsorbed on soil particles and seldom constitute a pollution problem. But nitrogen in solution is only partially used by plants or adsorbed by the soils, and it is the primary fertilizer pollutant (1). When the rain comes, this chemical is washed away with the surface runoff and eventually goes into the groundwater.

Animal wastes are confined within a limited area, in beef or milk production, so large amounts of waste are deposited on the ground. Thus, for the 120 to 150 days that a beef animal remains in a feedlot, it produces more than a half ton of manure on a dry weight basis. When thousands of animals are in a single feedlot, the natural assimilative capacity of the soil becomes overtaxed. Surface runoff in contact with the manure carries highly concentrated pollutants to subsurface waters. Animal wastes may transport salts, organic loads, and bacteria into the water and soil. Nitrate-nitrogen is the most important persistent pollutant that may reach the groundwater (2).

Sanitary systems have a significant impact on shallow aquifers in urban areas. Field observations revealed that contamination of groundwater is caused by infiltration of surface runoff polluted by municipal waste and sewage and/or leakage of sanitary effluents. It has increased the salt content of groundwater, particularly nitrates

Table 1. The Contaminants that may be Expected in Runoff[a]

1. Asbestos from brake and clutch linings
2. Bacteria and viruses from animals and birds, soils, litter, livestock hauling, livestock waste hauling and on-site sewage tanks and fields
3. Bromide from auto exhaust
4. Cadmium from tire fillers and insecticides
5. Chromium from moving engine parts and brake linings
6. Copper from bearing and bushing wear, moving engine parts, brake linings, and radiator repair
7. Cyanide and chloride from deicing road salts
8. Pesticides (fungicides, herbicides, and insecticides) from roadside maintenance
9. Iron from auto bodies, moving engine parts, bridges, guardrails, overpasses, lamp standards, and other structures
10. Manganese from moving engine parts and gasoline additives
11. Nickel from diesel fuel, lubricating oil, bushing wear, brake linings, and asphalt paving
12. Nitrogen from animal wastes, on-site sewage systems, vegetative matter, and fertilizers
13. Petroleum compounds from paving, fuels spills, engine blow-by, lubricant leaks, antifreeze, and hydraulic fluids
14. Phosphorus from animal wastes, on-site sewage systems, vegetative matter, and fertilizers
15. Potassium from fertilizers
16. Sulfate from roadbeds, road salts, and fuels
17. Zinc and lead from tire fillers, motor oil additives, automotive and radiator repairs, grease, and paint manufacturing

[a] *Source*: Ministry of Water, Land and Air Protection, Government of British Columbia.

and chlorides, and has reduced the oxygen content. In addition, introduction of pathogenic bacteria and viruses into groundwater has caused many outbreaks of waterborne disease.

Solid materials are frequently stockpiled near industrial plants and construction sites. These may be the raw materials awaiting use, or they may be solid wastes placed for temporary or permanent storage. Precipitation falling on unsheltered stockpiles may transport heavy metals, salts, and other inorganic and organic constituents as pollutants to the groundwater.

Urban runoff pollutants are many and varied, depending on land uses and pollutant sources in an urban area. Typically, loadings of urban pollutants are greatest from industrial and commercial areas. Although sources of specific pollutants may vary widely in urban areas, motor vehicles are recognized as a major source of pollutants; they contribute oils, greases, hydrocarbons, and toxic metals such as lead, zinc, copper, chromium, and arsenic.

BIBLIOGRAPHY

1. Todd, D.K. (1995). *Groundwater Hydrology*. Wiley, Toronto, Canada, p. 332.
2. Gillham, R.W. and Webber, L.R. (1969). Nitrogen contamination of groundwater by barnyard leachates. *J. Water Pollut. Control Fed.* **41**(10): 1752–1762.

SALINE SEEP

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Jackson (1) defines saline seep as an intermittent or continuous saline water discharge at or near the soil surface under dryland conditions that reduces or eliminates crop growth. Human induced salinization of land and water resources due to water table rise is as old as the history of human settlement and irrigation (2). Early settlements in the valleys of the Tigris and Euphrates flourished about 4000 B.C.: however, the irrigated farming of wheat resulted in salt accumulation, and in time the area was abandoned. Historic evidence from Russia, China, India, Pakistan, South American, United States, Canada, and Australia show that saline seeps are a worldwide problem. The number of saline seeps will probably increase in the future because an increase in world population will be accompanied by increases in irrigation.

Saline seeps result from a combination of geologic, climatic, and management factors. Development of a seep starts at the recharge area. As the water moves through the aquifer, the water dissolves and accumulates salts. Saline seeps are formed by mobilization of salt stored in the soil profile. The very act of irrigation is the cause for salinity because every irrigation event adds some salt to the soil. Land clearing or irrigation can cause the groundwater to rise. The additional water moves the water table closer to the land surface. When the water table is within 2–3 feet of the surface, capillary action can lift the water to the surface where it evaporates and leaves salts behind (Figs. 1 and 2).

The salt can also move laterally to affect streams. The common soil forming minerals calcium, sodium, magnesium, and potassium form water-soluble salts in the soil.

Techniques for controlling seeps originated in Montana and Alberta (3). The two major methods to control seeps are (1) cut off the recharge water and (2) reclaim the seep area. Installing subsurface tiles to intercept the groundwater flow might cut off recharge water. The second method is to increase water use in the recharge area by changing the type of crop. Alfalfa is an excellent crop substitute because it is a deep-rooted perennial capable of

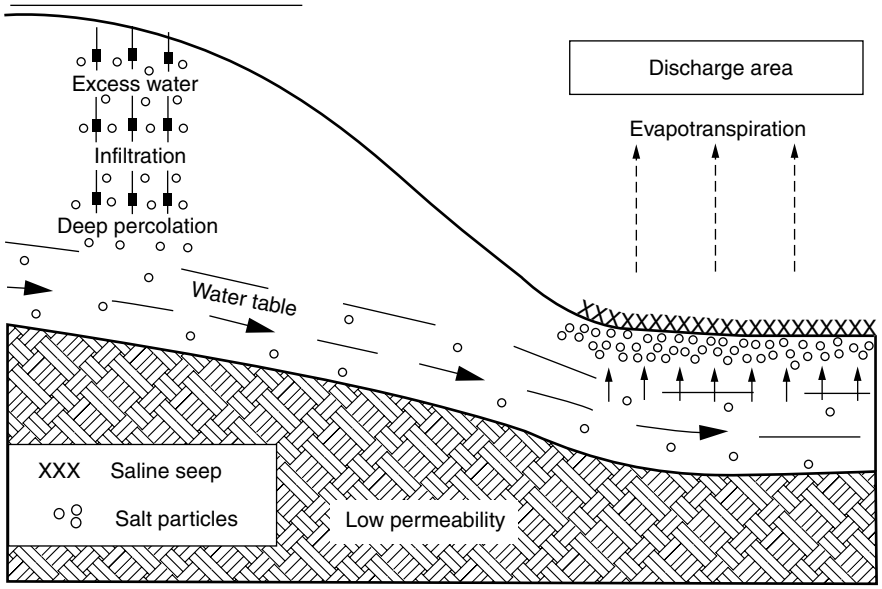


Figure 1. Water movement to seep.

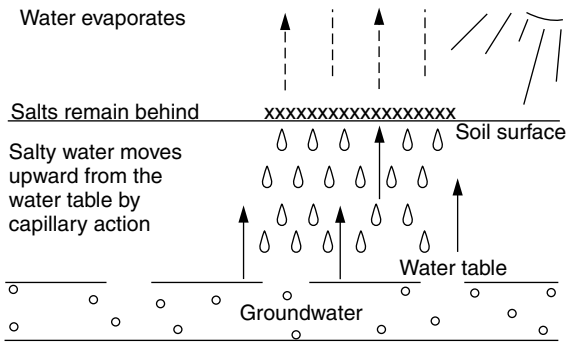


Figure 2. Evaporation and salt concentration.

using large amounts of water. Seeps have been reclaimed within 5 years by planting alfalfa in the recharge area (4).

In southeast Australia, the replacement of deep-rooted native vegetation by dryland and irrigated agriculture has resulted in a major change in surface water and groundwater systems in the Murray–Darling basin. The Murray River has a salinity of less than 25 mg/L in the headwaters and 480 mg/L downstream. Water that was previously used by vegetation for transpiration is now leaking past the vadose zone and entering the water table. The salinization process is closely linked to groundwater changes. In both irrigation and dryland farming, salts are remobilized into the production zone. The salts were originally stored in the aquifer or the vadose zone. Evaporation concentrates the salts in the near surface zone to levels where the plants are. For salinization to occur, it is necessary to have both a hydrologic change and a source of salt.

Saline soils and sodic soils are quite common in parts of western North Dakota and Montana. Most saline seeps have developed recently (postsettlement). The formation of saline seeps is closely related to the practice of summer fallow for moisture conservation (5).

Colorado River has 25 mg/L salt in the headwaters and 825 mg/L downstream at Imperial Dam. In the San Joaquin River in California, salinity increased from 330 mg/L in the 1930s to 600 mg/L in the 1970s. In the former Soviet Union, the salinity of the Syr Darya River which discharges to the Aral Sea increases from 300 mg/L to 2000 mg/L downstream.

The water table rise in agricultural areas of the world has contributed to the salinization of large areas. The development of land and water resources of the earth will be more difficult and more expensive than in the past. The control of population and the efficient use of developed resources will be essential in the future.

BIBLIOGRAPHY

1. Jackson, J. (1997). *Glossary of Geology*. American Geological Institute, p. 769.
2. Ghasemi, F. et al. (1994). *Water table rise and the expansion of land and water resources salinsation: a global view: IAH Congress Proceedings*. Water Down Under, Adelaide, Australia, pp. 607–610.
3. Brown, P.L. et al. (1983). *Saline seep diagnosis control and reclamation*. USDA-ARS conservation Research Report No. 30.
4. Lamon, R.E. and Whitney, D.A. (1992). *Management of Saline and Sodic Soils:MF-1022 Cooperative Extension Service*. Kansas State University, Manhattan, KS.
5. Wentz, D. (1997). *Dryland Saline Seeps-Types and Causes*. Alberta Agriculture.

GROUNDWATER SAMPLING TECHNIQUES FOR ENVIRONMENTAL PROJECTS

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Groundwater sampling techniques are important for accurate project results and understanding aquifers whether the project is sampling a groundwater monitoring well as part of an environmental assessment or regular sampling of a potable water supply well. Detailed groundwater sampling information can be obtained from Testa (1), Jacobs (2), the American Society for Testing Materials (3), the California Regional Water Quality Control Board (4), and Driscoll (5). Although there are numerous differences in groundwater sampling and record keeping techniques, regional variations, and specific regulatory requirements that vary from state to state, a generalized summary of selected environmental groundwater sampling techniques is given below.

PURPOSE OF GROUNDWATER SAMPLES

Groundwater samples are collected for a variety of reasons. Groundwater can be collected as a "grab" sample or from a monitoring well. Groundwater samples are used to define the vertical and aerial extent of groundwater contamination, to monitor target chemical concentrations over time, to provide a measurement for detecting a contaminant plume front, to evalvate unexpected changes in plume size or direction of flow, to determine the extent of interaquifer movement of contaminants, to determine aquifer characteristics such as permeability, transmissivity, etc.), to estimate the rate of contaminant plume movement, to develop a data base for designing remedial measures, to determine the effects of the remedial measures, to assist in performing the remedial work (provide hydraulic control and contaminant removal), to provide data base for groundwater modeling, and to evaluate the aquifer during regular sampling over the yearly hydrologic cycle (6).

GRAB GROUNDWATER SAMPLING

A "grab" groundwater sample is collected without the use of a fully installed groundwater monitoring well. Methods include using a bailer or jar to collect groundwater from an excavation or trench made with a backhoe or excavator. Other "grab" samples can be collected using a drilling rig wherein a sampler is drilled or pushed to the target depth and the sampler is pushed a bit further into the aquifer. Water is allowed to collect in the sampler. The

water is removed from the sampler using a bailer or by using a peristaltic pump and tubing, check-ball valve with tubing or other similar methods. These methods, frequently called punch methods, are commonly used with hollow stem auger rigs or direct push technology rigs. Cone penetrometer (CPT) rigs can use specialized groundwater containers that are inserted into a cavity of the water sampler tip. The groundwater containers are under a vacuum. At the proper depth, the sampler is opened, the groundwater container is pierced, and water enters the container.

Temporary wells are used occasionally in environmental investigations. A temporary well consists of a well screen below a casing riser placed in an open borehole. Several well volumes can be purged prior to sampling. A bailer or other method is used to bring the water to the surface. After groundwater sampling is completed, the borehole is usually tremie grouted to seal the annulus.

WATER WELLS

Water wells are installed using a variety of rigs: hollow stem auger, mud or air-rotary, air percussion, diamond coring, cable tool, and others. After well installation, wells are developed within a day to several days of installation to remove residual drilling materials from the well bore and to improve well performance by removing any fine material in the filter pack that can pass from the native soil into the well. Well development techniques include pumping, bailing, surging, jetting, and airlifting. In most cases, surging and pumping are satisfactory. Development water is inspected for turbidity, product sheen, odors, and sediment. A minimum of several casing volumes is removed during development. The well is considered fully developed when consistent pH, temperature, and conductivity readings indicate characteristic groundwater for the aquifer. If the aquifer is slow to recharge, development will continue until the well is pumped dry. Cross contamination of wells from pumps is avoided by using dedicated equipment and proper decontamination procedures.

Due to the large volumes of purge water generated during groundwater sampling and the costs for storage and disposal of the water, some regulatory agencies are now allowing various low-flow groundwater sampling techniques for compliance groundwater monitoring. Proponents of micropurging suggest that evacuation of a specific volume of water may increase turbidity from agitation or mixing of the well water column. Larger purge volume may increase the risk of colloid mobilization. Proper well development immediately after well construction is essential when using low-flow sampling (7).

Micropurging is the evacuation of tubing, sampling devices, and other items from the well prior to sampling groundwater. There is no purging prior to sample collection with micropurging, so there is no method for determining if the well contains stagnant well water or water representative of the aquifer. For this reason, many regulatory agencies do not approve micropurging. Instead, when minimal purging is requested, low-flow sampling is preferred.

The low-flow sampling method, typically used in 2-inch diameter groundwater monitoring wells, relates to the amount of drawdown in a well during purging. The indicator parameters are collected before and during purging and allowed to stabilize prior to groundwater sample collection. Purge rates may be higher than sample rates to maximize purge efficiency. Prior to the collection of the groundwater sample, the pump rate may be lowered to lower sample turbidity and entrained air in the sample, and to mimic conditions that may exist in the natural aquifer. High turbidity in water samples being analyzed for metals requiores filtering to remove colloidaland suspended sediments that may contain metals.

Discrete sampling systems are designed to collect groundwater samples form the formation at a specific depth or multiple target depths without significant purging prior to sample collection.

GROUNDWATER SAMPLING PROTOCOL

Depth to the top of the water and free-product thickness within wells are monitored by using a water level meter or an interface probe. Water level data collected from areas that have multiple wells are used to develop groundwater contour maps for the project site. Groundwater flow is perpendicular to equipotential lines drawn on the map. If free-product is detected, a product sample is sometimes collected for source identification. In environmental projects, where several chemicals are to be analyzed for a given well, individual samples are collected in order of decreasing volatility. When the results from previous sampling are known, it is recommended to start sampling the cleanest wells first, moving to the most contaminated wells later in the sampling event.

Each chemical analysis requires specific sample preservation techniques or additives. Sealed chemical ice is placed in the coolers to maintain samples at a temperature of 4 °C. Where several types of chemicals are to be analyzed for a given well, individual samples are collected in the following order: volatile organic compounds, purgeable organic compounds, purgeable organic halogens, total organic compounds, total organic halogens, extractable organic compounds, total metals, dissolved metals, phenols, and cyanide.

QUALITY CONTROL OF GROUNDWATER SAMPLES

A QC program, which is independent of the laboratory's program, verifies sample integrity and includes the submittal of duplicates, field blanks, and travel blanks to the laboratory. The QC samples are packaged and sealed in the same manner as the other samples and are assigned independent sample numbers.

A duplicate sample is collected for about 5% of the samples or one per sampling round, whichever is greater. The duplicate sample is acquired by filling separate containers from the same well bailer as the actual sample. The contents of the bailer are evenly divided between the actual and duplicate samples to ensure duplication. The field blank is submitted to the laboratory for the

same analyses as the rest of the sampling set. The field blank is acquired by dispensing deionized water from a clean sampling bailer into the containers in the same manner as groundwater samples. When sampling groundwater for analyzing volatile compounds, travel blanks are used to detect the introduction of contaminants during transportation from the field to the laboratory. The travel blank generally contains deionized water, which has been poured into the container prior to being taken into the field.

BIBLIOGRAPHY

1. Testa, S.M. (1994). *Geologic Aspects of Hazardous Waste Management*. CRC Press, Boca Raton, FL, pp. 145–187.
2. Jacobs, J. (2000). Monitoring well construction and sampling techniques. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 11.46–11.68.
3. American Society for Testing Materials. (1984). Standard Practice for Description and Identification of Soils (Visual-Manual Procedure), Method D 2488-84. Philadelphia, PA.
4. California Regional Water Quality Control Board. (1989). Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure, Sacramento, CA.
5. Driscoll, F.G. (1986). *Groundwater and Wells*, 2nd Edn. Johnson Filtration Systems, St. Paul, MN, pp. 268–339.
6. Sisk, S.J. (1981). *NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites*. EPA-330/9-81-002. U.S. Environmental Protection Agency, Denver, CO.
7. Puls, R.W. and Barcelona, M.J. (1996). Low-flow (minimal drawdown) ground water sampling procedures. EPA Groundwater Issue, April.

GROUNDWATER SAMPLING WITH PASSIVE DIFFUSION SAMPLERS

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INTRODUCTION: DIFFUSION-BASED GROUNDWATER SAMPLING METHODS

Passive diffusion-based sampling methods have been used to monitor environmental contaminants, particularly trace metals and certain lipophilic compounds including polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and pesticides, for many years. In particular, dosimeter-type and semipermeable membrane devices (SPMDs) are commonly used in limnology, oceanography, and ecotoxicology for evaluating ultralow concentrations and potential bioavailability of contaminants (1–4). These types of samplers are most frequently used for sampling sediment porewater and surface water (i.e., rivers, estuaries, harbors) and have occasionally been used for groundwater characterization in contaminant toxicology studies (5). These types of sampling devices are composed of a "trapping" phase, such as hexane, activated carbon, or triolein (a prominent fish lipid), contained within a semipermeable membrane (such as dialysis-type cellulose or a synthetic polymer). On deployment, contaminants diffuse through the membrane and are subsequently retained in the trapping phase until analysis. After the SPMD is removed, the contaminants must typically be extracted from the trapping phase before analysis. A significant disadvantage with SPMDs and dosimeter-type devices for groundwater sampling is that back-calculation to actual *in situ* aqueous concentrations may not be straightforward due to nonlinear and/or nonequilibrium sorption behavior of the trapping phase (5).

Passive diffusion (PD) samplers are similar to dosimeter-type and SPMD sampling methods in that they generally consist of a sealed container with a semipermeable membrane. The PD sampler is suspended in a monitoring well, and the solutes of interest diffuse across the membrane into the sampler. However, unlike dosimeter-type devices and SPMDs, PD samplers do not contain a trapping phase but are instead filled with water or air. Therefore, once the PD sampler is retrieved from the well (after equilibration), the concentration measured in the sampler is assumed to relate directly to *in situ* analyte concentrations at the deployment location. Passive diffusion samplers are less expensive to construct than SPMDs and easier to analyze because no extraction step is required. Furthermore, the correlation between the contaminant concentration measured in the PD sampler and the surrounding environment is straightforward: for water-filled PD samplers deployed in groundwater the concentrations are equivalent.

Passive diffusion-type sampling methods have been used in a variety of applications for many years, including dissolved gas measurement in seawater and groundwater (3,6,7). Generally, PD samplers offer several potential advantages for monitoring many common groundwater contaminants, compared to conventional sampling techniques. For sites with ongoing monitoring programs, significant cost savings may be realized due to reduced sampling-related labor and minimal sampling-related waste generation. For dissolved constituents with large Henry's Law constants, such as volatile organic compounds (VOCs) and dissolved gases, analyte loss due to volatilization can be greatly minimized. In some cases, analytical matrix interferences may be reduced if the membrane is selective against interfering constituents (i.e., the matrix in the PD sampler may be comparatively less complex). Additionally, multiple PD samplers can be deployed to provide solute concentration measurements across very discrete intervals. For example, PD samplers with dialysis-type membranes have been used to characterize ion and trace metal concentration profiles on the scale of a few centimeters in sediment (3).

MEMBRANE MATERIALS AND SPECIFIC CONSTRUCTION EXAMPLES

Because of the potentially significant costs savings and technical advantages noted above, the use of PD samplers for groundwater monitoring at contaminated sites is greatly increasing [particularly water-filled PD samplers using low-density polyethylene (LDPE) membranes].

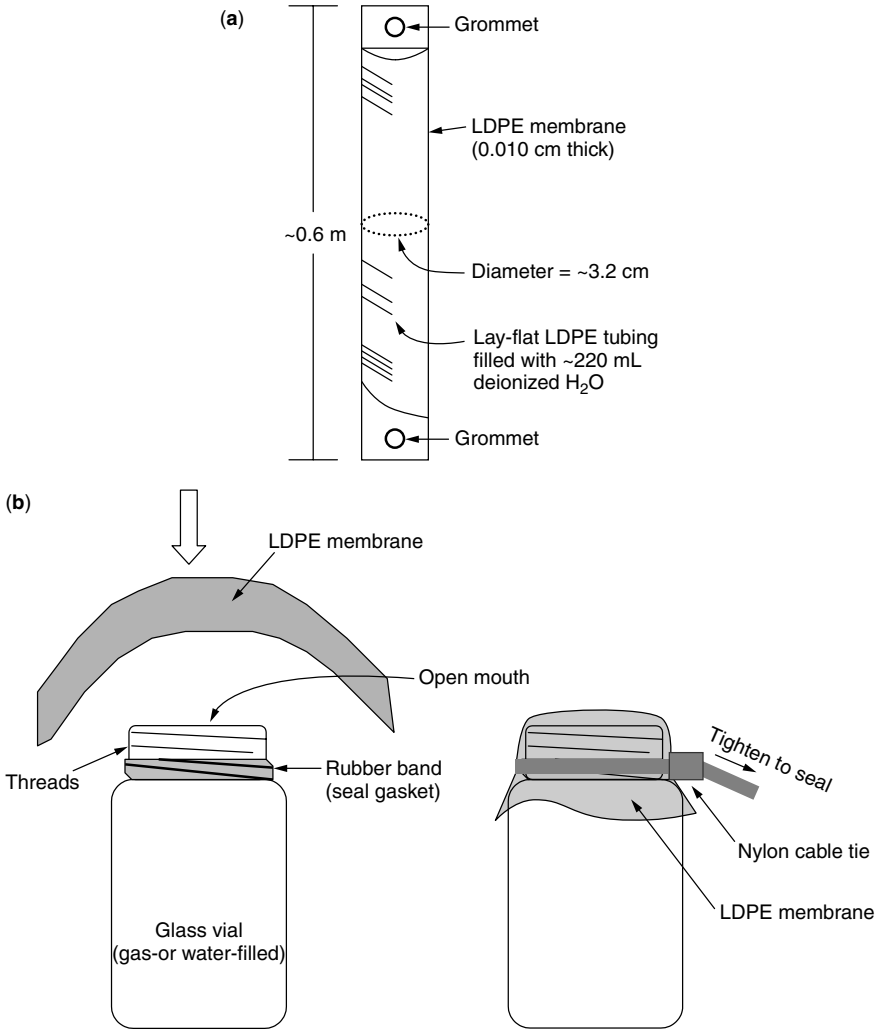


Figure 1. Schematics of passive diffusion samplers.

Laboratory and field compatibility tests indicate that LDPE membranes are suitable for most fuel and solvent VOCs; however, it has been demonstrated that the LDPE membrane is generally not suitable for measuring inorganic ions, metals, pesticides, explosives, semivolatile organics, alcohols, organic acids, and ethers [including methyl-*t*-butyl ether (MtBE)] with PD samplers (8,9). Dissolved gases, such as He, Ne, H_2, O_2, and N_2, can be measured by PD samplers with LDPE (10) or silicone (7) membranes. Passive diffusion-type samplers (also known as dialysis samplers or "peepers") that use other membrane materials, such as cellulose acetate, can be used to monitor major ions, metals, nutrients, dissolved gases, and pH (3,11).

Passive diffusion samplers can be constructed easily from inexpensive materials. As shown in Fig. 1a, the open mouth of a glass laboratory vial can be covered with a membrane and sealed with a rubber band gasket and nylon zip tie. Drop sheeting, which is widely available in the painting supply sections of hardware stores, can be used for LDPE membranes and is offered in a range of thicknesses. PD samplers filled with water can be constructed while submerged in deionized water to prevent entrapment of air bubbles. Passive diffusion samplers made of lay-flat LDPE tubing filled with deionized water are commercially available from EON Products, Inc. (Snellville, Georgia) and Columbia Analytical, Inc. (Kelso, Washington). A schematic of this type of sampler, which is also known as a PD "bag" sampler is shown in Fig. 1b. For a description of peepers and other PD samplers with dialysis-type membranes, see Davison et al. (3).

EQUILIBRATION TIME FOR PASSIVE DIFFUSION SAMPLERS

To prevent biased-low measurements, PD samplers must be deployed long enough in a well for equilibration to occur. Based on empirical laboratory and field studies, a minimum of 2–3 days is required for equilibration for most VOCs using commercially available LDPE PD bag samplers (8). Carnigan (12) found that some dialysis-type samplers require equilibration times of 3–20 days for measuring inorganics in porewater. Based on these general results, a minimum equilibration time of approximately 2 weeks is commonly recommended as a conservative approach in field studies (8,9). However, note that this is a generic rule of thumb. As equilibration is a diffusion process, the specific equilibration time depends

on sampler volume, membrane surface area, membrane thickness, and the diffusion coefficient of the solute in the membrane material.

Sanford et al. (2) present the following solution that describes the concentration within the PD sampler as it equilibrates with the surrounding groundwater:

$$C_s(t) = C_r H \left[1 - e^{\left(\frac{-D_m A t}{\forall L_m} \right)} \right] \quad (1)$$

where

$C_s(t)$ concentration within the sampler at time t after PD sampler deployment [M L^{-3}],

C_r resident concentration at the measurement location [M L^{-3}],

D_m effective constituent diffusion coefficient for the membrane material [L^2 T^{-1}],

H solute dimensionless Henry's law constant [ ],

A surface area of the PD sampler membrane [L^2],

t deployment time [T],

$\forall$ internal volume of the PD sample [L^3], and

L_m membrane thickness [L].

This solution assumes Fickian solute diffusion across a thin membrane, a constant C_r concentration at the measurement location, and a well-mixed reservoir in the PD sampler. As presented, Equation 1 incorporates air–water partitioning and is applicable to gas-filled PD samplers deployed in groundwater, such as those described by Sanford et al. (7) and Divine and McCray (10). For conditions where no phase partitioning occurs (such as a water-filled PD sampler deployed in groundwater), Henry's law constant (i.e., the gas-water partition coefficient) is treated as unity.

As clearly shown in Eq. 1, the rate at which a PD sampler equilibrates relates directly to the D_m value of the solute, the sampler dimensions ($A, \forall$), and the thickness of the membrane (L_m). Therefore, PD samplers can be constructed to minimize equilibration times by using a thin membrane and increasing the $A/\forall$ ratio. The effective D_m value is temperature-dependent and specific to both the membrane and solute. Divine and McCray (10) estimated that a practical range is $1–4 \times 10^{-7}$ cm^2 s^{-1} for D_m values of several dissolved gases and VOCs for LDPE membranes. Sanford et al. (2) measured D_m values for helium and neon of 4×10^{-7} cm^2 s^{-1} for silicone membranes. Based on these D_m ranges, equilibration times are predicted using Eq. 1 for several PD samplers, including both constructed (Fig. 1a) and commercially available (Fig. 1b) samplers. The specific parameter values and resulting equilibration times are summarized in Table 1, and the predicted PD sampler concentration histories are shown in Fig. 2.

These results show the relative importance of the various parameters for equilibration times. For example, increasing the $A/\forall$ ratio reduces the equilibration time, and this can be accomplished for constructed PD samplers (Fig. 1a) by filling the sampler with inert sand or glass beads (i.e., compare results of Scenario 3 with Scenario 4). It is also important to note that Eq. 1 is valid only for advection-dominated systems. If the groundwater velocity is very low (diffusion-dominated systems), a concentration gradient will develop outside of the sampler, and equilibration times can be much longer (13). Equation 1 is appropriate, however, for most shallow aquifer systems.

CASE STUDY: APPLICATION OF PASSIVE DIFFUSIONS SAMPLERS AT A HETEROGENEOUS SITE

Passive diffusion samplers measure water quality directly in contact with the membrane surface; therefore, they generally measure concentrations at relatively discrete intervals within a well. Conversely, samples collected by conventional purge-and-bail methods tend to integrate water quality across the entire well screen region and therefore are most significantly influenced by water quality conditions in the highest permeable zones across the well screen interval. In other words, PD samplers tend to measure porewater concentrations over relatively small intervals, and purge-and-bail type methods tend to measure flux-weighted concentrations. For vertically uniform plume distributions and homogeneous aquifer

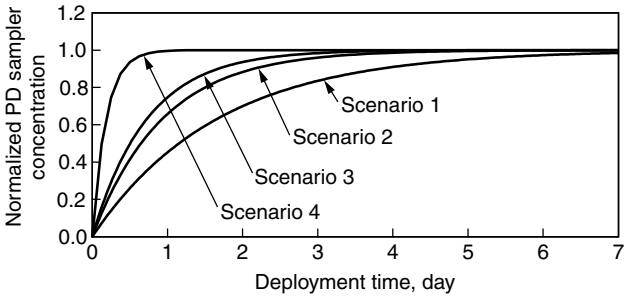


Figure 2. Passive diffusion sampler concentrations after deployment, predicted by Equation 1. The normalized concentration is defined as C_s/C_r (at equilibrium $C_s = C_r$; therefore, $C_s/C_r = 1.0$). The parameter values used in the models are summarized in Table 1.

Table 1. Passive Diffusion Sampler Dimensions, Membrane Thickness, Membrane Diffusion Coefficients, and Predicted Equilibration Times for Various Constructed (Fig. 1a) and Commercially Available (Fig. 1b) PD Samplers. The Equilibration Time is Defined by Equation 1 when $C_s \geq 0.95C_r$)

	A, cm^2	$\forall$, mL	L_m, cm	D_m, (cm^2 s^{-1})	Equilibration Time, Day
Scenario 1 *Commercial "bag" sampler*	350	220	0.010	4.0×10^{-7}	0.7
Scenario 2 *Commercial "bag" sampler*	350	220	0.010	2.5×10^{-7}	2.7
Scenario 3 *Constructed sampler: sand-filled 20-mL glass vial*	3.2	12.9	0.005	2.5×10^{-7}	2.8
Scenario 4 *Constructed sampler: 20-mL glass vial*	3.2	23	0.005	2.5×10^{-7}	5.1

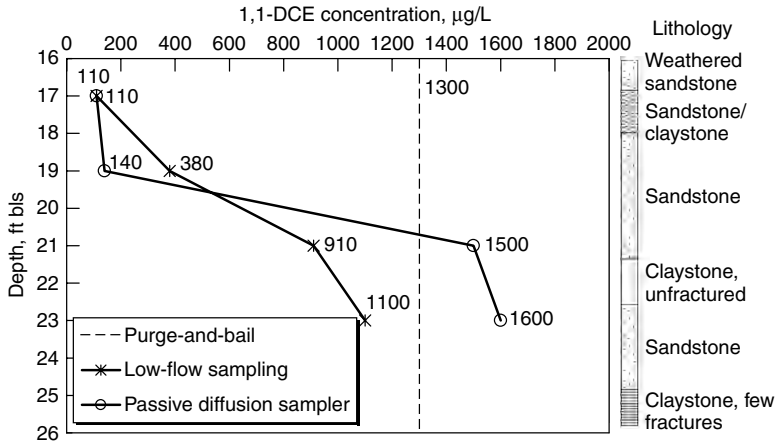


Figure 3. Comparison of sampling results for purge-and-bail, low-flow, and passive diffusion sampling methods for a single monitoring well.

conditions, results from these two sampling methods may be equivalent. However, these two methods may yield significantly different concentration values for a specific well at a heterogeneous site with plume stratification.

To illustrate this potential behavior, the concentrations of 1,1-dichloroethene (1,1-DCE) (a common VOC) measured at a monitoring well by purge-and-bail, low-flow [another discrete-type sampling technique; see Puls and Barcelona (14)]. PD sampling methods are shown in Fig. 3. The aquifer at this study site is highly heterogeneous, and this is clearly expressed in the results of the various sampling methods. Only one value (1300 µg/L) is obtained by the purge-and-bail method; however, the low-flow and PD sampling methods characterize concentrations at various discrete depth intervals and show significant contaminant stratification (approximately an order of magnitude over several vertical feet).

Figure 4 compares the results of purge-and-bail with PD sampling methods at several wells at the same heterogeneous site. The purge-and-bail measurements are generally higher than the average discrete PD sampler measurements, possibly indicating that the majority of the contaminant mass exists in highly permeable zones. These data provide additional characterization information and have potentially important implications for the site. At some sites, a similar targeted dual-method sampling strategy (i.e., use of both purge-and-bail and PD sampling methods) may be useful for evaluating contaminant distribution, remedial system design and performance, and long-term plume behavior.

Clearly, using PD samplers under heterogeneous aquifer conditions, particularly in an ongoing compliance monitoring program, requires careful consideration of ways to interpret measurement data and satisfy monitoring program objectives. For example, determining the appropriate intervals for PD sampler placement may be challenging (i.e., Fig. 3). Additionally, as indicated by the circled values in Fig. 4, the PD sampling method measured low concentrations of some nontarget VOCs at a few discrete intervals in certain wells, but these compounds were not measured above the analytical quantitation limit by the purge-and-bail method. Assuming that these differences are related to the differing averaging natures of the sampling methods, interpreting the discrete interval

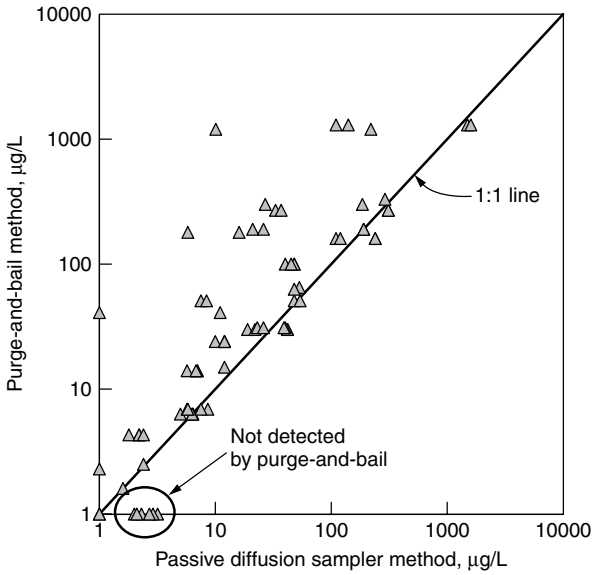


Figure 4. Comparison of sampling results (various VOCs) for purge-and-bail and passive diffusion sampling methods for a series of wells at a heterogeneous site.

measurement within site objectives or regulatory requirements may be challenging. For example, an analytical water quality goal or regulatory limit may be met by one method and not by another at the same well simply due to the inherent averaging characteristics of the sampling methods. For additional discussion of the results of this study, see Divine et al. (15).

BIBLIOGRAPHY

1. Sordergren, A. (1987). Solvent-filled dialysis membranes simulate uptake of pollutants by aquatic organisms. *Environ. Sci. Technol.* **21**(9): 855–859.
2. DiGiano, F.A., Elliot, D., and Leith, D. (1988). Application of passive dosimetery to the detection of trace organic contaminants in water. *Environ. Sci. Technol.* **22**(11): 1365–1367.
3. Davidson, W., Fones, G., Harper, M., Teasdale, P., and Zhang, H. (2000). Dialysis, DET, and DGT: *In situ* diffusional techniques for studying water, sediments, and soils. In: *In Situ Monitoring of Aquatic Systems*. J. Buffle and G. Horvai (Eds.). John Wiley & Sons, New York, Chapter 11.

4. Dunn, R.K., Teasdale, P.R., Warnken, J., and Schleich, R.R. (2003). Evaluation of diffusive gradient in a thin film technique for monitoring trace metal concentration in estuarine waters. *Environ. Sci. Technol.* **37**(12): 2794–2800.
5. Gustavson, K.E. and Harkine, J.M. (2000). Comparison of sampling techniques and evaluation of semipermeable membrane devices (SPMDs) for monitoring polynuclear aromatic hydrocarbons (PAHs) in groundwater. *Environ. Sci. Technol.* **34**(20): 4445–4451.
6. Dyck, W. and Da Silva, F.G. (1981). The use of ping-pong balls and latex tubing for sampling the helium content of lake sediments. *J. Geochem. Exploration* **14**: 41–48.
7. Sanford, W.E., Shropshire, R.G., and Solomon, D.K. (1996). Dissolved gas tracers in groundwater: Simplified injection, sampling, and analysis. *Water Resour. Res.* **32**(6): 1635–1642.
8. Vroblesky, D.A. and Campbell, T.R. (2001). Equilibration times, compound selectivity, and stability of diffusion samplers for collection of ground-water VOC concentrations. *Adv. Environ. Res.* **5**: 1–12.
9. Vroblesky, D.A. (2001). *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells, Part 1: Deployment, Recovery, Data Interpretation, and Quality Control and Assurance*. United States Geological Survey, Columbia, SC.
10. Divine, C.E. and McCray, J.E. (2004). Estimation of diffusion coefficients and equilibration times for LDPE passive diffusion samplers. *Environ. Sci. Technol.* **38**(6): 1849–1857.
11. Webster, I.T., Teasdale, P.R., and Grigg, N.J. (1998). Theoretical and experimental analysis of peeper equilibration dynamics. *Environ. Sci. Technol.* **32**(11): 1727–1733.
12. Carnigan, R. (1984). Interstitial water sampling by dialysis, methodological notes. *Limnol. Oceanogr.* **29**: 667–670.
13. Harrington, G.A., Cook, P.G., and Robinson, N.I. (2000). Equilibration times of gas-field diffusion samplers in slow-moving ground water systems. *Ground Water Monitoring Remediation* **20**(2): 60.
14. Puls, R.W. and Barcelona, M.J. (1996). *Low-Flow (minimal Drawdown) Ground-Water Sampling Procedures*. EPA/540/S-95/504, Ada, OK.
15. Divine, C.E., Madsen, L., Andrews, S.D., and Santangelo-Drieling, T. (in press). Passive diffusion ground water samplers at a heterogeneous site: Pilot study results. *Ground Water Monitoring and Remediation*.

SPECIFIC CAPACITY

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The specific capacity of a well is the pumping rate of the well divided by the drawdown at that rate:

$$S_c = \frac{Q}{\Delta h}$$

where S_c=specific capacity
Q=constant pumping rate, and
Δh=drawdown

Water well contractors often report specific capacity to characterize the performance of a well and use specific capacity to estimate the optimum depth for installing a pump to obtain the desired yield. Units typically associated with specific capacity are liters per second per meter of drawdown (l/s/m), cubic meters per day per meter of drawdown (m^3/day/m), cubic feet per day per foot of drawdown (ft^3/day/ft), or gallons per minute per foot of drawdown (gpm/ft).

When taking measurements to compute specific capacity, the pumping rate should be constant, and the period of pumping should be sufficiently long that the rate of change in drawdown is small. The specific capacity of a well tends to become smaller as the pumping rate and duration of pumping increase. At high pumping rates, nonlaminar flow losses are larger and result in an increased rate of drawdown. Water level drawdown in unconfined aquifers results in reduced aquifer transmissivity near pumping wells; larger drawdown at high pumping rates then results in progressively smaller transmissivity and smaller specific capacity. A specific capacity value remarkably smaller than expected may result when the well is not screened in the correct water-bearing zone or when well screen openings are clogged due to incomplete well development, precipitation of minerals in the screen openings, or biofouling. After many years of pumping, if the specific capacity declines to about half the original value, well rehabilitation should be considered.

Specific capacity may be used to estimate the maximum potential pumping rate of a well by multiplying the available drawdown by specific capacity. The available drawdown is the difference between the depth at which the pump is set and the depth to the nonpumping water level in the well.

Specific capacity may be used to estimate the transmissivity of aquifer media in the vicinity of the pumping well. Theis (1) suggested that specific capacity could be used to estimate the transmissivity of an aquifer using the equation,

$$T^* = \frac{Q}{\Delta h}\frac{2.3}{4\pi}\log\frac{2.25T^*t}{r^2S}$$

where $\frac{Q}{\Delta h}$=specific capacity
t=time
r=radius of pumping well
S=aquifer storativity
T^*=transmissivity; an initial guess of the value of T is made and substituted in the equation. The equation is then solved for Δh. After the initial solution, the value of T must then be adjusted until the calculated value of Δh is reasonably close to the measured value.

Driscoll (2) indicated that transmissivity could be estimated as

$$T = S_c \times 2,000 \text{ for confined aquifers}$$

or

$$T = S_c \times 1,500 \text{ for unconfined aquifers}$$

where T is in gpd/ft and
S_c is specific capacity.

Razack and Huntley (3) gave an empirical relationship between transmissivity and specific capacity as follows:

$$T = 15.3(S_c)^{0.67}$$

where T is in m^2/day
S_c in m^3/day/m,

or

$$T = 33.6(S_c)^{0.67}$$

where T is in ft^2/day
S_c in ft^3/day/ft.

Using specific capacity data to estimate transmissivity can be useful when trying to estimate potential pumping rates or estimating how much available head is needed to produce a specified pumping rate. But, as in any estimation technique, it is not always applicable or advisable. These instances may include situations where substantial drawdown occurs because the pumping duration is too short for the specific capacity test, too small a pumping rate is used for an adequate specific capacity test, or well construction is inefficient.

BIBLIOGRAPHY

1. Theis, C.V. (1963). Estimating the Transmissibility of Aquifers from the Specific Capacity of Wells. In: *Methods of Determining Permeability, Transmissibility, and Drawdown*. R. Bentall, compiler, U.S. Geological Survey Water-Supply Paper 1536-I, pp. 331–340.
2. Driscoll, F.G. (1986). *Groundwater and Wells*, 2nd Edn. Johnson Filtration Systems, Inc., St. Paul, MN.
3. Razack, M. and Huntley, D. (1991). Assessing transmissivity from specific capacity in a large and heterogeneous alluvial aquifer. *J. Ground Water* **29**(6): 856–861.

SOIL WATER

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Soil water is a measure of the quantity of water present within a unit volume of soil. Soil-water content can vary from fully saturated, in which case the water content equals the soil porosity, to oven-dry, in which case all free water has been evaporated.

Wet soils are characterized as having high water contents, which means that more soil pores are filled with water, whereas dry soils have more pores that are filled with air.

The volumetric water content, θ, is defined as the volume of water, V_w, per unit volume of soil, V_s:

$$\theta = \frac{V_w}{V_s} \tag{1}$$

where the range in water content is from a minimum, or residual, saturation, θ_r, to a maximum equal to the saturated porosity, θ_s, so that $\theta_r < \theta < \theta_s$.

The water content can also be defined with a gravimetric, or mass, measurement, θ_g, such that

$$\theta_g = \frac{M_w}{M_s} \tag{2}$$

where M_w is the water mass and M_s is the soil mass. We can readily convert between these two measures by using:

$$\theta = \theta_g \frac{\rho_w}{\rho_s} = \frac{\theta_g}{\rho_s} \tag{3}$$

where $\rho_w = M_w/V_w = 1$ kg/L is the water density and $\rho_s = M_s/V_s$ (kg/L) is the bulk density of the soil.

The soil water content can also be reported as a relative saturation, Θ, which is defined using

$$\Theta = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{4}$$

where θ_r and θ_s are the residual and saturated water contents, respectively. The relative saturation varies from zero for a dry soil to a maximum of one for a fully saturated soil, $0 < \Theta < 1$.

MEASURING WATER CONTENTS

Water contents are commonly measured with time-domain reflectometry (TDR) devices, as shown in (Fig. 1). TDRs determine the water content with the electromagnetic properties of a wave pulse passing through a conducting set of rods (such as 3-mm stainless-steel welding rods) placed in the soil.

The principle of TDRs is that the velocity of electromagnetic waves along a conductor is a function of the *dielectric* coefficient of the media around the conductor. Liquid water has a dielectric constant of 80.2 at 20 °C, whereas ice is 3.2, petroleum is 1.8 to 2.2, quartz is 4.3, and air is only 1.00.

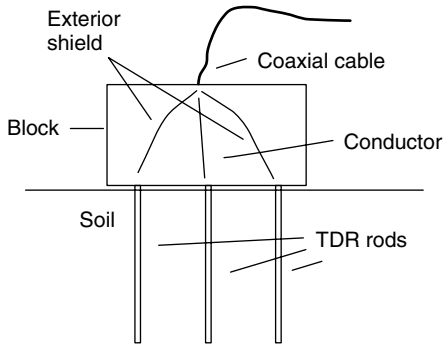


Figure 1. Time-domain reflectometer (TDR) probe that measures soil-water content. The three-rod assembly is placed within the soil. Coaxial cable connects probe to the water content tester. Center wire of coaxial cable connects to the central rod, whereas the exterior shield is connected to the two outer rods.

As the water dielectric constant is so much greater for water than for soil or air, the wave velocity is substantially retarded as the water content of a soil increases, because larger dielectric constants cause slower wave velocities and, hence, longer travel times.

Before the use of TDRs, neutron probes used the thermalization of neutrons to determine the water content (1). This older method has fallen out of favor, however, because of the rigorous licensing and inspection requirements associated with radioactive materials.

MATRIC TENSION

Water molecules in the unsaturated zone are bound by *adhesive* forces to soil surfaces and by *cohesive* forces to other water molecules, which are *surface tension* forces, and they result in fluid pressures that are less than atmospheric.

Rather than use negative pressure heads, $p < 0$, to describe the soil potential, we employ soil, or matric, tensions, $\psi > 0$. The matric tension is the negative fluid pressure head, $\psi = -p$, which increases as the pressure head becomes more negative (more tightly bound) and decreases as the pressure head becomes less negative (less tightly bound).

The total head within the soil pore fluids, h, is the difference between the elevation, z, and the matric tension:

$$H = z + p = z - \psi \tag{5}$$

Capillary theory can relate the matric tension, ψ, to the fluid potential associated with the radius of curvature, r, of fluid films within pores:

$$\psi = \frac{2\sigma \cos \alpha}{\gamma r} \tag{6}$$

where σ (Pa·m) is the surface tension and α is the contact angle at the air–water–solid interface.

The matric tension of a wet soil, $0 < \psi < 0.7$ bar, can be measured with tensiometers, as shown in (Fig. 2), which determine the negative pressure head of fluids inside a probe. The fluid within the probe is allowed to reach equilibrium with the soil fluids using a semiporous ceramic or metal filter that prevents air from entering the probe.

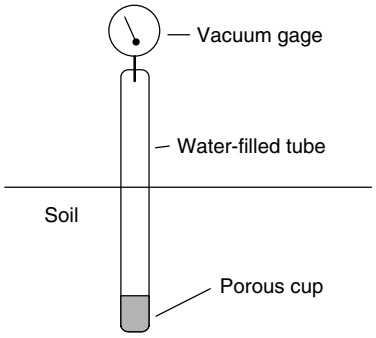


Figure 2. Soil-water tensiometer probe that monitors soil-tension. A porous cup allows water to exchange between the soil and a reservoir of water within the tube assembly. A vacuum pressure gauge monitors the water pressure inside the water reservoir.

Psychrometry is a useful technique in drier soils, $\psi > 5$ bar (2). The dewpoint temperature of the pore atmosphere is measured with a thermocouple psychrometer. The dewpoint temperature can then, along with the pore temperature, determine the relative humidity of the pore atmosphere. The matric tension can be readily determined from the relative humidity, as shown in Table 1.

MOISTURE CHARACTERISTIC CURVES

The amount of water contained within soil can be related to the fluid tension, or negative pressure, present within the water. Dry soils contain water that is held by strong adhesive forces to soil surfaces along with strong cohesive forces to other water molecules. These forces are reflected in the tension that holds the water against the force of gravity.

Each soil has a unique relationship between soil tension and water content. This relationship, termed the soil *moisture characteristic curve*, is a function that describes how water content and matric tension are related. The characteristic curve for each material varies with the pore size distribution—a soil with larger pores releases water at a lower tension than does a soil with smaller pores.

A number of formulations have been proposed that relate the relative saturation, Θ, to matric tension, ψ. The *Brooks and Corey* equation has the form:

$$\Theta = \left(\frac{\psi}{\psi_b}\right)^{-\lambda} \tag{7}$$

where ψ_b is the *bubbling pressure* and λ is a *pore-size distribution index*. This equation only holds for $\psi > \psi_o - \Theta = 1$ otherwise.

Another common formulation is the *van Genuchten* equation:

$$\Theta = \left[1 + (\alpha\psi)^n\right]^{(1-n)/n} \tag{8}$$

where α and n are empirical coefficients.

Moisture characteristic curves are commonly estimated with *pressure plates* (shown in (Fig. 3)) or *Tempe pressure cells*. In both methods, one or more soil samples are placed on top of a *porous plate* within a sealed chamber. Nitrogen gas under high pressure is forced into the chamber, and water is forced out of the soil samples through the porous

Table 1. Measures of Soil Tension

Fluid Pressure (bars)	Soil Tension (m)	Pore Radius	Relative Humidity (%)
0	0	∞	100
0.1	−1	15 μm	99.993
1	−10	1.5 μm	99.93
15	−150	100 nm	98.9
100	−1000	15 nm	93.
500	−5,000	3 nm	70.
1,000	−10,000	1.5 nm	48.
5,000	−50,000	3 Å	2.6
10,000	−100,000	1.5 Å	0.068

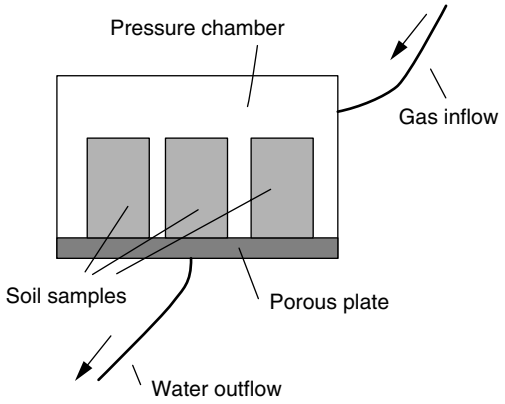


Figure 3. Pressure plate procedure for determining the soil moisture characteristic curve. A gas pressure is applied to soil samples within the chamber, and water is released through the porous plate. The water content, θ, is found for each pressure, ψ.

plate, which is permeable to water but not to air. The resulting water content of the samples can be determined once the outflow has stopped.

SAMPLING SOIL WATER

Soil water samples are more difficult to collect in the unsaturated zone than in the saturated zone because water does not freely flow into a well or piezometer. Commonly, a soil *lysimeter* collects water samples by placing a suction within a hollow tube that has a *porous cup* placed within the soil. Water flows through the porous cup into the hollow tube where it can then be collected.

Soil lysimeters are limited to conditions where the soils are wet, $\psi < 0.7$ bar. For drier conditions, soil samples can be collected and returned to the laboratory, where mechanical or gas pressure can be applied to the samples to force pore fluids out of the sample.

BIBLIOGRAPHY

1. Elder, A.N. and Rasmussen, T.C. (1994). Neutron probe calibration in unsaturated tuff. *Soil Sci. Soc. Am. J.* **58**(5): 1301–1307.
2. Rasmussen, T.C. and Rhodes, S.C. (1994). Energy-related methods: Psychrometers. In: *Vadose Zone Characterization and Monitoring; Principles, Methods and Case Studies*. L.G. Wilson, L. Everett, and S. Cullen (Eds.). Lewis Publishers, Boca Raton, FL.

SOIL AND GROUNDWATER GEOCHEMISTRY AND MICROBIOLOGY

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DEFINITIONS

Geochemistry can be defined as the study of the chemical composition of, and of actual or possible chemical changes in, a geological matrix, including *soil*, that complex mixture of minerals, life, and organic material on the surface of the earth. *Groundwater*, of course, is water located in the saturated zone of the earth. *Microbiology* is the study of small forms of life, usually including the bacteria and archaea domains and protists and fungi of the eukaryaceae domain, and naturally also covers numerous subcategories.

The interdisciplinary studies of the interactions among microflora, earth materials, and chemical reactions are often linked under *geomicrobiology* or *biogeochemistry*.

ORIGINS

The relationship between life in soil and earth materials appears to go back to the very origins of life on earth. Bacterial and archaeans (superficially bacteria-like microflora that have entirely different genetic operations, biochemistry, and cell membranes) were interacting with iron and other minerals as part of energy transformations since within a few 100 million years of the coalescence of the planet. Many archaeans specialize in methanogenesis and adaptation to extreme environments at the present time, such as geothermal waters, undersea hydrothermal vents, and hypersaline lakes (e.g., Dead Sea, Great Salt Lake, and solar salt lagoons). Biochemical evidence suggests that they may have developed in association with such conditions, which were common early in earth history.

Bacteria and cyanobacteria (colloquially known as blue-green algae) strongly affected the earth environment from early in the Archean era ($\pm$4 billion years before present, b.y. BP). Cyanobacteria, with a photosynthetic mechanism similar to algae and plants, used carbon dioxide and expended oxygen as a waste product in shallow anoxic seas. Ferrous iron (Fe), common in water and the earth's crust, scavenged the oxygen, forming various FeIII minerals, including magnetite, hematite (recently confirmed on Mars), goethite, and less-organized mineral forms. Such iron-containing Archean sediments were deposited as banded iron formations, with iron bands in a cherty matrix, which are important iron ores worldwide where they occur (such as the Mesabi Range in Minnesota). When much of the available free oceanic FeII was depleted, oxygen began to build up in the atmosphere, with a recognizably modern atmosphere dating from 1.7 b.y. BP.

Bacteria have the most diverse biochemical and respiratory capabilities among forms of life. Although others require oxygen for respiration, bacteria can respire using sulfur, forms of nitrogen, carbon dioxide, and metals (primarily Fe and Mn) as electron acceptors. Such respiration is used to process a wide variety of organic compounds, including recalcitrant ring structures. Such versatility appears to be a very ancient capability.

In ancient shallow marine settings, cyanobacteria formed stromatolites, laminations of organic and sedimentary structures formed as sand and debris, and coprecipitated minerals were trapped in cyanobacterial masses. Although many stromatolites are found as fossil structures, a number of locations exist on the modern-day Earth

where stromatolites are still forming, which are one form of the common microbial phenomenon, biofilm formation.

From there on, microbial processes and mineral-biological interactions, and the environment-manipulating "behavior" known as biofilm formation (all developed in the Archean era), have continued in action until the present.

- Bog ores (important to the development of an iron industry in the United States during the nation-forming period) and gold and copper placer ores are younger manifestations of the ancient microbial practice of depositing metals.
- Bacteria reduce oxides of Fe, Mn, N, and S to accumulate "reducing power" to oxidize ("digest") complex organic compounds. These capacities are exploited in groundwater contamination remediation. The presence of high levels of Fe and Mn in well water samples is also an indicator that organic carbon compounds are present in groundwater accessed by a well.
- Microbe-mediated biogeochemical transformations alter groundwater quality by oxidizing or reducing Fe and Mn, and mobilizing them into solution. Recently, the reduction of insoluble arsenic minerals to soluble forms and As mobilization by microbes has attracted interest as a factor in As presence in groundwater.
- Biofilm-forming microflora coat, clog, and corrode engineered structures such as wells and drains in the saturated zone, resulting in *biofouling* (further discussed in the article Biofouling in Water Wells).

SOIL MICROBIOLOGY

Soil microbiology is a special category of geomicrobiology focused on the earth's regolith, and specifically *soil*, which is a complex of mineral, organic, and biological components. Although beyond the scope of a short article, soil microbiology has traditionally been distinguished from groundwater or geomicrobiology. This distinction has origins in academic discipline; however, studies indicate that surficial soils have species richness and total microbial biomass values that are much higher than in earth materials below the soil zone. Protists and fungi are common in soil but limited in type and numbers (but not entirely absent) in aquifers.

Soil microbiology is much more thoroughly known compared with that of less-accessible earth materials. It is also much more thoroughly influenced by human activities, which include cultivation, fertilization, construction, and application of contaminants (both deliberately and accidentally). Soil microflora and soil structure experience close interactions with animals and plants. Changes in such macroflora and fauna communities can trigger sweeping changes in soil microbiology. Clearing and cultivation of forest and prairie soils result in simplification in microbial community structure. The introduction of Eurasian earthworms into North American boreal soils (where they have been absent since the Pleistocene glaciations) has resulted in measurable shifts in the availability of organic matter and nutrients to native plants. In turn, changes in vegetation affect soil and watershed hydrology.

OVERCOMING CHALLENGES IN MICROBIOLOGICAL METHODS IN GROUNDWATER STUDIES

Background

Environmental microbiology and geomicrobiology are the oldest disciplines within the broader field of microbiology. However, industrial, public health, and clinical interests quickly overshadowed the study of the microbiology of natural environments. Until the 1970s, scientific preconceptions in many circles, based on observations of engineered filters, limited methods (and limited reading) and placed limits on groundwater microbiology. Considerations of the chemistry of groundwater assumed that chemical transformations occurred in an environment devoid of life. A notable exception was that of the microbiologists in the Soviet petroleum industry of the 1950s and 1960s, who described the microbiology of petroleum reservoirs and systems.

Analysis

Methods for the analysis of groundwater environments for microbes were very limited prior to the 1980s. The principal analytical method was culturing, which recovers only a small fraction of bacteria. It was generally assumed that water passing through the soil was purified by active microbial processes and by filtration.

Interest in the occurrence of biofouling microflora in groundwater and concerns about groundwater contamination in the 1970s and 1980s motivated innovation in methods suitable for groundwater microbiology. As groundwater contamination became more and more evident in the United States and other western nations during the 1980s, the motivation for understanding groundwater environments increased. In addition, new methods in microbiology, based on advances in molecular biology, provided microbiologists with new tools to explore this difficult-to-sample microbial habitat. Among these are phospholipid fatty acid methyl ester (PL-FAME) and nucleic acid testing, described further in Evaluation of Microbial Components of Biofouling. Such methods provide the means to describe microbial associations in a meaningful way, as cultivation and phenotypic classification typically fail to do so.

Classification, in particular, is a problem in description. With micro-organisms, it often depends on making comparisons with libraries of known genotypes or phenotypes. Some deep subsurface communities are so isolated and specifically adapted that comparisons with described forms are weak. A general recognition exists in the geobiological community that the task of describing aquifer and other deep subsurface communities compares with the task of describing the recently discovered deep-sea hydrothermal vent ecosystems.

Sampling

Acquiring samples is perhaps the most difficult aspect of the microbiology of the deep subsurface. Such sampling is relatively expensive, at times technically challenging, and prone to sample compromise. Typically, methods for both solid and liquid sample acquisitions are adapted

from those developed for other purposes (borehole and core drilling, pumped or zonal sampling). Only coring can deliver solid samples isolated from drilling contamination. A variety of water sampling techniques exist to obtain discrete samples.

However, if properly interpreted, available sampling and analytical techniques appear to be sufficient to gain an understanding of deep subsurface microbial ecology.

NOTABLE DISCOVERIES

1. Microbial community diversity: PL-FAME and rRNA analysis reveal subsurface communities that are diverse and typically adapted to coping with starvation and exploiting resource "windfalls" when they occur. Bacteria can persist in viable but nonculturable and inactive states when conditions dictate. Microbial communities can have biomass that rivals surface soils and may include fungi and protozoa where pore sizes permit.
2. Microbial communities and numbers vary significantly between hydraulically transmissive and confining formations in the same wells and boreholes.
3. Community biochemical adaptability: Bacteria that form biofilms and readily exchange genetic potential can be quite plastic in their ability to exploit resources. Early in the effort to employ bioremediation in treating contaminated groundwater and soil, it was recognized that natural communities were capable of degrading a variety of anthropogenic compounds, especially hydrocarbons.
4. Iron and sulfur biogeochemical cycles are particularly important in deeper systems, whereas nitrogen is strongly cycled in the soil and shallow saturated flow zones. In deeper systems, carbon and nitrogen are cycled locally within biofilms.
5. Groundwater contamination locally alters oxidation-reduction systems, nutrient cycling, and community structure. Microbial communities react to influxes of organic carbon by increasing biomass and tipping toward anaerobic respiration as oxygen is depleted by hydrocarbon-using or other aerobic heterotrophs, which is closely analogous to eutrophication in surface water systems. For energetic reasons, the following are favored sequentially, switching to the next when the electron acceptor is depleted: nitrate, iron (and other metal) oxides, sulfate, and carbon dioxide (reduced to methane).
6. Microbial communities may include very long-lived and ancient lineages. Studies of communities in deep, isolated systems reveal communities that may be very ancient and existing in isolation from the surface.

An article of this length is insufficient to consider the subject comprehensively (considering that entire textbooks, conferences, and hundreds of webpages are devoted to the topic). Related subjects are considered elsewhere in the *Encyclopedia of Water*.

READING LIST

Ehrlich, H.L. (2002). *Geomicrobiology*, 4th Edn. Marcel Dekker, New York.

Krumbein, W.E. (Ed.). (1983). *Microbial Geochemistry*. Blackwell Scientific Publications, Oxford, UK.

Bitton, G. and Gerba, C.P. (Eds.). (1984). *Groundwater Pollution Microbiology*. Wiley-Interscience, New York.

Sinclair, J.L. and Ghiorse, W.C. (1989). Distribution of aerobic bacteria, protozoa, algae and fungi in deep subsurface sediments. *Geomicrobiology*. **7**(1–2): 15–32.

Chapelle, F.H. (1993). *Ground-Water Microbiology and Geochemistry*. John Wiley & Sons, New York.

Chapelle, F.H. (2000). *Ground-Water Microbiology and Geochemistry*, 2nd Edn. John Wiley & Sons, New York.

Madsen, E.L. and Ghiorse, W.C. (1993). Groundwater microbiology: subsurface ecosystem processes. In: *Aquatic Microbiology*. T.E. Ford (Ed.). Blackwell Scientific Publications, Boston, MA.

LeClerc, H. (2004). Microbiology of Natural Mineral Waters. Centre Evian. Available: http://www.centre-evian.com.

Madsen, E. (2004). Bibliography of important works in environmental microbiology. Available: http://www.micro.cornell.edu/faculty/Madsen/Bibliography_of_important_works_in_Environmental_Microbiology.htm.

Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., and Zuberer, D.A. (2005). *Principles and Applications of Soil Microbiology*, 2nd Edn. Prentice-Hall, New York.

CHARACTERIZING SOIL SPATIAL VARIABILITY

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SPATIAL VARIABILITY: DEFINITION, ORIGIN, SIGNIFICANCE, AND MEASUREMENT METHODS

Spatial variability refers to the variation in soil physical, chemical, mineralogical, and biological properties both laterally across the landscape and vertically through the soil profile. The spatial heterogeneity of soils is a consequence of interacting meteorological, pedological, and biological processes and anthropogenic factors over time. Within-field spatial variability of soil properties has been a primary concern within soil science ever since the classic paper by Nielson et al. (1) concerning the variability of field-measured soil water properties. The significance of soil spatial variability stems from its complex influence on any landscape-scale soil-related issue including solute transport in the vadose zone, precision agriculture, and soil quality assessment, to mention a few.

A variety of measurement methods are available for potentially characterizing soil spatial variability including ground penetrating radar (GPR), aerial photography, multispectral and hyperspectral imagery, time-domain reflectometry (TDR), and apparent soil electrical conductivity (EC_a). However, none of these approaches has been as extensively investigated with respect to characterization of within-field soil variability as EC_a (2).

Since its early agricultural use for measuring soil salinity, the application of EC_a has evolved into a widely accepted means of establishing the spatial variability of several soil physicochemical properties that influence the EC_a measurement. Geospatial measurements of EC_a are well suited for characterizing spatial variability for several reasons. Geospatial measurements of EC_a are reliable, quick, and easy to take. The mobilization of EC_a measurement equipment is easy and can be accomplished at a reasonable cost. Finally, and most importantly, EC_a is influenced by a variety of soil properties for which the spatial variability of each could be potentially established.

NEED FOR CHARACTERIZING SOIL SPATIAL VARIABILITY

The prospect of feeding a projected additional 3 billion people over the next 30 years poses formidable, but not insurmountable, challenges. Feeding the ever-increasing world population will require a sustainable agricultural system that can keep pace with population growth. Sustainable agriculture hinges on a delicate balance of economic sustainability, crop productivity, resource utilization, and minimized detrimental environmental impacts. These factors are influenced either directly or indirectly by soil spatial variability.

Spatial variability within a field amounts to an order of magnitude or more for soils (3,4) and to a factor of 2–4 or more for crops (5). Spatial variation in crops is the result of a complex interaction of biological (e.g., pests, earthworms, microbes), edaphic (e.g., salinity, organic matter, nutrients, texture), anthropogenic (e.g., irrigation efficiency, soil compaction due to farm equipment), topographic (e.g., slope, elevation), and climatic (e.g., relative humidity, temperature, rainfall) factors. To a varying extent from one field to the next, crop patterns are influenced by soil-related properties. Conventional farming is not as efficient as it could be because it currently treats a field uniformly. To maintain uniform crop production, conventional farming overcomes the inherent variability of soil and crop conditions between and within fields with an over application of inputs (i.e., irrigation water, pesticides, fertilizers, etc.) intended to meet the needs of areas of lowest productivity. Bullock and Bullock (6) pointed out the imminent need for efficient methods to accurately measure within-field variation in soil physical and chemical properties as a key component for precision agriculture.

The effective utilization of soil as a resource depends on assessing and maintaining its quality. A fundamental component of assessing field-scale soil quality is establishing the spatial distribution of the soil properties affecting the soil's intended management goal (e.g., maximize agricultural productivity, minimize environmental impact, and/or maximize waste recycling) and its intended function (e.g., biodiversity, filtering and buffering, nutrient cycling, physical stability and structural support, resistance and resilience, and water and solute flow). It is not sufficient to take a single measurement within a field to characterize its soil quality. Rather, a sufficient number of measurements must be taken and at specific locations to representatively characterize the spatial distribution of the existing soil conditions that influence the soil's intended use. Therefore, assessing soil quality requires quantitative knowledge of each indicator property associated with a soil's quality and the spatial variability of those indicator properties.

Furthermore, spatial variability has a profound influence on environmental impacts, particularly of non-point source pollutants. This result is because of its influence on the fate and transport of agrochemical inputs (e.g., pesticides, fertilizers, etc.) in an agroecosystem. In fact, it has become clear that the real constraint on modeling solute transport is not the detail of the model structures, but defining the characteristics of individual places (7). Jury (3) provides an excellent fundamental discussion of the spatial variability of soil properties and its impact on solute transport in the vadose zone. As Jury points out, "any hope of estimating a continuous spatial pattern of chemical emissions at each point in space within a field must be abandoned due to field-scale variability of soils."

The characterization of spatial variability is without a doubt one of the most significant areas of concern in soil science because of its broad reaching influence on all field- and landscape-scale issues. Research in the characterization of spatial variability has advanced tremendously over the past decade in large part because of georeferenced EC_a measurements.

EDAPHIC FACTORS INFLUENCING EC_a MEASUREMENTS

The earliest field applications of geophysical measurements of EC_a in soil science, which occurred in the early 1980s, involved the determination of salinity within the soil profile of arid zone soils. However, it soon became apparent that the measurement of EC_a in the field as a quantification of soil salinity was more complicated than initially anticipated because of the complexity of current flow pathways originating from the spatial heterogeneity of properties influencing current flow in soil.

Three pathways of current flow contribute to the EC_a of soil: (1) a liquid phase pathway via dissolved solids contained in the soil water occupying the large pores, (2) a solid–liquid phase pathway primarily via exchangeable cations associated with clay minerals, and (3) a solid pathway via soil particles that are in direct and continuous contact with one another (8). Of these three pathways, the solid pathway is usually negligible; hence, most soil can be approximated with a dual-pathway parallel conductance equation.

An analysis of this dual-pathway system indicates that EC_a will be influenced by a complex interaction of soil properties including salinity, soil texture, water content, ρ_b, and temperature. The ρ_b is directly influenced by clay content (soil texture) and organic matter (OM). Furthermore, the exchange surfaces on clays and OM provide a solid–liquid phase pathway primarily via exchangeable cations; consequently, the cation exchange capacity (CEC) and OM are recognized as additional factors that can influence EC_a measurements. Measurements of EC_a *must* be interpreted with these influencing factors in mind.

MOBILE EC_a MEASUREMENT EQUIPMENT

An EC_a survey to characterize spatial variability uses mobile geophysical equipment coupled with a global positioning system (GPS) to georeference each EC_a measurement. Mobile EC_a equipment has been developed by a variety of researchers (9–11). The development of mobile EC_a measurement equipment has made it possible to produce EC_a maps with measurements taken every few meters.

Mobile EC_a measurement equipment has been developed for both electrical resistivity (ER) and electromagnetic induction (EMI) geophysical approaches. In the case of ER, four stainless-steel electrodes are inserted into the soil generally at equal distances and connected to a resistivity meter. Current is applied to the two outer electrodes with the two inner electrodes serving as the potential electrodes. Fixing the electrode array and mounting it on or pulling it from a vehicle saves considerable time for measurements. By coupling the fixed electrode array to a datalogger and GPS georeferences the EC_a measurement, geospatial ECa measurements can be taken. Veris Technologies[1] (Salinas, KS; www.veristech.com) has developed a commercial mobile system for measuring EC_a using the principles of ER. In a similar fashion, an EMI unit can be mobilized by pulling a sled-mounted EM-38 unit (Geonics Ltd., Mississaugua, Ontario, Canada) behind a vehicle and logging the EMI data simultaneously along with real-time GPS position information. Measurements of EC_a with EMI generally involve taking readings in the horizontal coil configuration (EM_h), which is a shallow reading penetrating to a depth of about 0.75–1.0 m, and/or in the vertical coil configuration (EM_v), which is a deep reading penetrating to a depth of about 1.5 m.

EC_a-DIRECTED SAMPLING DESIGNS

Despite the complexities of the EC_a measurement, the fact that EC_a is influenced by several soil properties has broadened its utility and enabled it to play a major role in addressing the issue of characterizing spatial variability. Geospatial measurements of EC_a have been successfully used for (1) identifying the soil physicochemical properties influencing crop yield patterns and soil condition, (2) establishing the spatial variation of these soil properties, and (3) characterizing the spatial distribution of soil properties influencing solute transport through the vadose zone (4,12–14).

In a typical field survey, the spatial distribution of various soil properties can often be adequately determined with conductivity survey information in conjunction with some type of soil sampling plan. Either probability (design) or prediction (model) based sampling strategies can identify the soil properties that correlate best with EC_a in a particular field. Prediction-based sampling strategies objectively select sampling locations based on the observed spatial ECa pattern and thus are often referred to as "sensor-directed" sampling plans (15). Characterizing spatial variability with EC_a-directed soil sampling is based on the hypothesis that when EC_a correlates with a soil property or properties, then spatial EC_a information can identify sites that reflect the range and variability of the property or properties. In instances where EC_a correlates well with a particular soil property, an EC_a-directed soil sampling approach can optimally establish the spatial distribution of that property while minimizing the corresponding sampling and labor costs (2,15,16). Also, if EC_a is correlated with crop yield, then an EC_a-directed soil sampling approach can identify those soil properties that are causing the variability in crop yield (13). Details for conducting a field-scale EC_a survey for the purpose of characterizing the spatial variability of soil properties influencing soil quality or crop yield variation can be found in Corwin and Lesch (16).

Figure 1 shows EM_h and EM_v maps of an EC_a survey performed on a 6.5-ha field in Maricopa, AZ, along with the associated soil sample sites selected with a specific type of EC_a-directed sampling methodology known as spatial response surface sampling design (15,16). Once soil cores are taken at the selected sites and the corresponding soil physicochemical properties are analyzed, the properties that are well correlated with EC_a can be identified. Statistical prediction models can then be derived that spatially map (predict) these correlated soil properties with the calibrated EC_a survey data. Figure 2 shows the corresponding EC_a-predicted 0–0.9-m percent water content patterns for the field shown in Fig. 1.

GUIDELINES FOR CONDUCTING AN EC_A-DIRECTED SOIL SAMPLING SURVEY TO CHARACTERIZE SPATIAL VARIABILITY

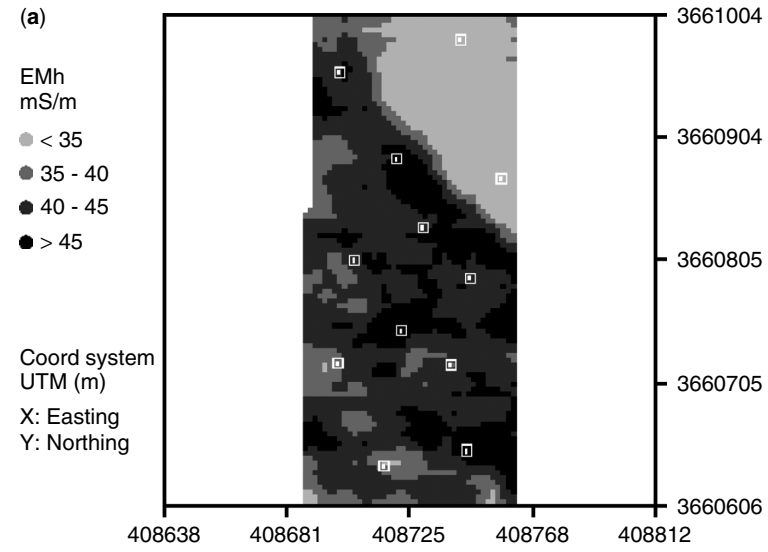
The basic elements of a field-scale EC_a survey for characterizing spatial variability include (1) EC_a survey design, (2) georeferenced EC_a data collection, (3) soil sample design based on georeferenced EC_a data, (4) soil sample collection, (5) physicochemical analysis of pertinent soil properties, (6) spatial statistical analysis, (7) determination of the dominant soil properties influencing the EC_a measurements at the study site, and (8) GIS development. The outlined steps of an EC_a-directed soil sampling survey are provided in Table 1.

LIMITATIONS AND PRECAUTIONS

At present, no other soil measurement provides a greater level of spatial information than that of geospatial EC_a measurements. Even so, are limitations exist to the use of EC_a to characterize soil spatial variability. Awareness of these weaknesses is crucial for the proper use and interpretation of geospatial EC_a measurements. The complex spatial heterogeneity of the soil system has subtle influences on geospatial EC_a measurements that can have significant interpretive impacts. The ability to recognize and interpret these influences can be the difference between the successful or failed application of EC_a measurements for characterizing spatial variability.

First and foremost, in the absence of soil sample information, geospatial measurements of EC_a by themselves do not directly quantify soil spatial variability.

[1]Product identification is provided solely for the benefit of the reader and does not imply the endorsement of the USDA.



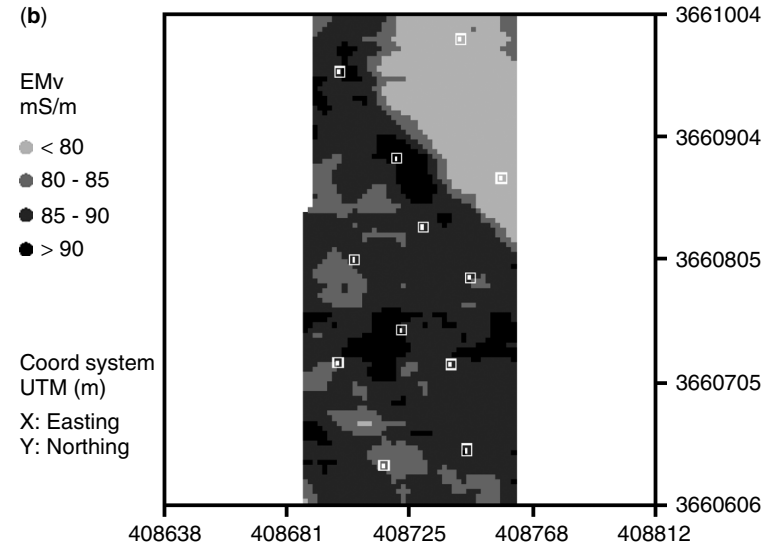


Figure 1. Maps of EC_a survey data and EC_a-directed soil sampling sites for a field in Maricopa, AZ: (**a**) EM38 horizontal and (**b**) EM38 vertical. White square symbol represents the soil sample site locations. UTM = universal transverse mercator grid system in meters.

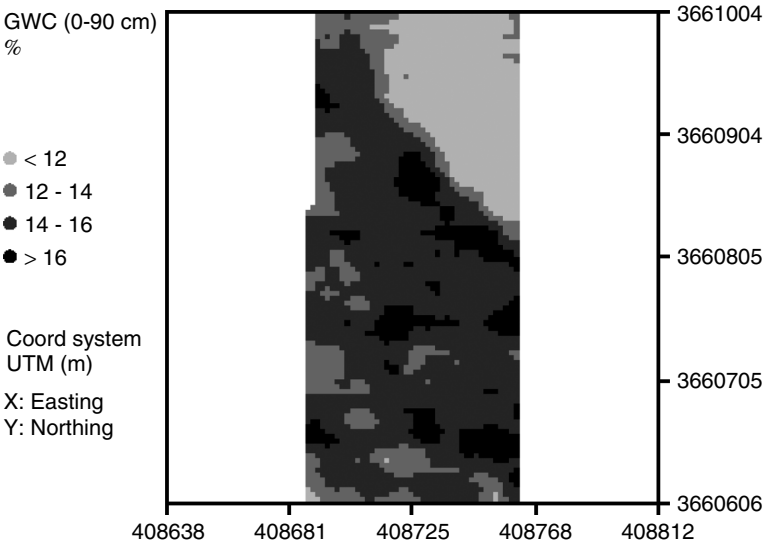


Figure 2. Map of spatial variability of percent gravimetric water content (GWC) for the 0–0.9-m sampling depth, as determined from the survey data and EC_a-directed soil sampling sites shown in Fig. 1 ($R^2 = 0.85$ for predicted and measured GWC). UTM = universal transverse mercator grid system in meters.

Table 1. Outline of Steps to Conduct an EC_a Field Survey

1. Site description and EC_a survey design
   a. record site metadata
   b. define the project's/survey's objective
   c. establish site boundaries
   d. select GPS coordinate system
   e. establish EC_a measurement intensity
2. EC_a data collection with mobile GPS-based equipment
   a. georeference site boundaries and significant physical geographic features with GPS
   b. measure georeferenced EC_a data at the predetermined spatial intensity and record associated metadata
3. Soil sample design based on georeferenced EC_a data
   a. statistically analyze EC_a data using an appropriate statistical sampling design to establish the soil sample site locations
   b. establish site locations, depth of sampling, sample depth increments, and number of cores per site
4. Soil core sampling at specified sites designated by the sample design
   a. obtain measurements of soil temperature through the profile at selected sites
   b. at randomly selected locations, obtain duplicate soil cores within a 1-m distance of one another to establish local-scale variation of soil properties
   c. record soil core observations (e.g., mottling, horizonation, textural discontinuities, etc.)
5. Laboratory analysis of appropriate soil physicochemical properties defined by project objectives
6. If needed, stochastic and/or deterministic calibration of EC_a to EC_e or to other soil properties (e.g., water content and texture)
7. Spatial statistical analysis to determine the soil properties influencing EC_a and/or crop yield
   a. soil quality assessment:
      1. perform a basic statistical analysis of physicochemical data by depth increment and by composite depth over the depth of measurement of EC_a
      2. determine the correlation between EC_a and physicochemical soil properties by composite depth over the depth of measurement of EC_a
   b. precision agriculture applications (if EC_a correlates with crop yield, then):
      1. perform a basic statistical analysis of physicochemical data by depth increment and by composite depths
      2. determine the correlation between EC_a and physicochemical soil properties by depth increment and by composite depths
      3. determine the correlation between crop yield and physicochemical soil properties by depth and by composite depths to determine depth of concern (i.e., depth with consistently highest correlation, whether positive or negative, of soil properties to yield) and the significant soil properties influencing crop yield (or crop quality)
      4. conduct an exploratory graphical analysis to determine the relationship between the significant physicochemical properties and crop yield (or crop quality)
      5. formulate a spatial linear regression (SLR) model that relates soil properties (independent variables) to crop yield or crop quality (dependent variable)
      6. adjust this model for spatial autocorrelation, if necessary, using restricted maximum likelihood or some other technique
      7. Conduct a sensitivity analysis to establish dominant soil property influencing yield or quality
8. GIS database development and graphic display of spatial distribution of soil properties

Source: Ref. 16. With permission.

Rather, EC_a-survey measurements provide the spatial information necessary to direct soil sampling. It is the combined use of both the EC_a-survey and the corresponding sample data that makes this sort of surveying technology invaluable for characterizing spatial variability. In other words, the primary strength of geospatial EC_a measurements lies in their effectiveness as a means to direct soil sampling (using a minimum number of sample sites) that best characterizes the spatial variability of those soil properties influencing EC_a in the landscape of interest.

Second, EC_a-directed soil sampling can only spatially characterize soil properties that correlate with EC_a. This correlation may be caused by a direct or indirect influence on the EC_a measurement, or the correlation may be a complete artifact. For example, salinity and water content will directly influence EC_a and CEC will indirectly influence EC_a through its influence on current flow at the

surface of soil minerals. Likewise, in many instances, B and salinity distributions are similar. Consequently, a strong correlation between B and salinity (and thus EC_a) can result, even though no cause-and-effect relationship exists between B and EC_a. Thus, a solid understanding of the soil properties that directly influence and/or are indirectly measured by EC_a at a specific site is particularly essential in temporal surveying applications, because over time these correlations may or may not persist.

Third, as previously mentioned, often a dynamic and complex relationship exists between EC_a and those properties that influence EC_a. Ground-truth soil samples are obligatory if spatial measurements of EC_a are to be used for quantifying soil variability. Geospatial measurements of EC_a do not supplant the need for soil sampling, but they do minimize the number of samples necessary to characterize spatial variability. Additionally, users of EC_a survey data must exercise caution and be aware of what EC_a is actually measuring at the site of interest. Normally, the only way to establish those soil properties that influence EC_a at a specific location is by collecting representative soil samples and then determining the relationship between EC_a and the particular property or properties of interest. This process requires that every EC_a survey has an associated soil sampling design. The location and number of sites can be established (after acquiring the EC_a survey data) using model-based sample design software such as ESAP (17).

Finally, the temporal stability of EC_a measurements at a site may be of potential concern because EC_a is a product of both static and dynamic factors, which adds another dimension to the complexity of understanding and interpreting geospatial EC_a measurements. For this reason, caution must be taken to characterize spatial variability with EC_a when dynamic conditions influencing EC_a are significant. Apparent soil electrical conductivity surveys are generally conducted (1) within a set time frame to minimize the effects of dynamic properties (such as temperature and water content), (2) when the soil is at or near field capacity (to avoid current-flow problems), and (3) with regard for subtle topographic effects (e.g., bed-furrow). Protocols for conducting an EC_a survey that consider all previously discussed limitations are presented by Corwin and Lesch (16).

FUTURE DIRECTION

Because of the heterogeneous nature of soils, characterization of soil spatial variability is a fundamental component of any landscape-scale process that cannot be overlooked or superficially addressed. Significant technological advances have occurred over the past two decades, particularly in the area of sensor technology and in precisely locating a geographic position with GPS. These advances have helped the progress of research in characterizing spatial variability at field and landscape scales.

Geospatial measurement of EC_a stands out among the ground-based sensor technologies, contributing to an improved ability to characterize spatial variability. Numerous soil samples are required for representative estimates of field-scale spatial variability using traditional grid sampling, which makes grid sampling impractical because of labor and cost intensiveness. Soil sampling directed by geospatial EC_a measurements provides a viable alternative for characterizing spatial variability of a variety of soil-related physicochemical properties. Geospatial EC_a measurements provide a means of significantly reducing the number of soil samples needed to characterize spatial variability, provided that the target soil properties are well correlated with the conductivity survey data.

Directed soil sampling with geospatial EC_a measurements has its limitations in characterizing spatial variability, particularly when the soil properties of interest are not measured either directly or indirectly by the EC_a survey data. In these instances, other types of sensors should be used (if available) or a more intensive soil sampling strategy must be adopted. A robust methodology for the integrated use of multiple remote and ground-based sensors has yet to be developed. The successful integration of multispectral and hyperspectral imagery, TDR, GPR, aerial photography, and EC_a sensors is needed to provide the redundant and supplemental data necessary to unravel the spatial complexity of soil. This type of integrated methodology represents the future direction of soil spatial variability research.

BIBLIOGRAPHY

1. Nielsen, D.R., Biggar, J.W., and Erh, K.T. (1973). Spatial variability of field-measured soil-water properties. *Hilgardia* **42**(7): 215–259.
2. Corwin, D.L. and Lesch, S.M. (In press). Apparent soil electrical conductivity measurements in agriculture. *Comput. Electron. Agric.*
3. Jury, W.A. (1986). Spatial variability of soil properties. In: *Vadose Zone Modeling of Organic Pollutants*. S.C. Hern and S.M. Melancon (Eds.). Lewis Publishers, Chelsea, MI, pp. 245–269.
4. Corwin, D.L. et al. (2003). Assessment and field-scale mapping of soil quality properties of a saline-sodic soil. *Geoderma* **114**(3–4): 231–259.
5. Verhagen, A., Booltink, H.W.G., and Bouma, J. (1995). Site-specific management: Balancing production and environmental requirements at farm level. *Agric. Syst.* **49**: 369–384.
6. Bullock, D.S. and Bullock, D.G. (2000). Economic optimality of input application rates in precision farming. *Prec. Agric.* **2**: 71–101.
7. Beven, K.J. (2002). Towards an alternative blueprint for a physically-based digitally simulated hydrologic response modeling system. *Hydrol. Process.* **16**(2): 189–206.
8. Rhoades, J.D., Chanduvi, F., and Lesch, S. (1999). Soil Salinity Assessment: Methods and Interpretation of Electrical Conductivity Measurements, FAO Irrigation and Drainage Paper #57, Food and Agriculture Organization of the United Nations, Rome, Italy, pp. 1–150.
9. McNeill, J.D. (1992). Rapid, accurate mapping of soil salinity by electromagnetic ground conductivity meters. In: *Advances in Measurements of Soil Physical Properties: Bringing Theory into Practice*. G.C. Topp, W.D. Reynolds, and R.E. Green (Eds.). *SSSA Special Publication* No. 30, ASA-CSSA-SSSA, Madison, WI, pp. 201–229.
10. Rhoades, J.D. (1993). Electrical conductivity methods for measuring and mapping soil salinity. In: *Advances in*

Agronomy. D.L. Sparks (Ed.). Vol. 49, Academic Press, San Diego, CA, pp. 201–251.

11. Jaynes, D.B., Colvin, T.S., and Ambuel, J. (1993). Soil type and crop yield determinations from ground conductivity surveys. ASAE Paper No. 933552, 1993 ASAE Winter Meetings, 14–17 Dec. 1993, Chicago, IL, ASAE, St. Joseph, MI.
12. Corwin, D.L. et al. (1999). Evaluation of GIS-linked model of salt loading to groundwater. *J. Environ. Qual.* **28**: 471–480.
13. Corwin, D.L. et al. (2003). Identifying soil properties that influence cotton yield using soil sampling directed by apparent soil electrical conductivity. *Agron. J.* **95**(2): 352–364.
14. Corwin, D.L., Lesch, S.M., Oster, J.D., and Kaffka, S.R. (In press). Characterizing spatio-temporal variability with soil sampling directed by apparent soil electrical conductivity. *Geoderma*.
15. Lesch, S.M. (In press). Sensor-directed response surface sampling designs for characterizing spatial variation in soil properties. *Comput. Electron. Agric.*
16. Corwin, D.L. and Lesch, S.M. (In press). Characterizing soil spatial variability with apparent soil electrical conductivity: I. Survey protocols. *Comput. Electron. Agric.*
17. Lesch, S.M., Rhoades, J.D., and Corwin, D.L. (2000). ESAP-95 Version 2.10R: User Manual and Tutorial Guide, Research Rpt. 146, USDA-ARS George E. Brown, Jr. Salinity Laboratory, Riverside, CA.

DEEP SOIL-WATER MOVEMENT

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Soil water refers to subsurface water between the Earth's surface and the regional water table, called the unsaturated, or vadose zone. Figure 1 illustrates the components of flow within this zone. Deep soil-water movement usually implies the migration of water below the root zone, and is also called deep percolation.

Soil water is held by adhesive forces to soil surfaces and by cohesive forces to other water molecules. Measurements of soil-water pressures are usually negative—water does not freely drain into a well. Some soil water may exist with positive pressures, such as water that is perched in a saturated zone above a layer of lower permeability. Water under positive pressure flows freely into a well.

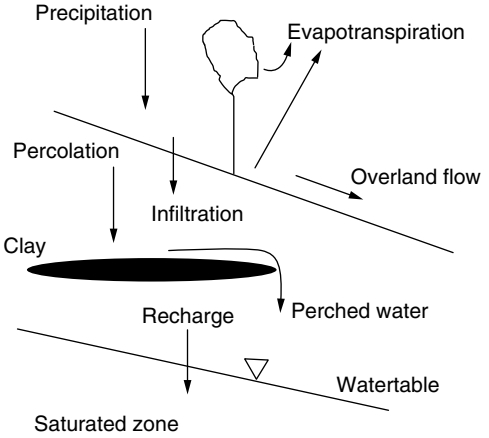


Figure 1. Flow components in the unsaturated zone.

FORCES THAT CONTROL WATER MOVEMENT

Gravity is the dominant force that controls soil-water movement. The downward force of gravity acts in conjunction with geologic media to control the magnitude and direction of fluid flow.

A second important force is the matric tension (or soil-water tension), which causes water to move from zones of lower tension to zones of higher tension. The soil tension, ψ, is the negative of the water pressure head, $\psi = -P/\gamma$, where P is the fluid pressure relative to atmospheric pressure and γ is the freshwater specific weight.

The total head, H, combines the gravitational and tension forces using $H = z - \psi$, where z is the elevation of the point of measurement.

In some circumstances, osmotic forces can also affect water movement. Osmotic forces develop when solute concentration gradients are present, causing water to move from zones of low salt concentration to zones of higher concentration. When osmotic forces are present, the total head must include the osmotic potential, ϕ, as noted in Section GW456 (head).

MATERIAL PROPERTIES

In addition to the total head, the characteristics of the geologic medium are also important for controlling the magnitude and direction of deep soil-water movement (1). The important material properties that affect soil-water movement are the unsaturated hydraulic conductivity functions and the soil-water characteristic curves.

Unsaturated Hydraulic Conductivity

The unsaturated hydraulic conductivity, $K(\psi)$, is commonly written as:

$$K(\psi) = K_r(\psi)\, K_s \tag{1}$$

where K_r is the relative unsaturated hydraulic conductivity function that varies with matric tension, ψ, and K_s is the saturated hydraulic conductivity.

As soil dries, the tension increases and the relative hydraulic conductivity decreases, whereas wetting soils show a decrease in tension and an increase in relative conductivity. The relative conductivity ranges from a theoretical minimum of zero in dry soil, $K_r \to 0$ as $\psi \to 0$, to a maximum of one in saturated soil, $K_r \to 1$ as $\psi = 0$, so that $0 < K_r \leq 1$.

Both the relative and saturated hydraulic conductivities vary with the pore-size distribution of the geologic media. Sandy materials may have a large saturated hydraulic conductivity, but a rapidly declining relative hydraulic conductivity, whereas finer materials may have a smaller saturated hydraulic conductivity but a slowly

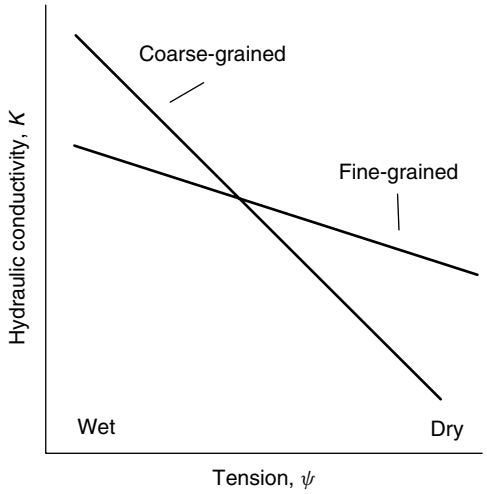


Figure 2. Unsaturated hydraulic conductivity, K, as a function of tension, ψ, for two materials. The coarser material is more conductive under wet conditions (smaller values of tension), whereas the finer material is more conductive under drier conditions.

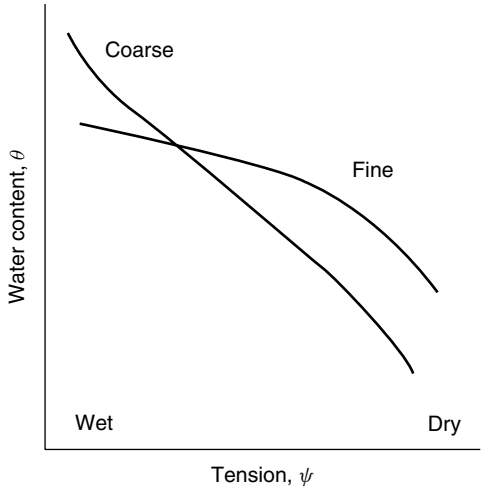


Figure 3. Soil water content, θ, as a function of tension, ψ, for two materials. The coarser material holds more water under wet conditions (smaller values of tension), whereas the finer material holds more water under drier conditions.

declining relative conductivity. This effect is shown if Fig. 2.

The crossover of the two curves shown in Fig. 2 results in the interesting phenomenon that coarser materials have a larger unsaturated hydraulic conductivity than finer material in the wet range, but a smaller conductivity in the drier range.

Thus, the flow behavior for wet conditions may be very different from the behavior under dry conditions in heterogeneous materials. Coarser materials (such as sands, fractures, and other large openings) generally dominate flow under wet conditions, whereas finer materials (such as silts, clays, and consolidated materials) can dominate flow under drier conditions.

Moisture Characteristic Curves

The ability of the unsaturated zone to hold water as a function of the soil tension is called the moisture characteristic curve. The characteristic curve for each material varies with the pore size distribution—a soil with larger pores releases water at a lower tension than a soil with smaller pores.

Figure 3 shows two soil characteristic curves, one for a coarser material and a second for a finer material. Like the unsaturated hydraulic conductivity function, the finer soil can hold more water under dry conditions, whereas the coarser soil holds more water under wetter conditions.

The water retention properties of soils also affect water movement. Changes in water flux with depth can be attributed to the uptake and release of water as the soil tension changes. For example, a wetting front may move downward with time from the surface after a large rain event, only to be absorbed by the dry soil underneath. The ability to absorb the moisture is a function of the ambient moisture tension—an already wet soil will have little ability to absorb additional water.

In some cases, water percolating down from above may not immediately reach the water table because the dry soils mediate the pulse of water. This water is retained by the soil and then slowly released over time. The initial pulse of water at the surface is transformed into a slow drainage at depth.

Only in materials with little water storage capacity (i.e., in wet soils or in materials with limited water holding capacity) will the downward movement of water be rapid. In these cases, the water that reaches the water table may or may not be the same water that was added at the surface. In some situations, the added water merely displaces the water below it, causing an equivalent volume of water to move at depth. In other situations, the added water moves quickly through the unsaturated zone.

Spatial Variability

Local subsurface conditions can also affect deep soil-water movement. Hydrogeologic units that dip in one direction, such as bedded sedimentary materials, can cause water to flow in the down-dip direction. Microscopic layering in features such as sand dunes can also affect the direction of movement.

Vertical features, such as fractures and joints, may focus water movement during wet conditions. Localized zones of preferential flow can also be found in soils with a defined structure, such as in soil with aggregates. These soils form a dual-porosity network consisting of fine pores within the aggregates and larger macropores between the aggregates.

Many explanations exist for preferential flow within soils, including bypass flow, macropore flow, fracture flow, boundary layer flow, mobile zone flow, finger flow, funnel flow, media heterogeneities, ion exclusion, and colloid transport (2).

WATER VAPOR MOVEMENT

Water vapor movement in deep systems can also be important, especially in very dry media where liquid flow

is small. Water vapor is generally in equilibrium with the liquid phase and can be related to the matric tension of the pore fluids (3):

$$RH = \frac{e}{e_s} = \exp\left(\frac{g\psi}{RT}\right) \quad (2)$$

where RH is the relative humidity, e is the actual vapor pressure, e_s is the saturated vapor pressure, R is the water vapor gas constant, and T is the absolute temperature. Dissolved solids in soil water can lower the relative humidity—and increase the tension—because of osmotic forces.

The diffusion of water vapor through the subsurface can be predicted using a variety of approaches that depend on the specific conditions within the subsurface, which is because additional forces become important when considering subsurface vapor movement, including thermal effects and barometric pressure changes.

Temperature variation affects water movement because the saturated vapor pressure increases with temperature. The natural temperature increase with depth is called the geothermal gradient. Deeper water is warmer and has a higher vapor pressure than water at a shallow depth. This vapor pressure gradient causes water vapor to move upward toward the cooler zones, where it may condense.

Also, barometric fluctuations cause oscillations in the vertical movement of soil gasses, leading to the vertical advective transport of water vapor. The vertical movement may be amplified when extreme barometric pressure conditions are present, such as during a hurricane when extremely low surface barometric pressures cause an upward air pressure gradient within the unsaturated zone.

BIBLIOGRAPHY

1. Evans, D., Rasmussen, T.C., and Nicholson, T.J. (2001). Flow and transport through unsaturated fractured rock: An overview. In: *Flow and Transport Through Unsaturated Fractured Rock*, 2nd Edn. D.D. Evans, T.J. Nicholson, and T.C. Rasmussen (Eds.). *Geophysical Monograph* 42. American Geophysical Union, Washington, DC.
2. Rasmussen, T.C., Baldwin, R.H., Dowd, J.F., and Williams, A.G. (2000). Tracer vs. pressure wave velocities through unsaturated saprolite. *Soil Sci. Soc. Amer. J.* **64**(1): 75–85.
3. Hillel, D. (1971). *Soil and Water: Physical Principles and Processes*. Academic Press, New York.

SPECIFIC GRAVITY

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The density of water and other materials varies with temperature as well as with the amount of dissolved and suspended matter within them. The specific gravity is the observed density of a material divided by a reference density, which is usually taken to be water at its maximum density, i.e., 1 kg/L. Thus, variations in the specific gravity are a direct measure of the variation in density. The specific weight of a material equals the product of its density and the gravitational constant. The specific gravity is important because it is needed to correct for the water density in wells to determine the freshwater head. Well construction also relies on the specific gravity of drilling muds to prevent the collapse of borehole walls in unconsolidated media.

The specific gravity is a measure of the density, or weight, of a fluid or solid. Denser materials have a larger specific gravity than do less dense materials. The specific gravity, ϱ, is defined using

$$\varrho = \frac{\rho}{\rho_o} \quad (1)$$

where ρ is the density (mass per unit volume) of the material and ρ_o is the density of a reference material.

The density of water at 4 °C, $\rho_o = 1$ kg/L, is generally the reference density for liquids and solids. Table 1 provides the specific gravity for a range of elements, including very light metals, such as aluminum and titanium, to very dense metals, such as gold and platinum. Note that for liquids and solids, the specific gravity equals the density because the standard density of water is 1 kg/L. The density of hydrogen is common for gasses.

The specific gravity of a pure substance can be affected by temperature. Table 2 provides the specific gravity and specific weight for water from 0 °C to 100 °C. Note that the specific gravity decreases more rapidly as the temperature increases.

Changes in physical properties of solids, such as their crystalline structure or porosity, can also result in a change in their density. The specific gravity can also be affected by any components present within the material, including dissolved gasses, liquids, and solids, as well as suspended gasses, liquids, and solids.

For example, water with high concentrations of suspended solids (such as drilling fluids) or dissolved solids (such as brines) has higher specific gravities than does clear water. Also, a column of air bubbles rising within a water column can reduce the fluid density.

The specific gravity is also related to the specific weight, $\gamma = \rho g$, where $g = 9.807$ m/s^2 is the gravitational constant. The specific weight commonly converts measured pressures to an equivalent hydraulic head because an increase

Table 1. Specific Gravity of Selected Elements

Material	Specific Gravity
Aluminum	2.70
Titanium	4.51
Iron	7.87
Copper	8.96
Silver	10.50
Lead	11.30
Mercury	13.50
Uranium	19.10
Gold	19.30
Platinum	21.50

Table 2. Variation of Pure Water with Temperature

Temperature (°C)	Density (kg/L)	Specific Weight (Pa/m)
0	0.99984	9,805.4
10	0.99970	9,804.1
20	0.99821	9,789.4
30	0.99565	9,764.3
40	0.99222	9,730.7
50	0.98803	9,689.6
60	0.98320	9,642.2
70	0.97778	9,589.1
80	0.97182	9,530.6
90	0.96535	9,467.2
100	0.95840	9,399.0

in depth, Δz, is accompanied by a concomitant increase in pressure, ΔP, which yields $\gamma = \Delta P/\Delta z$.

MEASURING THE SPECIFIC GRAVITY

A traditional technique for measuring the fluid density uses a *hydrometer*, which compares the weight of the fluid to a standard fluid. The hydrometer is allowed to float within the fluid, and the fluid density is determined from how much higher or lower the hydrometer level is compared with pure water (Fig. 1). Heavier fluids cause the hydrometer to rise relative to clear water because of buoyancy.

An alternative method for determining the fluid density is to employ a differential pressure transducer to measure the change in fluid pressure over a known depth. The resulting ratio between the measured pressure and the depth yields an estimate of the specific weight, $\gamma = \Delta P/\Delta z$.

Pressure transducers have recently measured the concentration and particle size distribution of suspended sediments (1). The particle size distribution is determined using Stokes's law, whereas the sediment concentration is found using

$$C = \frac{\varrho_f - 1}{\varrho_s - 1} \tag{2}$$

where ϱ_f is the measured specific gravity of the fluid and ϱ_s is the specific gravity of the suspended sediments.

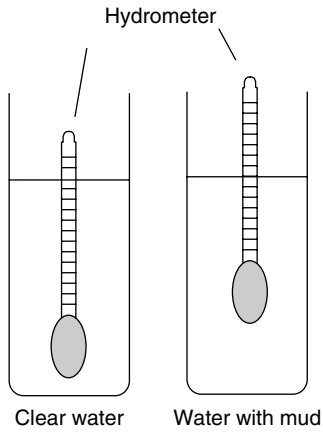


Figure 1. Hydrometer technique for measuring fluid density. Clear water causes the hydrometer to float at a constant level. Denser fluids cause the hydrometer to rise, whereas lighter fluids cause the hydrometer to sink lower in the water column.

IMPORTANCE OF SPECIFIC GRAVITY

Head Measurement

The use of water levels in wells to determine the hydraulic head within an aquifer is complicated when the density of the fluid within the borehole is not a constant (2). As noted in HEAD, changes in density affect the head according to the relationship:

$$H = z_o + \varrho \Delta z \tag{3}$$

where H is the freshwater head, z_o is the midpoint elevation of the screened zone within the aquifer, $\varrho = \gamma/\gamma_o$ is the specific gravity of the fluid within the well, $\Delta z = z - z_o$ is the height of the column of water within the monitoring well above the screened zone, and z is the water surface elevation in the well.

Drilling Fluids

The specific gravity of the drilling fluid is important during well construction. In loose materials, the process of drilling a well is complicated by the tendency of the unsupported walls to collapse.

Borehole walls can be temporarily supported until a casing is emplaced by using drilling fluids that are denser than water. The weight of the drilling fluid places an outward force on the borehole walls that helps to support them.

Heavier drilling fluids place a correspondingly heavier force on the borehole wall. One important drawback is the tendency of the drilling fluid to accumulate on the walls and within the formation, which causes a reduction in well yield if it is not removed during well development.

Lighter drilling fluids, such as foams and air, can also be used. In this case, the inflow of water from the formation into the borehole prevents the buildup of materials on the borehole wall, which eases well development. This technique is suitable in *consolidated media* where borehole collapse is not a problem.

Table 3. Specific Gravities of Selected Drilling Fluids

Drilling Fluid	Specific Gravity
Air	0.001
Mist	0.020
Stiff foam	0.100
Wet foam	0.200
Polymers	1.020
Polymers w/ NaCl	1.200
Bentonite clay	1.300
Polymers w/ CaCl	1.400
Bentonite w/ barite	2.200
Barite ($BaSO_4$)	4.200

Table 3 presents approximate specific gravities for a range of drilling fluids. Notice the wide range in specific gravities, from a low of 0.01 for air to a high of 4.2 for barite.

The values in Table 3 are approximate because the final density is a function of the relative concentrations of the liquids, solids, and gasses within the drilling fluid. Also note that the specific gravity of the air and mist are related to the density of water.

BIBLIOGRAPHY

1. Lewis, A.J. and Rasmussen, T.C. (1999). Determination of suspended sediment concentration and particle size distributions using pressure measurements. *J. Environ. Qual.* **28**: 1490–1496.
2. Driscoll, F.G. (1986). *Groundwater and Wells*, 2nd Edn. Johnson Filtration Systems, Inc., St. Paul, MN.

HOT SPRINGS

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Springs have been important in the social, cultural, and economic history of humankind. They have been an important source of water for humans. Our ancestors did not have drilling equipment, so in the absence of surface water, they had to rely on springs. Many early towns in Greece, Egypt, Mesopotamia, India, and China developed around springs. Many towns in the United States have taken their names from springs: Steamboat Springs, Colorado; Glenwood Springs, Colorado; Springfield, Missouri; and Rock Springs, Wyoming, are a few examples.

For centuries, hot springs and mineral springs were considered of medicinal or therapeutic value. Bottled "springwater" is still considered by many people of higher quality than ordinary tap water. This belief is at least partially responsible for the current high-volume sale of bottled water. Unfortunately, this association of springwater with purity is not based on fact. Springwater can contain higher concentrations of dissolved solids than local public water supplies, and springs become easily contaminated. Springs become contaminated because they are open, unprotected, and accessible to human beings and animals. Contamination can also occur from surface water flow or flooding into spring collection systems.

More than 3400 public water supply systems (1992) in the United States obtain part or all of their drinking water from springs. These systems provide drinking water for more than 7 million people. However, the average number of people served by a single public supply system using springs as a water source is small. Springs are an important component of the drinking water supply in many states. Public water supplies that use springs are more numerous in the western United States. Wyoming has 80 springs that are used for public water supply. A box used to collect water from springs is shown in Fig. 1 (1).

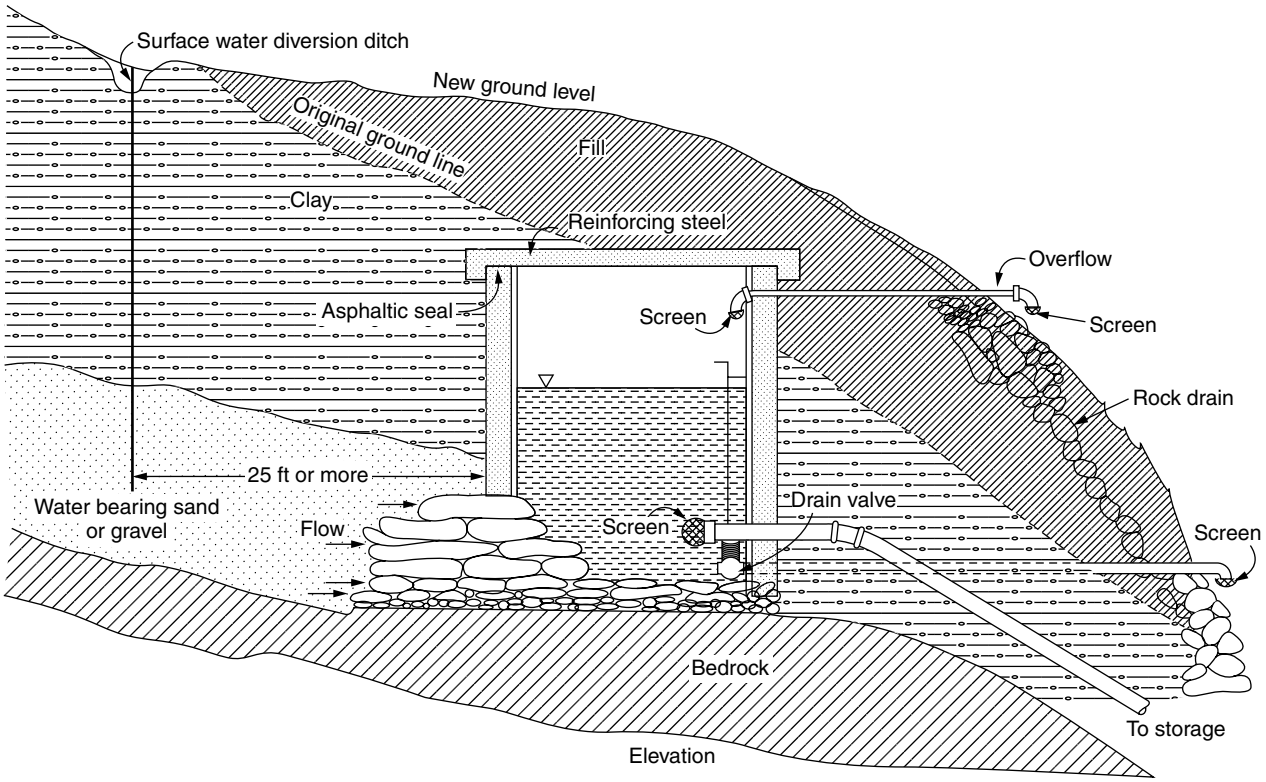


Figure 1. Diagram of a spring collection box (1).

A spring is a source of water that flows naturally from an aquifer or soil onto the land or into a body of surface water. Its occurrence depends on the nature and relationship of rocks (especially permeable and impermeable strata), on the position of the water table, and on topography.

Springs are generally classified as gravity springs and artesian springs. Thermal springs are typically considered a type of artesian spring. The vast majority of springs are gravity springs. Gravity springs are created by water that moves downgradient (downhill) and emerges at the surface. Two gravity springs, contact and fault springs are shown in Fig. 2. Artesian (nongravitational) springs occur when the potentiometric level of the groundwater system is above the land surface and water flows at the land surface under pressure either at the aquifer outcrop or from fractures or faults.

Springs are replenished by precipitation that recharges aquifers. The precipitation seeps into the soil and enters fractures, joints, bedding planes, or pore spaces in sand aquifers and sedimentary rocks. Springs occur when water flows through aquifers and discharges at the land surface through faults, fractures, or by flow along an impermeable layer. They can also occur where water flows from large orifices that result when the water dissolves carbonate rock (karst) and enlarges fractures or joints to create a passage (Fig. 2).

Springwater is sometimes forced to the surface along a fault from deep sources by thermal pressure gradients. Springs are associated with volcanism and fractures that extend to great depths in the earth's crust. Springs are a common feature in some hydrogeologic settings.

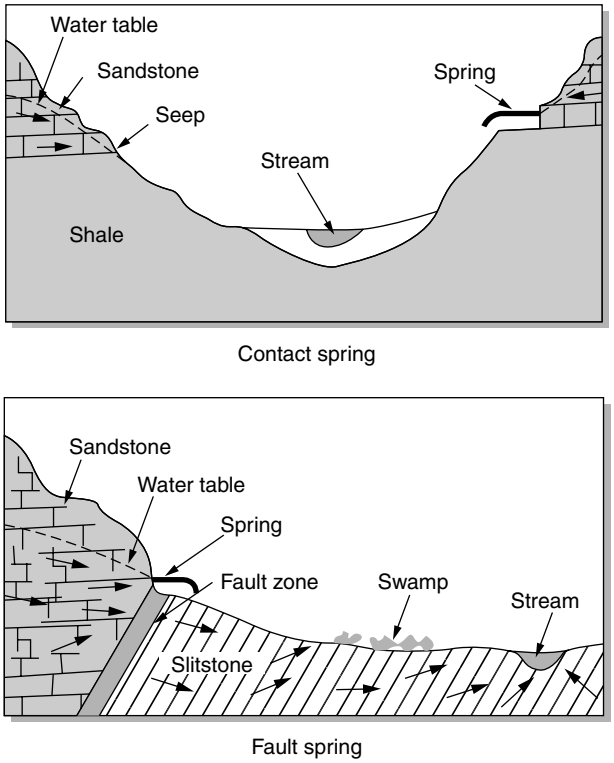


Figure 2. Contact and fault springs (2).

For example, springs are common in mountains and in watersheds that are underlain by fractured rock aquifers.

Springs can be regional (long flow paths) or local (short flow paths). Local springs are comparatively small, can have low flow, and are typically from shallow aquifers. The discharge from these springs often fluctuates either seasonally or in greater cycles, sometimes in response to local precipitation. Local aquifers are quickly recharged, and water movement through them is comparatively rapid, resulting in low water mineralization. Springs supported by local aquifers are more likely than regional flow springs to stop flowing periodically. Regional springs more typically have large discharges. Regional springs typically have nearly constant discharge and are more mineralized than local springs. Regional springs rarely stop flowing even during long droughts.

The discharge rate of a spring is a function of three main variables:

1. hydraulic conductivity (permeability) of the aquifer
2. area contributing recharge to the aquifer
3. quantity of recharge.

Springs are also classified based on hydrogeologic characteristics. The Water Resources Division of the U.S. Geological Survey recognizes eight principal types of springs based on hydrogeologic characteristics:

1. An artesian spring is a release of pressurized water from a confined aquifer at the aquifer outcrop or through an opening in the confining unit.
2. A depression spring is formed when the water table intersects a steeply sloping land surface. This type of spring is sensitive to seasonal fluctuations in groundwater storage and frequently disappears during dry periods.
3. A fracture spring (fault spring) is formed in fractured or jointed rocks. Water movement is through fractures, and springs form where the fractures intersect the land surface. This type of spring is particularly sensitive to seasonal fluctuations in groundwater storage and frequently disappears due to reduced flow during dry periods. Daily fluctuations of discharge of small springs are commonly the result of use of water by vegetation.
4. A contact spring occurs where a permeable water-bearing unit overlies a less permeable unit that intersects the ground surface.
5. A geyser spring is a periodic thermal spring resulting from the expansive force of superheated steam within constricted subsurface channels.
6. A perched spring occurs where infiltrating water discharges above the regional water table.
7. A seep spring discharges from numerous small openings in permeable material. These springs typically have very low discharge rates.
8. A tubular spring discharges from rounded channels (karst solution openings, lava tubes).

Springs occur in many sizes, types of discharge points, and locations with respect to topography. They occur in the highest elevations of mountainous areas and on valley floors. Many of the public water supply springs in the western United States are small; discharges are less than 5 gallons per minute. Springs vary in their physical and chemical compositions. They can be cold (50 °F) or hot (more than 10 °C above the air temperature). Shallow groundwater has a temperature within a few degrees of the ambient air temperature. Higher temperatures usually indicate deeper circulation. Thermal springs gain their temperature increases when the water comes in contact with recently emplaced igneous masses. Thermal and hot springs are due to deep-seated thermal sources and are classed as volcanic springs or fissure springs. Springs may occur singly or in groups that can include dozens of habitats in various sizes.

Springs may be highly mineralized, especially thermal springs and sometimes region springs that have a very long flow path. Thermal springs have pH values ranging from 7.2–7.6. Electrical conductance of spring water ranges from 2–10,000 milligrams per million.

A list of question that could be asked to evaluate spring conditions is shown below.

- Are there standing water and surface drainage around the spring?
- Is there deeply rooted vegetation in the spring collection area?
- Are there roots in the collection pits?
- Is there a lock-tight fence around the collection area?
- Is there a diversion channel capable of diverting surface water away from the collection area?
- Are there privies, septic systems, underground storage tanks, or barnyards near the spring?
- Is the collection chamber properly constructed (lockable)?

BIBLIOGRAPHY

1. U.S. Environmental Protection Agency. (1999). *Guidance Manual for Conducting Sanitary Surveys of Public Water Systems*.
2. Moore, J.E. et al. (1995). *Groundwater-a primer*. American Geological Institute, Arlington, VA.

READING LIST

Davis, S.N. and De Wiest, R.J.M. (1966). *Hydrogeology*. John Wiley & Sons, New York.

U.S. Environmental Protection Agency. (1997). *Investigation of Hydrogeologic Mapping to Delineate Protection Zones Around Springs-Report of Two Case Studies*.

Fetter, C.W. (2000). *Applied Hydrogeology*. Prentice-Hall, New York.

LaMoreaux, P.E. and Tanner, J.T. (2001). *Springs and Bottled Waters of the World*. Springer, New York.

Meinzer, O.E. (1923). *Outline of Ground Water Hydrology*. U.S. Geology Survey Water Supply Paper 494, p. 71.

Moore, J.E. (2002). *Field Hydrogeology*. Lewis, Boca Raton, FL.

Moore, J.E. et al. (in press). *A Field Guide to Evaluate Springs*. USEPA, Washington, DC.

Sanders, L.L. (1998). *A Manual of Field Hydrogeology*. Prentice-Hall, Upper Saddle River, NJ.

SQUEEZING WATER FROM ROCK

NASA Earth Science Enterprise
Data and Services

On December 16, 1811, an earthquake estimated at magnitude 7.0 to 8.0 on the Richter scale rocked the frontier town of New Madrid, Missouri, in the central United States. It was the first of three powerful earthquakes that would shake the central Mississippi River Valley that winter. Damages were reported as far away as Charleston, South Carolina, and Washington, DC. According to the U.S. Geological Survey, the New Madrid events were the most powerful earthquakes in recorded U.S. history.

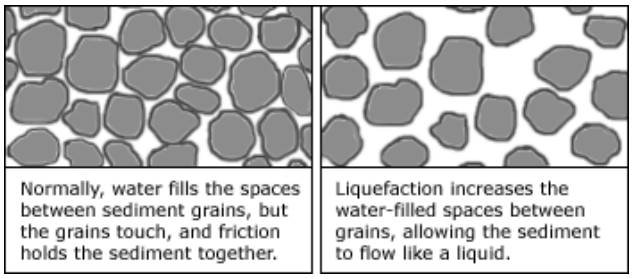
Survivors of the New Madrid earthquakes reported not only intense ground shaking and land movement, as would be expected during an earthquake, but also an unfamiliar phenomenon: water and sand spouting up through fissures, or cracks, in the Earth's surface. In a letter published in *Lorenzo Dow's Journal*, New Madrid resident Eliza Bryan (1) wrote in 1816:

> . . . the surface of hundreds of acres was, from time to time, covered over in various depths by the sand which issued from the fissures, which were made in great numbers all over this country, some of which closed up immediately after they had vomited forth their sand and water. . . 25 June 2003



Structures in the village of Bhuj, India, which was 80 kilometers (50 miles) from the earthquake epicenter, sustained considerable damage. (Image Copyright © James Mori, Research Center for Earthquake Prediction, Disaster Prevention Institute, Kyoto University)

This article is a US Government work and, as such, is in the public domain in the United States of America.



Modern earthquake researchers refer to this expulsion of water and sand from the ground as *earthquake dewatering*, which results from liquefaction. Liquefaction occurs when an earthquake vigorously shakes and compacts water-saturated sediments. As the compaction process displaces the water between the sediment pores, water and sand shoot upward and out of the ground.

"Imagine a cube full of sand and water. If you press it in from both sides (compressing and releasing it, then compressing it again), you build up what's called pore-water pressure," said Martitia Tuttle, geologist and consultant for the U.S. Geological Survey. "It's like shaking a coke can—when the pressure builds up and you release it, the fluid comes shooting to the surface." These fountains of water can sometimes shoot as high as 30 feet into the air, according to Tuttle (2).

Tuttle is part of a team that has been studying liquefaction in the New Madrid region in an effort to identify large prehistoric earthquakes in the geologic record. "Interpreting historic and prehistoric earthquake events involves a lot of uncertainty, due to the lack of data," Tuttle said. "We often don't know precisely where the earthquakes occurred or how big they were." What researchers needed was a modern-day event in a similar environment with which to compare the New Madrid earthquakes.

On January 26, 2001, a magnitude 7.7 earthquake near the village of Bhuj, located in the Kachchh region of northwestern India, provided scientists with just that analogue. Considered one of the two most damaging earthquakes in India's recorded history, the Bhuj earthquake killed about 20,000 people and caused an estimated $3.3 billion in damages.





The Bhuj earthquake struck the Kachchh region of northwestern India on January 26, 2001. The bottom image is a detail of the area indicated in red in the top map. (Images adapted from maps from the University of Texas at Austin General Libraries)

Earthquake Severity Table Adapted from What is Richter Magnitude? (A New Browser Window Will Open.)

Richter Magnitude	Earthquake Effects
Less than 3.5	Recorded but generally not felt
3.5 to 5.4	Often felt but rarely causes damage
Less than 6.0	Slight damage at most to well-constructed buildings; over small regions, can cause major damage to poorly constructed buildings
6.1 to 6.9	Can be destructive in populated regions up to 100 kilometers across
7.0 to 7.9	Major earthquake that can cause serious damage over areas larger than 100 kilometers across
8 or more	Great earthquake that can cause serious damage over areas several hundred kilometers across

According to Tuttle and co-authors (3) of a paper recently published in *Eos*, local residents and survey teams working in the area after the earthquake reported fountains of water and sediments surging from the ground during and immediately following the Bhuj earthquake. The water flow was significant enough to reactivate streams in previously dry river channels.

"The Bhuj earthquake provided an opportunity to study an earthquake that was very similar to the New Madrid event—it was a very large earthquake, and it occurred in an intraplate-like setting," said Tuttle. The New Madrid and Kachchh regions are both located more than 185 miles (300 kilometers) from active plate boundaries.

"Before the Bhuj earthquake, there was a lot of debate in the seismological community about the magnitude of the New Madrid earthquakes, but based on the similarity in intensity between the New Madrid and Bhuj events, there is a growing consensus among scientists that the New

Madrid earthquakes were probably larger than magnitude 7.5," said Tuttle. "The Bhuj earthquake is a modern event that helps us better understand the historic and prehistoric earthquake record in the New Madrid region."

But despite the unique study opportunity presented by the Bhuj earthquake, the area presented the researchers with some grave challenges. First, the Kachchh region of India is remote and difficult to reach. Second, it shares a politically sensitive border with Pakistan. These factors made it difficult for research teams to conduct field studies to verify liquefaction effects or the presence of water in some areas.

Bernard Pinty (4), research scientist at the Institute for Environment and Sustainability in the Joint Research Centre of the European Commission in Ispra, Italy, and colleagues found that water expelled during the earthquake could be detected in imagery from NASA's Multi-angle Imaging SpectroRadiometer (MISR) satellite sensor.

The MISR instrument, which flies aboard NASA's Terra satellite, views the sunlit face of the Earth at nine widely spaced angles simultaneously. As it passes over the Earth, its nine cameras successively view each piece of the planet's surface at a spatial resolution of 300 yards (275 meters).

The change in reflection at different angles provides a means for distinguishing different types of land surface covers. Since bright soils in India's Rann of Kachchh (also known as the Rann of Kutch) reflect most of the sun's near-infrared radiation, and water bodies absorb near-infrared radiation, MISR is able to detect the contrast and indicate where dewatering occurred.

According to Pinty, these features made MISR an ideal tool for studying liquefaction in the Bhuj earthquake. "MISR's multi-angle capability was instrumental in exposing the presence of free water close to the Pakistani border, a region where it is difficult, if not impossible, to take ground measurements," he said.

Most other satellite instruments only look straight down or towards the edge of the Earth. "It would take several more passes for another sensor to capture the entire region that the MISR imagery covers," said Tuttle. "The MISR images enabled us to see a large area both during and immediately after the earthquake, and we could see that dewatering was occurring over a huge region."

Scientists now know that the New Madrid earthquakes were not geologic flukes; similar events have occurred repeatedly in the geologic past. In fact, the central Mississippi Valley experiences more earthquakes than any other region in the United States east of the Rocky Mountains.

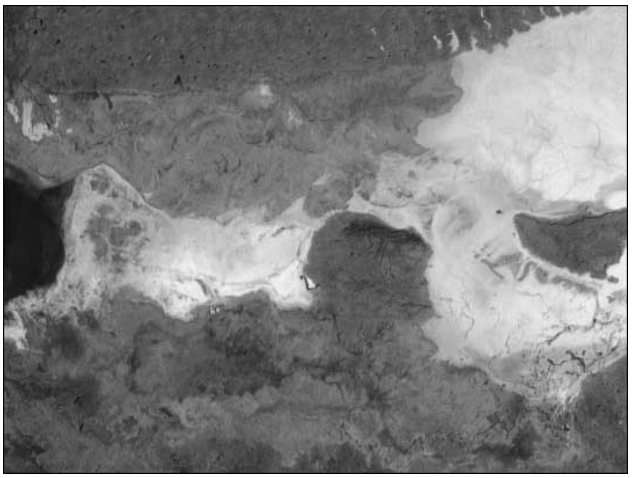
The New Madrid Seismic Zone, which includes parts of Tennessee, Kentucky, Missouri, Arkansas, Illinois, Indiana, and Mississippi, harbors a large liquefaction field. Scientists estimate the probability of a magnitude 6.0 or greater earthquake occurring in the New Madrid Seismic Zone within the next 50 years at 25–40 percent, according to the U.S. Geological Survey. But a similar event would have much more serious consequences today.

In 1811–1812, the central Mississippi Valley was a remote frontier. Today, the region is home to millions of people and includes the metropolitan cities of St. Louis, Missouri, and Memphis, Tennessee. In addition, most buildings in the region were not built to withstand earthquake shaking, as they often are in California and Japan.

Buildings and engineered structures are at much higher risk in areas where liquefaction occurs, due to increased ground motion. "The liquefaction process is extremely damaging to all sorts of engineered structures; it has



These cracks in the ground surface north of Chobari, India were caused by liquefaction induced during the Bhuj earthquake. (Image Copyright © James Mori, Research Center for Earthquake Prediction, Disaster Prevention Institute, Kyoto University)



This false-color MISR image was acquired after the Bhuj earthquake, on January 31, 2001. The image shows numerous areas where groundwater flowed up to the surface, including within the Rann of Kachchh, as well as near the Indo-Pakistani border. (Image courtesy of NASA/GSFC/LaRC/JPL, MISR Team) Click here for more information.

caused major destruction in both Anchorage and San Francisco," said Pinty.

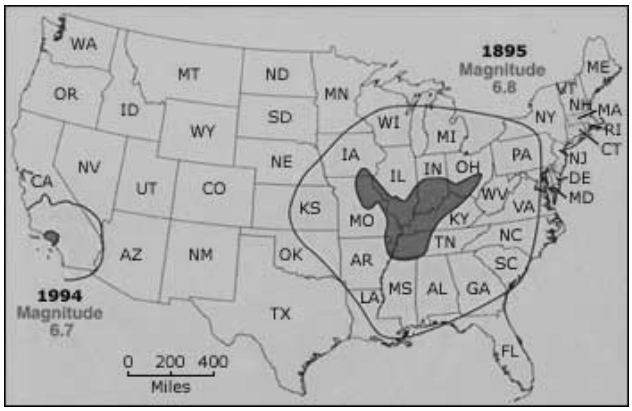
"The ground failure that resulted from liquefaction during the New Madrid earthquakes was severe. We're talking about vertical displacement of 3 to 6 feet (1 to 2 meters), and lateral displacement up to 33 feet (10 meters)," said Tuttle. "A recurrence of that type of event would have severe consequences for engineered structures."

According to Tuttle, in 1988 a magnitude 5.9 earthquake in Quebec, Canada, produced liquefaction. "Basements cracked, septic fields were disrupted, and people described water and sand shooting into their basements, out of their toilets, and into their bathtubs," she said. "And that was just a moderate-sized earthquake, not a big one."

MISR imagery, which is archived at the Langley Research Center DAAC, promises to be a boon to earthquake researchers seeking to minimize hazard risks.



The MISR instrument views the sunlit Earth simultaneously at nine widely spaced angles, providing ongoing global coverage at high spatial detail. (Image courtesy of NASA)



Although earthquakes in the central and eastern United States are less frequent than in the western United States, they affect much larger areas. This is shown by two areas affected by earthquakes of similar magnitude—the 1895 Charleston, Missouri, earthquake in the New Madrid Seismic Zone and the 1994 Northridge, California, earthquake. Red indicates regions of minor to major structural damage; yellow indicates areas where shaking was felt, but little or no damage to objects occurred. (Image courtesy of the U.S. Geological Survey)

"The interesting thing is that this project started as an 'after hours' sort of activity," said Pinty. "But it soon acquired its own momentum, giving us results that are of significant relevance to earthquake study applications. Our findings revealed that MISR can detect water and moist conditions on terrestrial surfaces, even under unfavorable spectral conditions."

"If we study modern earthquakes that produce liquefaction, we can better interpret the geologic record of liquefaction during past events. This helps us anticipate what is likely to happen in the future so that we can make informed decisions about reducing and mitigating hazards," said Tuttle.

For more information, visit the Langley Atmospheric Sciences Data Center DAAC. (A new browser window will open.)

"It's one of those things where people tend to think—if it hasn't happened during my lifetime, then it can't happen here," said Tuttle. "But the liquefaction field in the New Madrid region is very large. We're talking about a huge earthquake that could have a significant impact on society."

BIBLIOGRAPHY

1. Bryan, E. (1849). *New Madrid, Territory of Missouri*, March 22, 1816. In *Lorenzo Dow's Journal*. Published by Joshua Martin: 344–346. Quoted by The Virtual Times, The New Madrid Earthquake. Accessed June 5, 2003.
2. Tuttle, M.P. (2001). The use of liquefaction features in paleoseismology: Lessons learned in the New Madrid seismic zone, central United States. *Journal of Seismology*. **5**: 361–380.
3. Tuttle, M.P. et al. (2002). Observations and comparisons of liquefaction features and related effects induced by the Bhuj earthquake. *Earthquake Spectra*. **18**(Supp. A): 79–100.
4. Pinty, B. et al. (2003). Observing earthquake-related dewatering using MISR/Terra satellite data. *EOS, Transactions, American Geophysical Union*. **84**(5): 37–48.

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STORAGE COEFFICIENT

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DEFINITIONS

A coefficient is a mathematical quantity that relates two or more variables in an equation describing some physical process. In equations describing the flow of fluids in a porous medium (e.g., groundwater in an aquifer), the **storage coefficient** is the quantity that relates the change in fluid potential (i.e., hydraulic head) in the

aquifer to the change in the amount of water stored in the aquifer at a given point. In practical terms, the storage coefficient tells us the volume of water that can be removed from an aquifer for a given drop in hydraulic head.

There are three storage coefficients used in groundwater flow equations (the units of each are given in [brackets] following each definition):

Specific Storage (S_s) is the volume of water removed from a unit volume of a confined aquifer for a unit drop in hydraulic head [L^{-1}].

Storativity (S) is the volume of water removed from a unit area of an aquifer for a unit drop in hydraulic head; in confined aquifers, it is equal to the specific storage times the thickness of the aquifer, in unconfined aquifers, it is equal to the specific storage times the thickness of the aquifer plus the **specific yield** [–].

Specific Yield (S_y) is the volume of water removed from a unit volume of an unconfined aquifer for a unit drop in water level; this quantity is also defined as the volume of water that will drain by gravity from a saturated unit volume of an aquifer and is equivalent to the effective porosity [–].

Specific Storage (S_s)

The main equation that governs the flow of a fluid in a porous medium is given by

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} = S_s \frac{\partial h}{\partial t} \tag{1}$$

where q = specific discharge (i.e., groundwater flow) in the x, y, or z direction [$L \cdot t^{-1}$]
h = hydraulic head [L]
t = time [t]
x, y, z = lengths in the principal directions in our coordinate systems [L]
S_s = specific storage [L^{-1}]

Darcy's law

$$q = K\frac{dh}{dl} \tag{2}$$

where K = hydraulic conductivity [$L \cdot t^{-1}$]
dh/dl = hydraulic gradient, or change in head with length [–]

can be substituted for q to get the expanded version of the flow equation:

$$\frac{\partial\left(K_x \frac{\partial h}{\partial x}\right)}{\partial x} + \frac{\partial\left(K_y \frac{\partial h}{\partial y}\right)}{\partial y} + \frac{\partial\left(K_z \frac{\partial h}{\partial z}\right)}{\partial z} = S_s \frac{\partial h}{\partial t} \tag{3}$$

Equations 1 and 3 are specific versions of the **continuity** (or **conservation of mass) equation**,

$$I - O = \Delta S \tag{4}$$

where I = flux into a volume of a system [$L^3 \cdot t^{-1}$]
O = flux out of a volume of a system [$L^3 \cdot t^{-1}$]
ΔS = change in the amount stored in that same volume of the system [$L^3 \cdot t^{-1}$]

The left side of Eq. 3 corresponds to the left side of the continuity equation and describes the divergence of flux at a point in the aquifer. In other words, it describes the groundwater flow vector resolved into x, y, and z components (see Fig. 1).

The right side of Eq. 3 corresponds to the right side of the continuity equation and describes the change in storage at the given point in the aquifer. The term $\partial h/\partial t$ refers to the change in hydraulic head, with respect to time, at the same point in the aquifer. The term S_s is the **specific storage**, and it relates the changes in head in the aquifer to the change in the amount of water stored in the aquifer at a certain point. In other words, it is a quantity that tells us the volume of water that can be removed from a unit volume of a confined aquifer for a unit drop in head.

CONFINED AQUIFERS—A CONCEPTUAL UNDERSTANDING

Consider a confined aquifer that consists of a layer of sand overlain by an impermeable layer of clay that acts as a confining layer. If a well is drilled into the aquifer and water is pumped from the well, the heads around the well will lower and create a cone of depression in the potentiometric surface (Fig. 2). The more water that is pumped from the well, the larger the cone of depression. In the example shown in Fig. 2, the pumping well has removed a volume of water (represented by the volume in the barrel), and in response, the water levels in

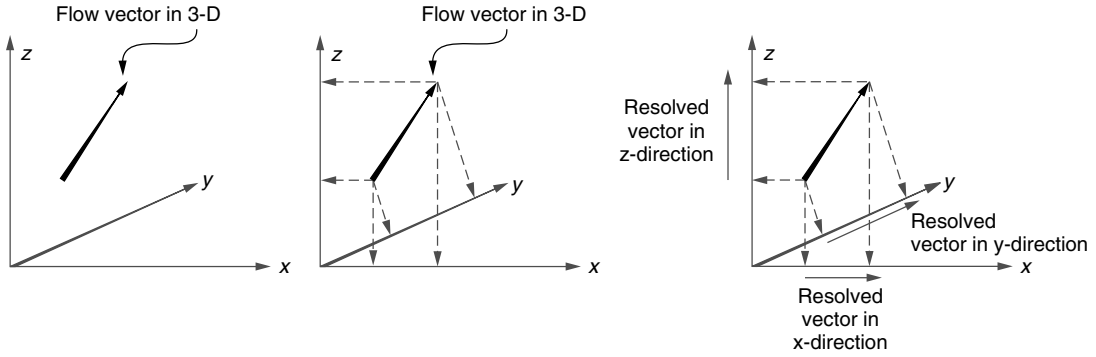


Figure 1. Flow vector resolved into component vectors in three dimensions.

the well and in the surrounding aquifer have dropped. However, the saturated thickness of the aquifer itself has not changed (i.e., the aquifer is still full to the base of the confining layer). What is the source of this water? The conceptual answer deals with elastic deformation and compressibility of the aquifer materials and the water.

This aquifer is made up of sand grains and pore spaces that are full of water. If there is no confining layer and the aquifer is simply recharged by water infiltrating from above, the pore spaces are full of water, and the pore fluid pressure is equal to atmospheric pressure plus the overlying column of water. In this case, the volume of water in the pore space is equal to the volume of the pore space.

However, if the aquifer is confined and an additional component of pressure is added to the water, that pressure will force a greater volume of water into the pores of the sand. It does this by compressing the sand grains slightly, pushing the sand grains around so that pore volume is increased, and compressing the water itself slightly. Increasing the pore fluid pressure causes the aquifer to undergo **elastic** (i.e., recoverable) **deformation**, so that a subsequent decrease in fluid pressure will cause an associated decrease in volume (Fig. 3).

This is the source of the additional volume of water. Pumping water from the confined aquifer lowers the excess fluid pressure (i.e., the pressure head above the top of the aquifer), causing the aquifer to 'relax' and yield water that is stored by the excess pressure.

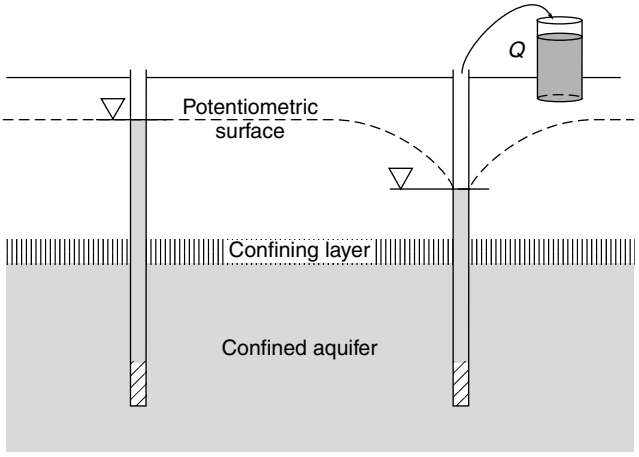


Figure 2. Pumping well in a confined aquifer.

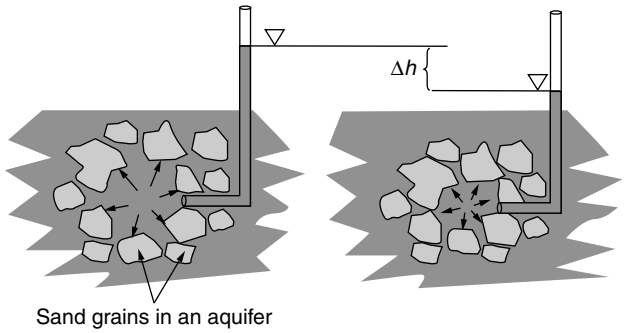


Figure 3. Elastic deformation in a sand aquifer.

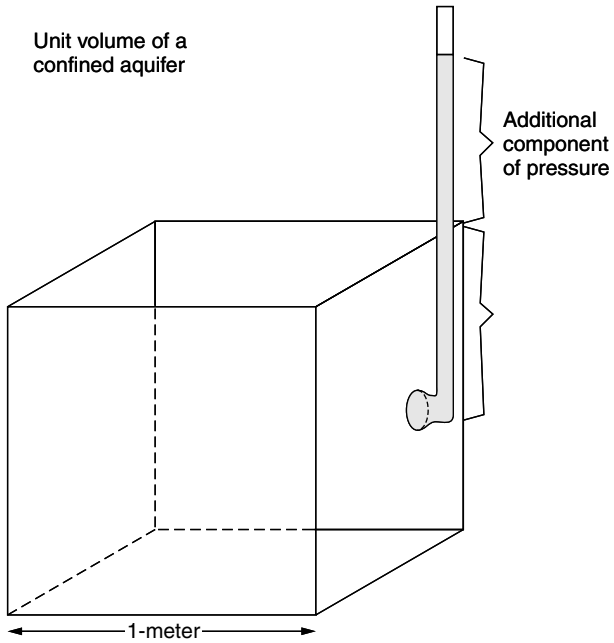


Figure 4. Unit volume of a confined aquifer.

CONFINED AQUIFERS—A MATHEMATICAL UNDERSTANDING

Consider a unit volume of a confined aquifer. This unit volume is saturated with water, and the water has an additional component of pressure that would cause the water level in a manometer to rise above the top of the cube (Fig. 4). If a volume of water is removed from the cube, it will reduce the additional component of pressure and lower the head in the cube. Removing more water will cause more head loss; less water will cause less head loss. Therefore, there is a specific volume of water that, if removed, will cause a unit drop in head. This volume of water that results in a unit drop in head in the unit volume of aquifer is the **specific storage**.

The specific storage is also called the **elastic storage coefficient**; it deals only with the amount of water removed from elastic storage. The specific storage is a function of the compressibility of the aquifer matrix (i.e., the material that makes up the aquifer) and the compressibility of the water and is strictly defined as

$$S_s = \rho_w g(\alpha + n\beta) \tag{5}$$

where ρ_w = density of water [M/L^3]
g = gravitational constant [L/t^2]
α = compressibility of the aquifer matrix [1/M/Lt^2]
n = porosity [–]
β = compressibility of water [1/M/Lt^2]

STORATIVITY IN CONFINED AQUIFERS

The specific storage actually refers to an infinitesimal point in the aquifer. However, in real aquifers, the thickness of the aquifer influences how much water the aquifer will yield; a thicker aquifer will transmit and yield more water than a thinner aquifer. Multiplying the specific storage by the saturated thickness of the aquifer results in **storativity** (S):

$$S = S_s b \tag{6}$$

where b = saturated thickness of the aquifer [L].

In other words, the storativity describes the volume of water removed from a unit *area* of aquifer for a unit drop in head.

UNCONFINED AQUIFERS AND SPECIFIC YIELD

In a confined aquifer, all the water pumped out through a well is provided by the release of water from elastic storage. In an unconfined aquifer, the same thing occurs—the changes in head result in a release of water from elastic storage in the aquifer. However, in an unconfined aquifer, the pumping well is dewatering a section of the aquifer (Fig. 5), and this part of the aquifer's response adds an additional volume of water to the volume withdrawn from elastic storage.

This additional volume of water is released from the pore spaces and is due to the **specific yield** of the aquifer. Specific yield is the volume of water that drains from a rock under the force of gravity and is directly related to the effective porosity of the aquifer matrix. The volume of water released from a unit volume of aquifer due to dewatering of the aquifer is therefore the unit volume times the specific yield.

So, in unconfined aquifers, the volume of water released from a unit volume of aquifer is a function of both the specific yield (i.e., the water removed from the pore space) and the specific storage (the water released from elastic storage in the aquifer). Therefore, in an unconfined aquifer, the storativity of the aquifer is the sum of the specific yield and the thickness times the specific storage.

$$S = S_y + bS_s \tag{7}$$

However, the magnitudes of these parameters are drastically different: specific yield values in an aquifer generally range from 1% to 50%, or 0.01 to 0.5; specific storage values generally range from 1×10^{-3} to 1×10^{-6}, or 0.001 to 0.000001, which means that, in an unconfined aquifer, the volume of water provided by release from elastic storage is orders of magnitude less than that provided by dewatering the pores; so the specific storage is generally considered negligible, and unconfined storativity is a function only of the specific yield.

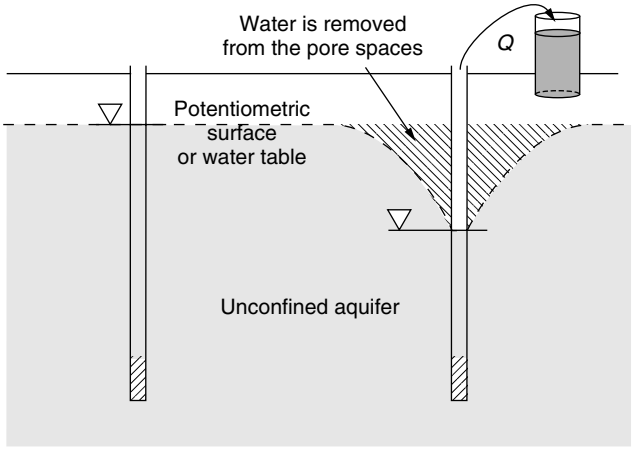


Figure 5. Pumping well in an unconfined aquifer.

QANATS: AN INGENIOUS SUSTAINABLE GROUNDWATER RESOURCE SYSTEM

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A qanat system consists of an underground tunnel that conveys water by gravity from highland aquifers to the ground surface at lower elevations. Blended with ingenuity, its purpose is simply to collect and bring underground water to the surface for use. Qanat, invented and originated in Iran more than 2700 years ago, is considered a hydraulic engineering system of an Old World era providing water to settlements since its invention. The overwhelming climate of Iran is arid and semiarid; two thirds of the country area in central, southern, and eastern parts receive an average of about 150 mm of rainfall annually. Yet, Iran is considered a farming country where diverse crops are grown. This remarkable achievement in agricultural development of arid lands has materialized partly by building qanats to tap underground water in regions where surface water is lacking or unreliable during seasons of high water demand. Numerous urban and rural qanat-watered settlements are vivid examples that not all civilizations were rooted by the sides of rivers. Qanats have helped to transform barren lands into productive assets. Thanks to its simple and efficient technique, the idea behind this sustainable water resource system was passed from one generation to the next and traversed geographic boundaries. Qanat's use is not confined to Iran and has been adopted in many regions across the world.

QANAT DESCRIPTION

Britannica characterizes a qanat as, "A qanat taps underground mountain water sources trapped in and beneath the upper reaches of alluvial fans and channels the water downhill through a series of tunnels, often several kilometres long, to the places where it is needed for irrigation and domestic use ...." The dictionary of

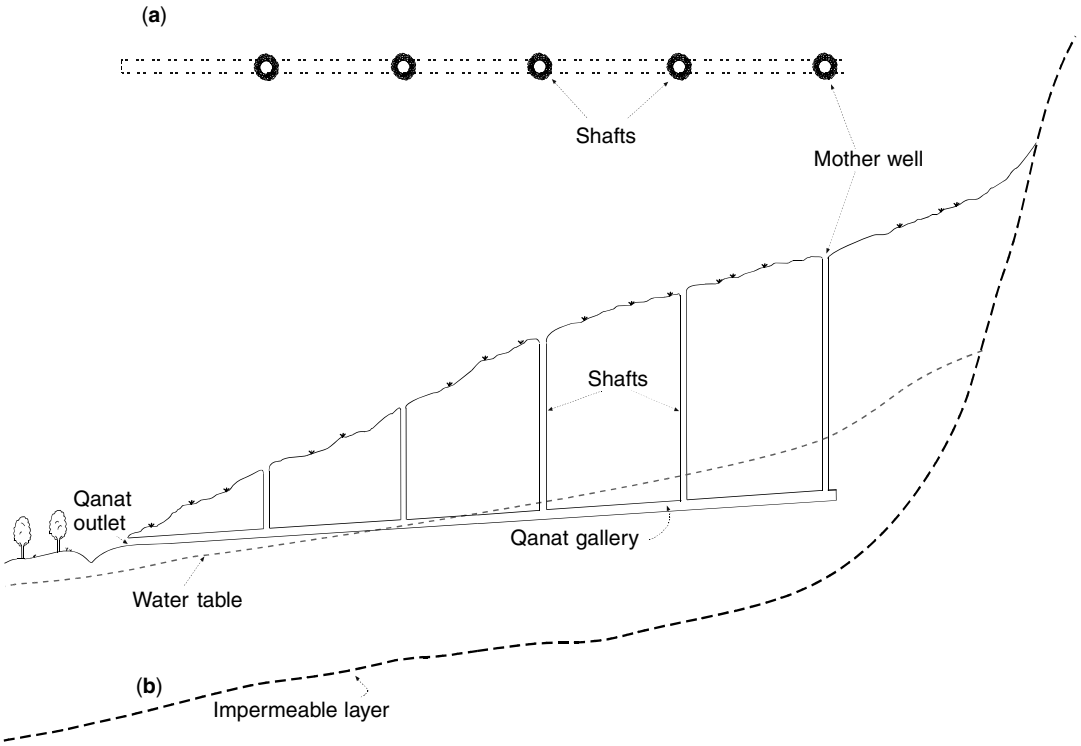


Figure 1. Schematic plan (**a**) and cross section (**b**) of a qanat system.

Islamic Architecture defines qanat as a "subterranean canal system usually used to bring water some distance from a river or mountains." More technically, Lightfoot (1) describes a qanat as "a form of subterranean aqueduct, or subsurface canal, engineered to collect groundwater and direct it through a gently sloping underground conduit to surface canals which provide water to agricultural fields."

As shown in Fig. 1, a qanat consists of a gently sloped underground tunnel, or gallery, penetrating the upland aquifer at one end and appearing in the ground surface at the other end. The gallery, is also vertically connected to the ground by several wells, or shafts, dug along its length, often at 20–30 m to a maximum of 100 m intervals, providing ventilation and access during construction and maintenance. Put differently, a qanat consists of a series of vertical shafts in sloping ground, inter-connected at the bottom by a tunnel with a gradient flatter than that of the ground. The excavated soil is piled up around the entrance of the wells to give some protection in times of storm surface runoff. The first shaft, called the mother well or main shaft, is usually sunk into the alluvial fan to a level below the groundwater table. The line of qanat wells looks like anthills in a distinctive plan view. The typical cross section of a qanat gallery is 1.5 m high and about 1 m wide, which is just sufficient to allow men and boys to do the digging and cleaning.

Qanats can be classified into hill and river-based. Hill qanats have their main shafts based in the aquifers located in hill slopes. This type of qanat is not very long. If this type of qanat taps a deep aquifer, it will enjoy a relatively constant discharge. A river-based qanat is normally recharged from a seasonal river, stretching over a long distance where the tunnel meets the ground surface.

Other terms for qanat, pronounced *kanat*, as it is called in different parts of the world, are karez (e.g., in Afghanistan and eastern Iran), foggora (e.g., in Algeria), hattara (e.g., in Morrocco), and falaj (e.g., in Oman).

HISTORY AND GEOGRAPHIC EXTENT OF QANATS

Written records and recent excavations prove that qanats first appeared in ancient Iran (then Persia). Wulff (2) describes the origin of qanat: "As early as the seventh century B.C., the Assyrian king Sargon II reported that during a campaign in Persia he had found an underground system for tapping water in operation near Lake Urmia. His son, King Sennacherib, applied the secret of using underground conduits in building an irrigation system around Nineveh, and he constructed a qanat on the Persian model to supply water for the city of Arbela." The earliest reports of qanats indicated that the water for the city of Ula northwest of Lake Urmia, located in northwest of Iran, was provided by qanats some 700 B.C. (3). English (4) reports that, based on early mining, the mountains of Kurdistan in western Iran, eastern Turkey, and northern Iraq were the birthplace of the qanat more than 2500 years ago.

The technique was then widely diffused during the expansion of Achaemenid dynasty, ruling the Persian Empire, beginning sometime in the fifth century B.C. Qanats were constructed in Mesopotamia to the shores of the Mediterranean to the west, in Egypt and the Arabian Peninsula to the south, and in Afghanistan,

Central Asia, and western China to the east. The Arabs introduced the idea further to the west during the second diffusion phase in the eighth century A.D. The greatest developments of qanat technology outside the Persian core area are in southern Morocco (Marrakesh and the Tafilalet) and southern Algeria (5). Wulff (2) reported the excavation of several particularly interesting qanats constructed by Arab rulers of early medieval times in the Middle East. These include a small qanat built by the caliph of Damascus to supply water for his palace in 728 A.D. A century later, presumably with the aid of Persian engineers, the caliph Mutawakkil in Iraq constructed a qanat that brought water to his residence at Samarra from the upper Tigris River 300 miles away.

Qanats are reported to exist in Spain, Sicily, Cyprus, the Canary Islands, and in South American countries such as Mexico, Peru, and Chile. The Madrid qanat system in Spain, bringing water for urban use, still functions. The qanat systems of Tehuacan and Parras in Mexico are believed of Spanish origin, but those of Parras (Coahuila) and Pica (Chile) may be pre-Columbian (6). English (5) and Beekman et al. (7) discuss scenarios of the diffusion of qanat technology throughout the world.

CONSTRUCTING A QANAT

The laborious construction of a new qanat is a task to be engineered by an expert, who usually heads a team of diggers. The diggers, called *muqannis*, are responsible for building and repairing qanats. The expert must decide on a number of key issues prior to qanat construction: the site of the mother well and the alignment and the slope of the underground gallery. In his work, the expert uses simple instruments such as a long rope and a level. As the mother well of a qanat is usually dug in an alluvial fan at the foot of a mountain or hillside, the expert watches for signs of seepage on the ground, slight variations in the vegetation, and available groundwater. Once the site is chosen, one or sometimes more trial wells are sunk. The muqannis then start digging the trial well, normally 1 m in diameter. They use a windlass at the top and haul up the soil excavated by their teammates. They continue the digging and spoil the material around the rim of the well until the water table is struck. The expert then should determine whether the aquifer water has acceptable water yield. If so, he measures the distance from the mother well to the qanat outlet, where water is planned for use. Once the general alignment of the qanat is determined, the expert calculates the slope of the qanat gallery. This slope must allow the water to flow, yet prevent erosion of the bottom and walls of the gallery. The slope for short qanats may run from 0.5 to 2 in 1000, whereas longer qanats usually have gentler slopes. In steep land, the slope of the gallery is maintained in a looping course. The work then proceeds from the outlet of qanat by excavating the tunnel back toward the mother well. Vertical shafts at a distance of 30 m, or so, are dug to provide ventilation and access. For shafts deeper than 100 m, the muqannis set up another windlass halfway within the shaft for a two-stage haul up of spoil. The muqannis maintain a straight course by sighting along a pair of burning oil lamps. The task requires great skill and endurance. Figure 2 shows a top view of qanat during construction.



Figure 2. A top view of a qanat during construction.

Muqannis may encounter a number of dangers in their work. Soft soil in the tunnel can cause collapse of the roof. In such cases, the tunnel cross section is braced with baked clay collars to control cave-ins (Fig. 3). Another danger is air low in oxygen. Any change in the burning of the illuminating oil lamps is an indication of such danger. And last, but not least, is the hazard during the breakthrough into the mother well, which must be emptied.



Figure 3. Cross section of a qanat gallery protected by a lining.

Muqannis are highly respected for their courage, hard work, and know-how. They are paid well for their work, and older muqannis are considered blessed or lucky.

QANATS AND WATER REGULATIONS

In Iran, the allotment of water delivered by qanats is regulated by certain laws, which are rooted in a traditional system of water rights. Normally a water master or bailiff, appointed by a qanat owner(s), supervises the water distribution according to each farmer's time share. As Wulff (2) has noted, "the bailiff is guided by an allocation system that has been fixed for hundreds of years. For instance, three hamlets in a region west of Iran, still receive the shares that were allotted to them in the 17th century by the civil engineer in the reign of Shah Abbass. The hamlets of Dastgerd and Parvar in central Iran are entitled to eight shares apiece. These allocations are built into outlets from the qanat distribution basin." English (4) provides a detailed overview of qanat ownership, the complex water distribution system, and, through some examples, how fragmentation of qanat water rights has taken place. He makes a note of strict and unforgiving adherence to communal methods of water rotation and upkeep of the water supply system serving to maintain the social cohesion of qanat-watered villages.

QANATS: COSTLY AND TIME-CONSUMING

Qanats are labor-intensive and time-consuming to build. Both the cost and time to build a new qanat varies with topography, depth of the water table, underground soil type, length of the qanat, type of ownership, availability and experience of muqannis, and local conditions. Thus, reports differ in figures provided for the cost and duration of construction of qanats.

Noting that qanats are long-lasting water resources systems if properly maintained, Wulff (2) believes that the agricultural production sustained by qanat water repays the investment in construction and maintenance by 10% to 25% depending on the size of the qanat, the water yield, and the crop type. Wulff's assessment of the cost in the 1960s showed that a 6-mile long qanat required US$13,500 to US$34,000 to build. The cost runs to about $90,000 for a qanat 10 to 15 miles long.

English (8), on the other hand, reported that it took 27 years to construct a 1-km qanat in Kerman, in central Iran, with a mother well 45 meter deep, due to three changes in ownership. Another 3-km qanat with two mother wells, 50 and 55 m deep, and a bifurcated tunnel took 17 years to build. The costs of these two qanats, respectively, were approximately $10,000 to $11,000 per km in the 1960s. As another example, the cost of constructing a 40-km long qanat near the city of Kerman with a mother well 90 m deep was roughly $213,000 when completed in 1950 (4). Such expenses adjusted for inflation can be raised only through government subsidies or large corporations in modern Iran. Due to high construction investment, qanat owners often try to increase the yield. They may extend branches from the main tunnel to reach additional aquifers or excavate the floor of the existing tunnel to tap water at a deeper level (2).

Note that, although agricultural production cannot repay the investment and maintenance costs of new qanats in some regions, existing qanats are still the second water supply system in volume providing for drinking and domestic use in Iran. Keeping the qanat cost and the enormous building effort in mind, individual farmers are unwilling and unable to fund the construction of new qanats or even maintain old ones. Thus, farmers have turned to drilled wells as the more affordable alternative.

QANAT VERSUS DRILLED WELL

People in arid regions rely on underground aquifers for their water supply. The aquifers can be tapped by a qanat, or alternatively by a drilled well, and the water is directed to an area where it is consumed. The volume of water produced by a qanat depends upon several factors: extent, type, yield, and recharge rate and area of the aquifer. Comparing a drilled well with a qanat system, there are advantages for each. The following compare the two systems:

- As history proves it, qanats are sustainable renewable water resource systems. However, they cannot meet today's increasing demand. Wells are the alternative at the expense of inducing negative water balance in the aquifers they exploit.
- Qanats need no extra energy to harvest water, whereas wells need diesel or electric power to bring water to the surface.
- Qanats can be built and maintained using low-technology tools and material locally available.
- Qanats can be used as a passive cooling system in conjunction with a wind tower (9).
- Qanats reinforce social cooperation, an important issue in traditional societies.
- Wells are dug in a short time, whereas qanat construction is slow, investment-intensive, and quite time-consuming. However, technology can be put to work to accelerate qanat construction by cutting the time and the cost.
- Only a portion of a qanat's water is used during nonirrigation season, unless conserved by other means. During periods of low water use in fall and winter, watertight gates can seal off the qanat outlet damming up the water. In spring and summer, night flow may be stored in small ponds for daytime use (10). A well pump can be switched off when water is not needed.
- A typical qanat's discharge is less than that of pumped wells. The latter are favored to meet growing demands, though, in a nonsustainable manner.

Experts in Iran now suggest an integrated approach of conjunctive use of qanats and wells. The location of a well must be optimized with respect to an existing qanat recharge area.

STATISTICS OF QANATS

No one knows how many qanats were ever built, how many are still in operation, and how much water they deliver. Available reports vary in numbers, albeit they have collected qanat statistics in different times. It is estimated that, as of the 1960s, between 40,000 to 50,000 qanats had been built in Iran during its history, of which some 27,000 running qanats were still used (11). Wulff (2) reported that some 22000 qanats in Iran, totaling 170,000 miles of underground conduits built by manual labor, had a total yield of 19,500 cubic feet of water per second, which amounts to 17 billion cubic meters of water annually. Two recent reports prepared in Iran put the total number of qanats, as of 1995, between 25,000 and 33,000, but it is unclear whether all are currently used. The reports, however, agree on the total volume of water provided by qanats at around 9 billion cubic meters. Having accepted this figure and the figure given by Wulff in 1968, an alarming decline of about 50% in water yield of qanats is inferred, which must be partly due to an excessive number of wells causing underground water tables to drop and affect qanat yield. The declining groundwater tables and increasing number of abandoned qanats have shrunk the share of water supplied by qanats to less than 10% of total use.

The discharge of individual qanats varies widely with the location and, in some cases, time of the year. Qanat discharges of a few liters to as much as 1 cubic meter per second have been reported.

There are some unique qanats in Iran described as follows:

1. Vazvan Qanat in Meimeh, Isfahan province, is 1800 m long. At a distance of 600 meter from its outlet, a stone dam has been built to store the water. A total of six gates have been installed at different elevations to control the flow of water, depending on the time and amount needed. This qanat system is essentially an underground dam.
2. The well-known and unique Moun Qanat in Ardestan, Isfahan province, is a twin-gallery qanat system, the only one of its kind reported in the world. The two galleries are independent conduits, about 3 m apart in elevation. A thin impermeable layer is believed to separate the two qanat conduits. The water in the layers is not mixed, as the upper conduit is bent around the shafts. The qanat is about 2 km long, and its total discharge waters 25 ha.
3. Gonabad region, in Khorasan province northeast of Iran, is known for some of the oldest qanats in Iran. Reports indicate that one qanat has a mother shaft with a depth of 140 meters and a length of about 70 kilometers. Another qanat is reported with a 270-m mother well.

BIBLIOGRAPHY

1. Lightfoot, D.R. (1997). QANATS in the Levant: Hydraulic technology at the periphery of early empires. *Technology and Culture* **38**(2): 451.
2. Wulff, H.E. (1968). The qanats of Iran. *Sci. Am.* **April**: 94–105.
3. Laessøe, J. (1951). The irrigation system at Ulhu, 8th century BC. *J. Cuneiform Stud.* **5**: 21–32.
4. English, P.W. (1998). Qanats and lifeworlds in Iranian plateau villages. *Yale F&ES Bull.* **103**: 187–205.
5. English, P.W. (1968). The origin and spread of qanats in the Old World. *Proc. Am. Philos. Soc.* **112**: 170–181.
6. Humlum, J. (1965). Underjordiske vandingskanaler: kareza, qanat, foggara. *Kultergeografi* **16**: 81–132.
7. Beekman, C.S., Weigand, P.S., and Pint, J.J. (1999). Old World irrigation technology in a New World context: qanats in Spanish Colonial Western Mexico. *Antiquity* **73**(279): 440–446.
8. English, P.W. (1966). *City and Village in Iran*. University of Wisconsin Press, Madison, WI.
9. Bahadori, M.N. (1978). Passive cooling systems in Iranian architecture. *Sci. Am.* **February**: 144–154.
10. Beaumont, P. (1989). The qanat: a means of water provision from groundwater sources. In: *Qanat, Kariz, and Khettara, Wishbech*. P. Beaumont, M. Bonine, and K. McLachlan (Eds.). Menas Press, pp. 13–31.
11. Goblot, H. (1979). *Les Qanats: Une Technique d 'Acquisition de l 'Eau*. Mouton, Paris.

LYSIMETERS

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Lysimetry is a measurement technique that employs sampling devices called lysimeters to measure the movement of water and solutes through a porous medium. Lysimeters have most commonly been used to quantify water movement (i.e., drainage) through soil and typically consist of a porous plate surface of varying pore sizes through which water moves from the soil into a collection reservoir.

BRIEF HISTORY OF LYSIMETERS

According to Joffe (1), lysimeter studies were initiated in the late eighteenth century to address the fate of precipitation in soil. Many lysimeter studies then shifted to consider leaching of soil and precipitation-deposited constituents, such as ammonium and sulfur (1). Gradually, lysimeters were adopted to investigate fertilizer losses from agricultural and nonagricultural soil (1).

Early lysimeter research involved greatly disturbed soil profiles, unrepresentative of natural soil properties. Lysimeter tanks were dug and refilled with soil after construction was complete (1). For this reason, the validity of drainage and leaching measurements were severely questioned, as they are today. Nonetheless, many technological and methodological advancements have been made since the late 1700s, but the same fundamental question remains today as it did then: how to measure natural water movement through undisturbed soil?

DRAINAGE LYSIMETERS

Two general types of lysimeters exist for monitoring water and solute fluxes through soil, weighing and nonweighing lysimeters. Weighing lysimeters are large-scale sampling devices typically used for measuring evapotranspiration, drainage, and solute leaching. Inputs and losses of moisture are evaluated on the basis of changes in mass in a containerized column of soil within the lysimeter (2). Weighing lysimeters are expensive, labor-intensive to construct, and usually involve filling the lysimeter by reconstructing a disturbed soil profile (3,4), although large weighing lysimeters that have undisturbed soil columns have been constructed, such as the monolith lysimeters near Coshocton, Ohio. However, nonweighing lysimeters are better suited for less burdensome, replicable field measurements of *in situ* water and solute fluxes.

Nonweighing lysimeters are well adapted to monitoring drainage and leaching from soils. Nonweighing lysimeters, also known as drainage or pan lysimeters, are typically much smaller than weighing lysimeters. An advantage of a nonweighing pan lysimeter is that replicable field measurements can be obtained below undisturbed soil profiles. As a result, site-specific information can be gathered relative to the mass flux of water and leachate concentrations of soluble organic and inorganic chemical species (3). Coupling drainage measurements with solute concentrations provides a means of estimating solute mass fluxes through an undisturbed soil profile.

DRAINAGE MEASUREMENTS USING NONWEIGHING LYSIMETERS

The collection of leachate through the porous surface of a lysimeter depends on two conditions: (a) minimal discontinuities in the flow path of moving water and (b) a driving force for water movement. Maintaining a capillary connection between the soil and the porous surface of the lysimeter is imperative for high-quality results. Neglecting to minimize potential sources of error may cause ponding, preferential, and bypass flow around the lysimeter (3).

Drainage lysimeters have been designed to operate where a variety of forces act on soil water. Drainage and solute fluxes are measured and replicated in the field by some variation of a nonweighing pan lysimeter operating under tension (i.e., tension lysimeters) or tensionless (i.e., zero-tension lysimeters). In soil or any other porous material, the bulk of the water moves in response to gradients in gravitational and/or matric potentials. Zero-tension lysimeters rely on the force of gravity for water movement through the lysimeter's porous plate surface. The effect of a matric potential gradient is created by applying suction to a tension lysimeter to quantify drainage and leaching.

Both types of nonweighing lysimeters have several significant disadvantages. Nonweighing lysimeters are commonly operated after the lysimeter has been filled with soil, similar to weighing lysimeters. As a result, soil horizonation, structure, pore size distributions, and many other physical properties no longer reflect natural soil conditions. Therefore, using a disturbed profile technique for general lysimeter installation may generate biased and uninterpretable results (4).

Kung (6) described another disadvantage of nonweighing lysimeters, in which funnel flow may divert percolating water based on the angle of inclination of coarse textured soil lenses. Lenses, or soil textural discontinuities, may cause water to bypass the lysimeter or channel water directly to it. In either case, results may be erroneous.

Tension or tensionless column lysimeters that have sidewalls extending above the soil surface pose additional challenges (7–9). Impeding runoff, as the design of extended-walled column lysimeters do, unnaturally alters the water status of the contained soil column by permitting ponding during winter months and following intense rainfall. Furthermore, crop management becomes more difficult as the extended sidewalls act as obstacles to plowing, seeding, and cultivating (9).

Zero-tension lysimeters rely on the formation of a saturated soil zone above the porous plate before drainage occurs by gravitational flow, which is an unlikely natural condition in most deep, well-drained and moderately well-drained soils and alters the water content and soil water potential of the rooting zone (7). The prerequisite of saturation above these sampling devices may cause drainage water to bypass the lysimeter (3) and create unnatural matric potential gradients that cause water movement from the saturated zone to the surrounding unsaturated soil matrix (10). Zero-tension lysimeters that have upwardly extended sidewalls (7,8,11) may promote preferential flow down the side of the soil column upon drying (11). In addition, lateral flow that normally occurs under field conditions would be restricted in containerized, column lysimeters with fine textured, clayey horizons (12).

Fixed-tension lysimeters improve the flow patterns around and through the lysimeter's porous plate surface. Stored water often moves through soil under some tension. Applying tension (i.e., suction or vacuum) to a porous surface produces more natural flow patterns through a soil profile than relying on gravity to generate drainage. However, fixed-tension lysimeters typically experience vacuum depletion shortly after vacuum application unless constant vacuum is maintained. Fixed-tension lysimeters do not reproduce natural soil water potential variations that can occur during a relatively short period of time. The transient nature of soil water potentials influences unsaturated hydraulic conductivity and thus alters drainage fluxes.

RECENT USAGE OF NONWEIGHING DRAINAGE LYSIMETERS

Drainage lysimeters, both tension and tensionless, have been frequently employed in numerous studies to accomplish a variety of research goals. Zero-tension lysimeters have been used to study salt and water movement and leaching losses under conventional and no-tillage maize [*Zea mays*; (13)]; collect mobile colloids transporting organic and heavy metal compounds (11); investigate nitrate (NO_3^-) and pesticide leaching from removed, but intact, soil columns (12,14); monitor the fate and cycling of ^{15}N on revegetated mine spoils in containerized, soil

mini-columns (7); determine the effect of irrigation on the nitrate leaching potential of agroecosystems (4); measure nitrate leaching from maize agroecosystems under zero, intermediate, and high fertilizer N rates (3); and elucidate the effect of various cropping systems on solute leaching and ^{15}N migration (8,9).

Jemison and Fox (10) evaluated the collection efficiency of zero-tension lysimeters. A bromide (Br^-) tracer method was used to determine an overall mean collection efficiency, based on lysimeter recovery of applied Br^-, of 52%, ranging from 13–92%, and high plot-to-plot variability of volumes were collected. Cumulative observed drainage, uncorrected for Br^- collection efficiency, measured from zero-tension lysimeters for 3 years, was consistently lower than LEACHM-predicted drainage (10). LEACHM (Leaching Estimation And Chemistry Model) is a complex computer model capable of simulating water infiltration and redistribution, solute transport and distribution in the soil, and tracer ion uptake by plants (15).

The use of fixed-tension drainage lysimeters has been somewhat more limited. Karnok and Kucharski (16) described the use of an underground rhizotron-lysimeter facility constructed to monitor root growth, evapotranspiration, and leaching under turf grass cover. Leaching losses from observation cells were collected under a continuous, fixed tension of −33.3 kpa. Dolan et al. (17) used wedge-shaped, fixed-tension microlysimeters to ascertain the effect of nitrogen placement on nitrate leaching below maize monoculture grown in sandy soil. Adams et al. (18) evaluated nitrate leaching from poultry litter and manure-amended pasture soil using pan lysimeters at a fixed tension of ~ -10 kpa. Despite several disadvantages, fixed-tension and tensionless nonweighing lysimeters have many potential uses and applications.

EQUILIBRIUM-TENSION LYSIMETERS

Equilibrium-tension lysimetry is an innovative and improved nonweighing drainage lysimeter technique that allows applied-lysimeter suction to mimic the surrounding bulk soil matric potential fluctuations; thus it minimizes the potential for bypass flow and preserves natural drainage patterns (19). A heat dissipation sensor (19,20) is used to monitor the bulk-soil matric potential, and suction applied to the lysimeters is varied as the bulk-soil matric potential varies. Lysimeter suction was originally set manually every several days (19), but a recently developed automated vacuum system maintains equilibrium between applied-lysimeter suction and bulk-soil matric potential fluctuations within seconds (21).

The use of equilibrium-tension lysimeters is relatively new and even more limited compared to the other types of nonweighing drainage lysimeters (Fig. 1). Equilibrium-tension lysimeters have been used to quantify drainage losses for a multiyear period in a water balance study of a restored prairie and maize agroecosystems in southern Wisconsin (22). At the same study site in southern Wisconsin, equilibrium-tension lysimeters have been used to quantify multiple years of nitrogen and carbon (23,24) and soluble phosphorus fluxes (25) in drainage water from below the root zones of a restored prairie and maize agroecosystems. Equilibrium-tension lysimeters have also been used to quantify heavy metal and antibiotic leaching from the root zone of tall fescue (*Festuca arundinacea*) amended with poultry litter in northwest Arkansas (unpublished data).

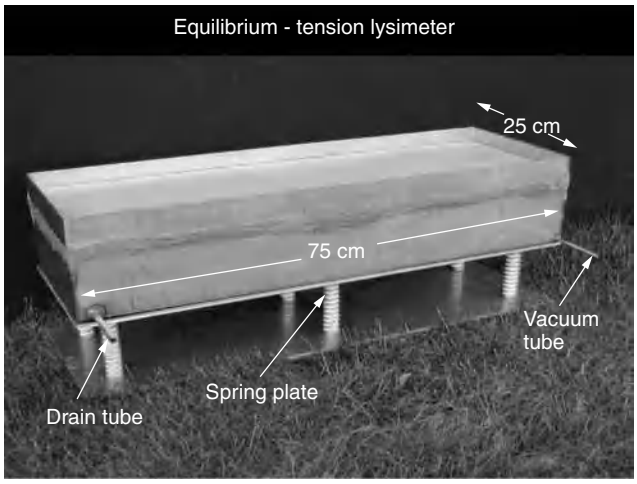


Figure 1. Stainless steel equilibrium-tension lysimeter (ETL) for measuring drainage and solute leaching below an undisturbed soil column.



Figure 2. Backhoe digging trench for lysimeter installation.



Figure 3. Rectangular cavity excavated in sidewall of the trench with nearly completed lysimeter installation.



Figure 4. Complete lysimeter installation with cavity protected from damage upon backfilling with treat plywood.



Figure 5. Soil surface following lysimeter installation and trench backfilling.

GENERAL TENSION-LYSIMETER INSTALLATION AND SAMPLING PROCEDURES

For the most representative results in a field setting, nonweighing drainage lysimeters are typically installed below an undisturbed soil column. A trench is dug by hand or with a backhoe, then a small cavity that extends into the plot or measurement area is excavated in the long sidewall of the trench (Fig. 2). The lysimeter is forced upward against the base of the undisturbed soil column. Some apparatus (e.g., a spring plate, shim, or screw jack) is installed below the lysimeter to provide the necessary upward force to maintain the capillary connection between the lysimeter's porous plate surface and the soil above (Fig. 3). Once the cavity is outfitted with the lysimeter, the trench can either be left open and accessible or completely backfilled. If the trench will be backfilled, tube extensions that extend upward out of the soil can be connected to the drain and vacuum tubes attached to the lysimeter. The lysimeter cavity itself is typically left open but protected with plywood from damage during backfilling (Fig. 4). The trench is backfilled by adding soil in the opposite order in which it was removed and is revegetated, if necessary, so that only the tube extensions and heat dissipation sensor wires if used, are visible above the soil surface (Fig. 5).

Water collected in the lysimeter's collection reservoir is typically removed under vacuum. The leachate volume is recorded, and, if necessary, a portion is saved and refrigerated for subsequent chemical analysis.

BIBLIOGRAPHY

1. Joffe, J.S. (1932). Lysimeter studies. I. Moisture percolation through soil profiles. *Soil Sci.* **34**: 123–143.
2. Soil Science Society of America (SSSA). (1996). *Glossary of Soil Science Terms*. Soil Sci. Soc. Am., Madison, WI.
3. Jemison, J.M. and Fox, R.H. (1994). Nitrate leaching from nitrogen-fertilized and manured corn measured with zero-tension pan lysimeters. *J. Environ. Qual.* **23**: 337–343.
4. Martin, E.C., Loudon, T.L., Ritchie, J.T., and Werner, A. (1994). Use of drainage lysimeters to evaluate nitrogen and irrigation management strategies to minimize nitrate leaching in maize production. *Trans. ASAE.* **37**: 79–83.
5. Owens, L.B. (1987). Nitrate leaching losses from monolith lysimeters as influenced by nitrapyrin. *J. Environ. Qual.* **16**: 34–38.
6. Kung, K.J.S. (1993). Laboratory observation of funnel flow mechanism and its influence on solute transport. *J. Environ. Qual.* **22**: 91–102.
7. Reeder, J.D. (1986). A non-weighing lysimeter design for field studies using nitrogen-15. *Soil Sci. Soc. Am. J.* **50**: 1224–1227.
8. Shipitalo, M.J. and Edwards, W.M. (1993). Seasonal patterns of water and chemical movement in tilled and no-till column lysimeters. *Soil Sci. Soc. Am. J.* **57**: 218–223.
9. Moyer, J.W., Saporito, L.S., and Janke, R.R. (1996). Design, construction, and installation of an intact soil core lysimeter. *Agron. J.* **88**: 253–256.
10. Jemison, J.M. and Fox, R.H. (1992). Estimation of zero-tension pan lysimeter collection efficiency. *Soil Sci.* **154**: 85–94.

11. Thompson, M.L. and Scharf, R.L. (1994). An improved zero-tension lysimeter to monitor colloid transport in soils. *J. Environ. Qual.* **23**: 378–383.
12. Bergstrom, L. and Johansson, R. (1991). Leaching of nitrate from monolith lysimeters of different types of agricultural soils. *J. Environ. Qual.* **20**: 801–807.
13. Tyler, D.D. and Thomas, G.W. (1977). Lysimeter measurements of nitrate and chloride losses from soil under conventional and no-tillage corn. *J. Environ. Qual.* **6**: 63–66.
14. Bergstrom, L. (1990). Leaching of chlorsulfuron and metsulfuron methyl in three Swedish soils measured in field lysimeters. *J. Environ. Qual.* **19**: 701–706.
15. Jemison, J.M., Jabro, J.D., and Fox, R.H. (1994). Evaluation of LEACHM: I. Simulation of drainage, bromide leaching, and corn bromide uptake. *Agron. J.* **86**: 843–851.
16. Karnok, K.J. and Kucharski, R.T. (1982). Design and construction of a rhizotron-lysimeter facility at the Ohio State University. *Agron. J.* **74**: 152–156.
17. Dolan, P.W., Lowery, B., Fermanich, K.J., Wollenhaupt, N.C., and McSweeney, K. (1993). Nitrogen placement and leaching in a ridge-tillage system. pp. 176–183. In: *Conference Proceedings on Agricultural Research to Protect Water Quality*. Feb. 21–24, 1993. Minneapolis, MN. Soil Water Conserv. Soc., Ankeny, IA.
18. Adams, P.L. et al. (1994). Poultry litter and manure contributions to nitrate leaching through the vadose zone. *Soil Sci. Soc. Am. J.* **58**: 1206–1211.
19. Brye, K.R., Norman, J.M., Bundy, L.G., and Gower, S.T. (1999). An equilibrium tension lysimeter for measuring drainage through soil. *Soil Sci. Soc. Am. J.* **63**: 536–542.
20. Reece, C.F. (1996). Evaluation of a line heat dissipation sensor for measuring soil matric potential. *Soil Sci. Soc. Am. J.* **60**: 1022–1028.
21. Masarik, K.C., Norman, J.M., Brye, K.R., and Baker, J.M. (2004). An improved automated approach to equilibrium tension lysimeters. *J. Environ. Qual. In Press*.
22. Brye, K.R., Norman, J.M., Bundy, L.G., and Gower, S.T. (2000). Water budget evaluation of prairie and maize ecosystems. *Soil Sci. Soc. Am. J.* **64**: 715–724.
23. Brye, K.R., Norman, J.M., Bundy, L.G., and Gower, S.T. (2001). Nitrogen and carbon leaching in agroecosystems and their role in denitrification potential. *J. Environ. Qual.* **30**: 58–70.
24. Brye, K.R., Gower, S.T., Norman, J.M., and Bundy, L.G. (2002). Carbon budgets for a prairie and agroecosystems: Effects of land use and inter-annual variability. *Ecol. Appl.* **12**: 962–979.
25. Brye, K.R. et al. (2002). Phosphorus leaching under a restored tallgrass prairie and corn agroecosystems. *J. Environ. Qual.* **31**: 769–781.

STEADY-STATE FLOW AQUIFER TESTS

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Groundwater studies are conducted to evaluate the occurrence, availability, and quality of groundwater. There are numerous practical applications like optimum development of groundwater basins, safe withdrawal, groundwater recharge, seepage from canals and reservoirs, and drainage that require knowledge of the hydraulic characteristics of aquifers. Two basic aquifer properties needed to make a quantitative assessment of such applications are transmissivity and storage coefficient which represent, in a general sense, its abilities to transmit and store water, respectively. The other hydraulic properties of an aquifer are hydraulic resistance, leakage factor, and drainage factor. Performing an aquifer test is an effective way of determining these hydraulic properties of aquifers. Steady-state flow aquifer tests are conducted to determine transmissivity, hydraulic conductivity, and hydraulic resistance; more detailed unsteady-state tests are conducted if other hydraulic properties are also to be evaluated. The objective of this article is to discuss steady-state methods of determining aquifer characteristics.

AQUIFER TESTS

The procedure involves pumping water from a well for a certain time and at a certain rate and measuring its effect on the water table in the well and at a number of piezometers installed in the vicinity. When pumping is carried out in a well, the water level in its vicinity is lowered; the extent of lowering at any point is termed the, drawdown. The drawdown is maximum at the well point and reduces gradually with distance from the well, becoming zero at a certain distance termed the radius of influence. This distance varies with the well and depends on the well discharge, formation constants, and the duration of pumping. The lowering of the water level in the well during pumping creates a head difference or hydraulic gradient from the surroundings which causes the flow of water in the well. The hydraulic gradient increases as flow converges toward the well. The rate of flow is same through all the concentric cylindrical surfaces around the well, and the surface area decreases as one approaches the well. The form of the surface resembles a cone, and therefore it is known as the cone of depression, which is the characteristic feature of every pumped well. Its size and shape depend on the discharge, length of pumping, aquifer characteristic, and other factors.

Steady-State and Unsteady-State Flows

Both steady-state and unsteady-state groundwater flow conditions occur in nature and cannot be very distinctly separated. It is a matter of interpretation and choice as to which concept is used for practical utility. Although every phenomenon in nature is transient, it could be considered a series of successive steady-state events.

Steady-state groundwater movement requires that the boundary conditions of flow and aquifer characteristics remain unchanging with time. Even though the aquifer characteristics do not remain constant, they are assumed so for practical purposes. Thus, if a hydraulic disturbance like well pumping is created, even though the process is initially unsteady, eventually it becomes steady with time.

DEFINITION OF AQUIFER PROPERTIES

The transmissivity (T) of an aquifer is the rate of flow under a unit hydraulic gradient through a vertical strip of the aquifer of unit width and extending through the whole saturated thickness of the aquifer. It has the dimensions of length^2/time and, for example, may be expressed in m^2/day. T is the product of the average hydraulic conductivity (k) and the saturated thickness (b) of the aquifer.

Hydraulic conductivity (k) is the proportionality constant k in Darcy's law $v = ki$, where v is the specific discharge or Darcy's velocity (L T^{-1}) and i is the hydraulic gradient (dimensionless), which is the volume of water that will flow through a porous medium in unit time under a unit hydraulic gradient through a unit area measured at right angles to the direction of flow. k is a parameter that depends on both the properties of the porous medium and of the fluid and has units of length/time, for example, m/day.

Saturated thickness (b) is equal to the physical thickness of the aquifer between two confining layers in a confined aquifer. The saturated thickness for unconfined aquifers, equal to the difference between the free water table and the impervious layer, is not constant but varies with pumping.

Coefficient of storage (S) of an aquifer is the volume of water released from or taken into storage per unit surface area of the aquifer per unit change in head. In unconfined aquifers, S is known as the *specific yield* which represents the volume of water released from storage per unit surface area of aquifer per unit decline of the water table. Specific yield is also sometimes called effective porosity or drainable pore space. S is a dimensionless quantity.

Hydraulic resistance (c) is a property of semiconfined aquifers that characterizes the resistance of a water-bearing layer to vertical flow. It is also known as the reciprocal leakage coefficient and is given by b'/k' where b' and k' are the thickness and the hydraulic conductivity, respectively, of a semipervious layer. The dimension of the hydraulic resistance is time and is, for example, expressed in days.

Leakage factor (L) describes the spatial distribution of leakage through one or more semipervious layers into a leaky aquifer or vice versa. It is defined as $L = \sqrt{kbc}$, has the dimension of length, and it may be expressed in meters.

Of these aquifer parameters, transmissivity (T), hydraulic conductivity (k), and hydraulic resistance (c) are the properties that can be determined from steady-state aquifer tests.

STEADY-STATE METHODS OF DETERMINING AQUIFER PARAMETERS

Different well flow theories have been derived based on the consideration of a continuity equation in cylindrical or spherical coordinates, well depth, the fully or partially penetrating nature of wells; steady-state or unsteady-state flow conditions; gravity, artesian, leaky or nonleaky aquifer; constant or variable discharge conditions; and sinks or source. The methods of determining aquifer constants depend on the solution of the selected continuity equation and the specific boundary conditions. Steady-state solutions can be used to estimate transmissivity; the storage coefficient (S) cannot be determined because it does not appear in the solution. The following methods based on steady-state approaches can be used to determine the transmissivity of an aquifer.

Unconfined Aquifer Flows

Radial Flow to a Fully Penetrating Constant Discharge Well (Fig. 1). The flow is considered assuming that the aquifer is homogeneous, isotropic, of uniform thickness, and has an infinite aerial extent. The differential equation for groundwater flow in an unconfined aquifer may be written in cylindrical coordinates as

$$\frac{d}{dr}\left(\frac{r\,dh}{dr}\right) = 0 \tag{1}$$

In a well that fully penetrates the gravity aquifer, the flow will be axisymmetric. Neglecting the vertical component of the velocity as small, the equipotential surfaces may be considered coaxial cylinders. The flow across these cylinders at a distance r is given by $Q = av = 2\pi rh\left(-k\frac{dh}{dr}\right)$. Equation (1) may be integrated twice. The two constants may be obtained from an assumed boundary condition of a piezometric head at the well as $h(r_0) = h_0$ and the relationship of the well flow at a given distance r. The solution of Eq. 1 under the boundary conditions gives the phreatic surface of the flow as

$$h^2 = \frac{Q}{\pi k}\ln\frac{r}{r_0} + h^2 \tag{2}$$

Three methods may be developed from Eq. 2 to determine transmissivity.

Determination of T Using Two Observation Wells: Dupuit–Thiem Method. It can be seen from Eq. 2 that there is no fixed saturated thickness in gravity aquifers and only k appears in the solution describing phreatic surfaces. Thus, only k can be obtained from the solution. To obtain the transmissivity, k has to be multiplied by some average depth. Measuring heads at two distances $r_1, r_2 (r_2 \geq$

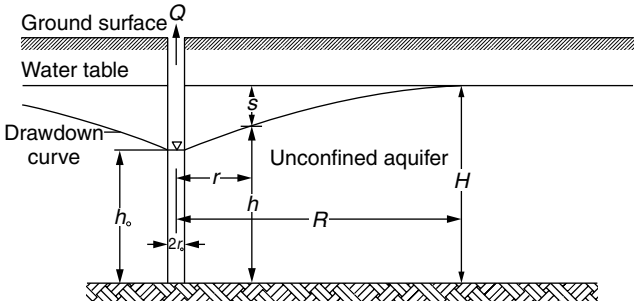


Figure 1. Flow to an unconfined aquifer.

$r_1), h(r_1) = h_1, h(r_2) = h_2$ in Eq. 2, an expression for k may be written as

$$k = \frac{Q}{\pi h(h_2^2 - h_1^2)} \ln \frac{r_2}{r_1} \tag{3}$$

Contrary to Dupuit's assumption, the vertical components of velocity are large in gravity flow and cannot be ignored. Equation 3, consequently, does not give correct results. Setting $h = H - s$, Eq. 3 can be rewritten as

$$kH = \frac{Q}{2\pi \left[\left(s_1 - \frac{s_1^2}{2H} \right) - \left(s_2 - \frac{s_2^2}{2H} \right) \right]} \ln \frac{r_2}{r_1} \tag{4}$$

where H is the saturated thickness of the aquifer, s_1 and s_2 are drawdowns and $s_1 - \frac{s_1^2}{2H}$ and $s_2 - \frac{s_2^2}{2H}$ are corrected drawdowns s_1' and s_2',

Transmissibility may be written in terms of corrected drawdowns or, neglecting correction terms, it may also be expressed as

$$T = kH = \frac{Q}{2\pi(s_1' - s_2')} \ln \frac{r_2}{r_1} \approx \frac{Q}{2\pi(s_1 - s_2)} \ln \frac{r_2}{r_1} \approx \frac{Q}{2\pi(h_2 - h_1)} \ln \frac{r_2}{r_1} \tag{5}$$

Determination of T Using a Single Observation Well. Due to constraints on funds for pumping tests, it may be possible to construct only one observation well. For such a situation, one may have observations only in a single well. For such conditions, setting $h(r_0) = h_0$ and $h(r_1) = h_1, (r_1 \geq r_0)$, an expression for k may be written as

$$k = \frac{Q}{\pi(h_1^2 - h_0^2)} \ln \frac{r_1}{r_0} \tag{6}$$

In the same way for such boundary conditions, T may be written in terms of corrected drawdowns. Considering that corrections have small values, they may be neglected to give approximate values of transmissivity as

$$kH = \frac{Q}{2\pi \left[\left(s_0 - \frac{s_0^2}{2H} \right) - \left(s_1 - \frac{s_1^2}{2H} \right) \right]} \ln \frac{r_1}{r_0} \approx \frac{Q}{2\pi(s_0 - s_1)} \ln \frac{r_1}{r_0} \approx \frac{Q}{2\pi(h_1 - h_0)} \ln \frac{r_1}{r_0} \tag{7}$$

Determination of T Using the Head in the Pumped Well. Due to further constraints on funds, one may not be able to make even a single observation well. For such a condition, measuring the head in the pumped well itself, $h(r_0) = h_0$, and considering an arbitrary radius of influence $h(R) = H$, the hydraulic conductivity may be obtained as

$$k = \frac{Q}{\pi(H^2 - h_0^2)} \ln \frac{R}{r_0} \tag{8}$$

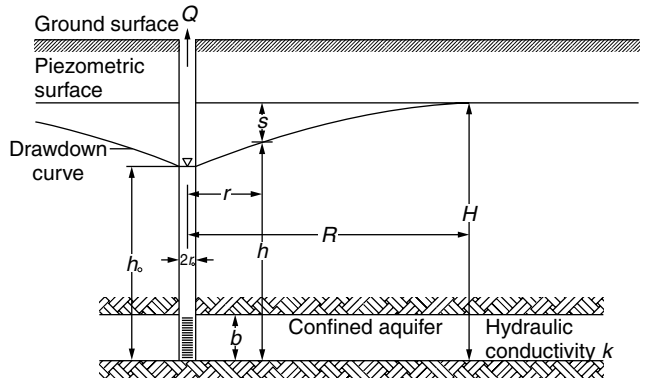


Figure 2. Flow to a confined aquifer.

Writing $h = H - s$, transmissibility may be written as

$$kH = \frac{Q}{2\pi \left(s_0 - \frac{s_0^2}{2H} \right)} \ln \frac{R}{r_0} \approx \frac{Q}{2\pi s_0} \ln \frac{R}{r_0} \tag{9}$$

Confined Aquifer Flows (Fig. 2)

Similar to the unconfined aquifer, flow is considered to take place assuming that the aquifer is homogeneous, isotropic, of uniform thickness, and of infinite aerial extent.

Radial Flow to a Fully Penetrating, Constant Discharge Well. Differential equations of the groundwater flow to a fully penetrating well in a confined aquifer may be written in cylindrical coordinates as

$$\frac{d}{dr} \left(r \frac{dh}{dr} \right) = 0 \tag{10}$$

In a fully penetrating aquifer of thickness b, the flow is axisymmetric, and the equipotential surfaces are coaxial circular cylinders. Flow across these cylinders in a fully penetrating artesian aquifer of thickness b at a given distance r from the well center is given as $Q = av = 2\pi rb \left(-k \frac{dh}{dr} \right)$. Equation 10 may be integrated twice under the assumed condition of the piezometric head at the well, $h(r_0) = h_0$, and the relationship of the well at a given distance r to give

$$h = \frac{Q}{2\pi kb} \ln \frac{r}{r_0} + h_0 \tag{11}$$

Thiem's (1906) Equilibrium Equation Using Two Observation Wells. To reduce errors because of losses in the well and through the well screen, Thiem (1) proposed measuring piezometric heads h_1, h_2 in two observation wells located at distances r_1, r_2 from a constantly discharging well Q. Thus, setting $h(r_1) = h_1, h(r_2) = h_2$ in Eq. 11 of an expression of transmissivity may be derived as

$$T = kb = \frac{Q}{2\pi(h_2 - h_1)} \ln \frac{r_2}{r_1} \tag{12}$$

Determination of T Using a Single Observation Well. Considering the head as $h(r_1) = h_1$ at a single piezometer installed at distance r_1 from the well, T may be obtained from Eq. 11 as

$$T = kb = \frac{Q}{2\pi(h_1 - h_0)} \ln \frac{r_1}{r_0} \tag{13}$$

Determination of T Using the Piezometric Head in the Pumped Well. By measuring the piezometric head in the pumped well itself and at an arbitrary radius of influence R, $h(R) = H$, T can be obtained from Eq. 11 as

$$T = kb = \frac{Q}{2\pi(H - h_0)} \ln \frac{R}{r_0} = \frac{Q}{2\pi s_0} \ln \frac{R}{r_0} \tag{14}$$

Spherical Flow to a Nonpenetrating, Constant Discharging Well in An Extensively Thick Artesian Aquifer (Fig. 3). The groundwater flow equation for such a flow system is described by a continuity equation in spherical coordinates as

$$\frac{d}{dr}\left(r^2 \frac{dh}{dr}\right) = 0 \tag{15}$$

The isopiestic surfaces to a nonpenetrating well consist of concentric hemispheres. The flow across a hemispherical surface at distance r is given by

$$Q = av = 2\pi r^2(-k dh/dr)$$

Considering the piezometric head at the well, $h(r_0) = h_0$, and the flow equation above, the piezometric surface can be obtained as

$$h = \frac{Q\left(\frac{1}{r_0} - \frac{1}{r}\right)}{4\pi k} + h_0 \tag{16}$$

Determination of k Using Two Observation Wells. It may be observed that from Eq. 16, only hydraulic conductivity can be determined as the thickness of the aquifer is not finite.

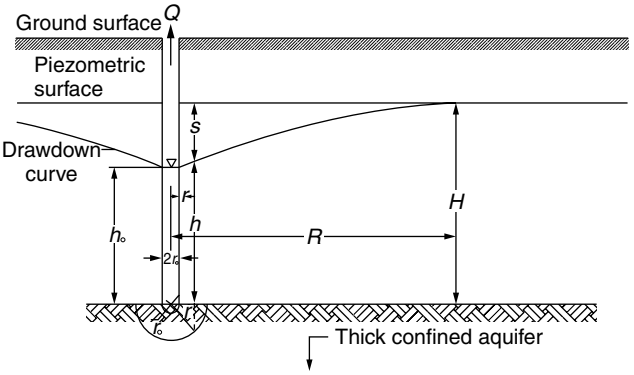


Figure 3. Spherical flow to a thick confined aquifer.

Considering heads at two observation wells located at distances r_1, r_2 as h_1, h_2, an expression for k may be obtained as

$$k = \frac{Q\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}{2\pi(h_2 - h_1)} \tag{17}$$

Determination of k Considering the Head in the Well. Using the measurement of the head in the pumped well itself, $h(r_0) = h_0$, and considering an arbitrary radius of influence R, an expression for k in terms of the head and drawdown $s = H - h$ may be written as

$$k = \frac{Q\left(\frac{1}{r_0} - \frac{1}{R}\right)}{2\pi(H - h_0)} = \frac{Q\left(\frac{1}{r_0} - \frac{1}{R}\right)}{2\pi s_0} \tag{18}$$

Considering that $R > r_0$, 1/R is negligible and can be neglected; this gives

$$k \approx \frac{Q}{2\pi r_0(H - h_0)} \approx \frac{Q}{2\pi r_0 s_0} \tag{19}$$

Semiconfined Aquifer Flows

Aquifer Constants from the Steady-State Flow of a Well in a Semiconfined Aquifer: Hantush and Jacob method (2) (Fig. 4). The solution is based on the assumption that the phreatic surface remains constant, so that the leakage through the semiconfining layer takes place in proportion to the drawdown of the piezometric level. Hantush and Jacob (2) obtained a solution for $L > 3D$, as

$$s_m = \frac{Q}{2\pi kb} K_0\left(\frac{r}{L}\right) \tag{20}$$

where s_m = steady-state drawdown in meters at distance r;
Q = discharge of the pumped well in cubic meters per day;
$L = \sqrt{kbc}$, leakage factor in meters;
$c = \frac{b'}{k'}$, hydraulic resistance of a semipervious layer in meters; and
$K_0(x)$ = modified Bessel's function of the first kind and zero order.

Hantush observed that if r/L is <0.05, Eq. 20 can be approximated as

$$s_m = \frac{2.3Q}{2\pi kb}\left(\log 1.12\frac{L}{r}\right) \tag{21}$$

A plot of s_m against r on semilog paper, with r on the logarithmic scale, will show a straight line relationship in the range where r/L is small. The slope of the straight line, the drawdown difference per log cycle of r, is expressed as

$$\Delta s_m = \frac{2.3Q}{2\pi kb}$$

$$kb = \frac{2.3Q}{2\pi \Delta s_m} \tag{22}$$

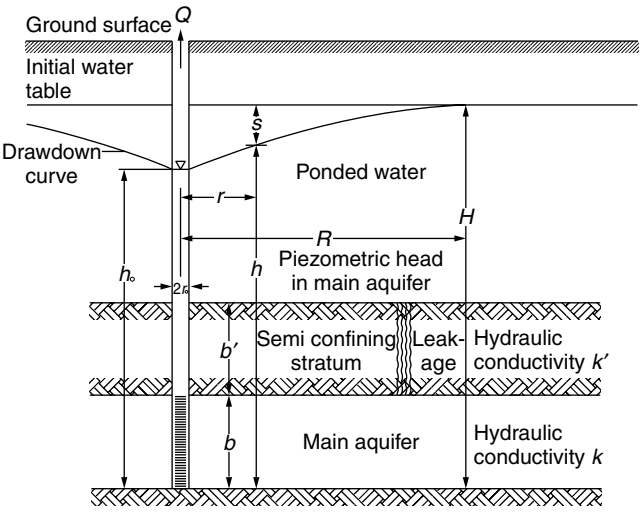


Figure 4. Flow to a semiconfined aquifer.

For any point s_m, r is selected on the straight line. Putting r in Eq. 21 gives $L.c$ can be obtained as

$$c = \frac{b'}{k'} = \frac{L^2}{kb}$$

Alternatively the extended straight line portion of the curve intercepts the r axis where the drawdown is zero. At the interception point, $s_m = 0, r = r_o$, and Eq. 21 reduces to

$$\left(\log 1.12\frac{L}{r}\right) = 0$$

or

$$1.12\frac{L}{r_0} = 1.12\frac{\sqrt{kbc}}{r_0} = 1$$

or

$$c = \frac{(r_0/1.12)^2}{kb}$$

Transmissivity from Steady Flow in a Semiconfined Aquifer: Ernst's Modification of the Thiem Method. The relationship is based on assuming that the well discharge is corrected by subtracting, from the total discharge, the amount of phreatic water obtained from the semipervious layer. The determination requires two piezometers installed in semipervious layers at distances r_1, r_2. The coaxial phreatic water from a circular area may be written approximately as $r_0 = r_1 + 1/3(r_2 - r_1)$.

The phreatic water delivered from a circular area is

$$Q' = \pi r_0^2 \Delta s' S' \times 24$$

where $\Delta s' =$ average drop of phreatic level in the semipervious layer during the last hour (m) and $S' =$ specific yield of the semiconfined aquifer (to be estimated from well logs). The transmissivity may be found from

$$kb = \frac{(Q - Q')\ln\dfrac{r_2}{r_1}}{2\pi(s_1 - s_2)} \tag{23}$$

Approximate Methods

Logan's (3) Method for confined aquifers. Equation 14 using the observation in the pumped well itself is also known as Logan's method. According to Logan (3), the accuracy of the calculation depends on the accuracy in measuring the maximum drawdown in the well s_0 and on the accuracy of the ratio R/r_0. The ratio R/r_0 may have a large value, but the ratio of the logarithm may be small. He suggested an approximate value of 3.33 for the log ratio. Putting this value in Eq. 14 gives the transmissivity as

$$kb = \frac{2.3Q}{2\pi s_0}\log\frac{R}{r_0} \approx \frac{1.22Q}{s_0} \tag{24}$$

Logan's (3) Method for Unconfined Aquifers. Using a similar approach and considering observation in the pumped well itself, the transmissivity in an unconfined aquifer may be obtained from Eq. 9 as

$$kH = \frac{2,3Q}{2\pi s_0'}\log\frac{R}{r_0} \approx \frac{1.22Q}{s_0'} \tag{25}$$

where $s_0' \equiv s_0 - \dfrac{s_0^2}{2H}$.

Transmissivity from Other Analytical Solutions

In principle, any analytical solution of a boundary value problem of groundwater flow can be used to estimate aquifer parameters, if other variables can be measured or estimated. A few steady-state solutions for estimating transmissivity are presented.

Two Equal, Constant Discharge, Mutually Interfering Wells. The relationships between two equal and constant discharge interfering wells distance B apart may be written as

$$Q_1 = Q_2 = \frac{2\pi kb(h_a - h_0)}{\ln\dfrac{R^2}{r_0 B}} \tag{26}$$

where $r_0 =$ well radius, $h_a =$ average piezometric head at the external boundary, $h_0 =$ piezometric head at the well, and $R =$ radius of influence ($R > B$).

Thus if the values of the constant equal discharges. Q, h_0, h_a, R, and B are known, the transmissivity may be determined from the relationship

$$kb = \frac{Q\ln\dfrac{R^2}{r_0 B}}{2\pi(h_a - h_0)} \tag{27}$$

Steady-State Flow to a Partially Penetrating Well. A relationship was obtained for such a flow system by De Glee (4) as

$$h_{2b} - h_0 = \frac{Q_p}{4\pi k}\left(\frac{2}{h_s}\ln\frac{\pi h_s}{2r_0} + \frac{0.20}{b}\right)$$

where h_s is the depth of the partially penetrating well, b is the aquifer thickness, h_{2b} is the initial piezometric head at distance 2b, and h_0 is the piezometric head in the well.

$$\text{Also} \quad 1.3\, h_s \le b; \frac{h_s}{2r_w} \ge 5$$

From this relationship and measuring other parameters, the transmissivity may be found as

$$kb = \frac{Q_p b}{4\pi(h_{2b} - h_0)} \left[\frac{2}{h_s} \ln \frac{\pi h_s}{2r_0} + \frac{0.20}{b} \right] \tag{28}$$

For a partially penetrating well in an unconfined aquifer where the drawdown is also small in relation to the saturated thickness, Eq. 28 can be used by replacing b by H.

Kozeny (5) proposed a relationship, by which transmissivity may be determined from

$$T = \frac{2.3 Q_p \log \dfrac{r}{r_0}}{2\pi(h - h_0)\, G} \tag{29}$$

where

$$G = \alpha \left(1 + 7 \sqrt{\frac{r_0}{2h_s}} \cos \frac{\pi\alpha}{2} \right)$$

Q_p is the discharge of a partially penetrating well, Q_f is the discharge of a fully penetrating well, $G = Q_p/Qf$ is a correction factor giving the ratio of the two discharges, α is the fractional penetration of the well screen h_s/b, and h_s is the depth of penetration of the aquifer.

PRACTICAL ASPECTS OF PUMPING TESTS (after Ref. 6)

Observation Well Size, Location, and Numbers

An observation well should be just large enough to allow accurate and rapid measurement of water levels. Small wells provide a fast response. Five-cm observation wells are usually effective when hand methods of measuring water levels are used. Larger pipes may be used with automatic recorders. Observation wells are commonly installed with 1–2 m long screens at the bottom embedded in the aquifer to measure the pressure head. Observation wells should be installed at about the same depth as the middle of the well screen in the pumped well.

Observation wells should be located at a reasonably large distance and not too close to the pumped well. Setting observation wells at distances of 30–100 m from the pumped well may work out best in most cases. When observation wells are too close to the pumped well, correct drawdown readings may be difficult. The cone of depression in a water table spreads at a slower rate than in an artesian formation, so the observation wells for a water table aquifer should be relatively closer to the pumped well.

The number of observation wells depend upon the amount of information required and the funds available for the test program. Drawdown data from the well itself or from a single observation well permit estimating the average hydraulic conductivity, transmissibility, and coefficient of storage of the aquifer. If two or more observation wells are placed at different distances, the test data can be analyzed both in terms of the time–drawdown and the distance–drawdown relationships. It is always better to have as many observation wells as conditions may allow. A minimum of three placed at varying distances and radially at equal angles around the well is desirable.

Measurement of Water Levels. The depth to water may be measured many times during the course of a pumping test. Observations should be taken at close intervals during the first 2 hours, and the time between readings should gradually increase as the test continues. The water level measurement may be recorded to the nearest 0.5 cm in the observation wells. Measurements may be made every half-minute during the first 5 minutes after starting the pump, then every 5 minutes for an hour, then every 20 minutes for about two hours. From this point on, readings at hourly intervals should be sufficient.

Water-level measurements can be taken in various ways, the wetted-tape method, mechanical sounder, electric water-level indicator, pressure gauge, or pressure logger. For detailed information on these devices, see Kruisman and De Ridder (7). Fairly accurate measurements of water levels can be made manually.

Measurements of Discharges. The other parameter that needs to be measured is the discharge from wells during pumping tests. To avoid complicated calculations later, the discharge rate should preferably be kept constant throughout the test. The discharge rate can be measured using various devices like commercial water meters, flumes, orifice weirs, containers or the jet-stream method. The procedures for installation and measurements using these devices are available in standard texts.

SUMMARY

An overview of steady-state approaches for determining the transmissivity of confined, unconfined, and semiconfined aquifers has been presented. Detailed procedures for determining transmissivity using drawdown data in a pumped well and one or two observation wells are discussed in the context of two most common methods of Thiem and Dupuit–Thiem. A few approximate methods and analytical solutions for determining aquifer constants have been briefly introduced. General guidelines for conducting pumping tests including measurement of discharge and groundwater levels and numbers and locations of observation wells have been furnished.

BIBLIOGRAPHY

1. Thiem, G. (1906). *Hydrologische Methoden*. Leipzig, p. 56.
2. Hantush, M.S. and Jacob, C.E. (1955). Non steady radial flow in an infinite leaky aquifer. *Trans. Amer. Geophysical Union*. **36**: 95–100.
3. Logan, J. (1064). *Estimating Transmissibility from Routine Production of Tests of Water Wells Ground Water* **2**(1): 35–37.

4. De Glee, G.J. (1930). *Over Grundwaterstroomingen bij Wateronttrekking Door Middle van Patten*. J. Waltman Jr., Delft, the Netherlands, p. 175.
5. Kozeny, J. (1933). *Theorie und Berech nug der Brunneu Wasser Kraft and Wasser Wartschift*. **28**: 88–92,113–116.
6. Johnson Div. UDP, Inc. (1972). *Ground Water and Wells*. 2nd Edn. Edward E. Johnson, St. Paul, MN, p. 440.
7. Kruisman, G.P. and De Ridder, N.A. (1970). *Analysis and Evaluation of Pumping Test Data, International Institute for Land Reclamation and Improvement*. Wageningen, the Netherlands.

TIDAL EFFICIENCY

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Ocean tides often cause water levels in coastal aquifers to fluctuate. These fluctuations result from two different causes. In confined aquifers, the additional weight of the water on the surface increases the pressure on the water at depth, which causes an increase in water levels in observation wells located near the coast. In this case, no movement of water between the ocean and the aquifer may have occurred. In unconfined aquifers, however, the loading effect does not occur. Instead, water that has moved directly through the pores within the aquifer has caused the water level response. Regardless of the mechanism, both processes can be described with the phase lag, or delay, between the tidal peak and the aquifer response peak, as well as the amplitude ratio between the magnitudes of the response and the tides

Water levels in wells located near the coast often fluctuate with a rhythm that mimics the rise and fall of the ocean. The tidal efficiency, TE, is the ratio of the change in water levels in wells, ΔW, to the change in tidal levels, ΔT:

$$TE = \frac{\Delta W}{\Delta T}$$

where both water levels are measured with the same type of units (e.g., feet, meters, psi). Tidal efficiencies can range from a maximum of one in poorly consolidated geologic media to a minimum of zero in rigid aquifers (1,2).

The tidal response in an aquifer can result from two types of phenomena, one in confined and a second in unconfined aquifers. As described in greater detail below, the confined aquifer response is caused by the increased load placed on the surface, whereas the unconfined aquifer response is caused by the movement of water in response to changing tidal water levels.

CONFINED AQUIFERS

In confined aquifers, coastal tides affect water levels because the surface load changes as ocean levels fluctuate. The weight of the ocean compresses the underlying aquifer, which causes a change in the fluid pressure. In this situation, no water moves between the ocean and the aquifer, which is similar to the effect that trains have as they pass a well in some confined aquifers—water levels rise and then fall as a train passes by (3).

The loading effect is greater in poorly consolidated aquifers where a greater proportion of the overlying load is borne by the fluid. Pore fluids in consolidated aquifers are less likely to carry the load, and so these aquifers have lower tidal efficiencies.

Coastal aquifers are not the only type of aquifer that shows a response to surface loads. The loading effect on confined aquifers can be observed in response to the placement or removal of any type of mass on the ground surface. Components of the water budget (such as precipitation, evaporatranspiration, and soil moisture) can immediately affect water levels in confined aquifers—even when no direct hydraulic communication is present (4).

An increase in water levels in a confined aquifer under a waste lagoon may be mistakenly attributed to contamination from the lagoon. The cause could be from downward leakage of water from above, or it could also be from the increased surface load causing a rapid increase in fluid pressure.

Another example of surface loading develops when barometric pressure changes cause water levels in wells to fluctuate. In these cases, the response is somewhat complicated because the barometric pressure also exerts a force on water levels in open wells. The tidal efficiency in confined aquifers is related to the barometric efficiency, BE, in that the two efficiencies must sum to unity, $TE + BE = 1$. Thus, aquifers with low tidal efficiencies have large barometric efficiencies, and vice versa. The reader is referred to BAROMETRIC EFFICIENCY for additional discussion of this topic.

UNCONFINED AQUIFERS

A second tidal influence occurs in unconfined, surficial coastal aquifers. In these aquifers, water levels change as the hydraulic perturbation created by changing ocean levels moves horizontally through the saturated zone toward the well. Unlike the confined case in which the load is transmitted without concomitant fluid movement, water is free to move through the unconfined aquifer.

For a simple, one-dimensional flow geometry (i.e., a well placed at some distance from a linear shoreline), the response is a function of the distance of the well from the shoreline, L, and the aquifer *hydraulic diffusivity*, $D = T/S$, where T and S are the aquifer transmissivity and storativity, repsectively. Nearby wells in more diffusive aquifers respond more rapidly than do more distant wells in aquifers with lower diffusivity. The response is a function of a dimensionless variable, $\kappa = D\tau/L^2$, where τ is the response time.

This type of response is not limited to coastal areas, however. A similar type of response is found in surficial aquifers next to streams. In this case, changing water levels during floods cause a loss of water from the stream into the adjacent aquifer, with a reversal of flow later in the flood hydrograph. This type of response is also referred to as *bank storage* (5).

SINUSOIDAL OSCILLATIONS

Many types of loading phenomena display periodic variation, tides being a common example. In addition to the gravitational affects of the sun and moon on the oceans, gravitational forces also cause changes in atmospheric pressure, called *atmospheric tides*, and even in the solid earth, called *earth tides*.

These periodic variations can be characterized with the *period* of the oscillation (e.g., 24 hours for solar tides) and the *amplitude*, or *magnitude*, of the oscillation. When observing the tidal response in confined aquifers, the tidal efficiency is equal to the ratio of the magnitude of the water level fluctuation in the well to the magnitude of the ocean tides. For example, if peak daily ocean levels vary by 1 m and the peak daily groundwater levels vary by 10 cm, then the tidal efficiency is 0.10, or 10%.

Another influence is the *phase lag*, which is the delay between when the ocean tide and the aquifer water levels peak. Normally, an insignificant delay occurs between the ocean tide and a confined aquifer response; yet this delay can be large in cases in which significant borehole storage exists.

The tidal efficiency and phase lag in unconfined aquifers can determine the aquifer diffusivity. The transmissivity and storativity can be only determined, however, if the flow of water can be determined, which requires measurements of the flow rate between the ocean (or stream) and the aquifer.

BIBLIOGRAPHY

1. Bear, J. (1972). *Dynamics of Fluids in Porous Media*. Dover Publications, New York.
2. Walton, W.C. (1970). *Groundwater Resource Evaluation*. McGraw-Hill, New York.
3. Jacob, C.E. (1940). On the flow of water in an elastic artesian aquifer. *Am. Geophys. Union Trans.* **21**: 574–586.
4. vanderKamp, G. and Schmidt, R. (1997). Monitoring of total soil moisture on a scale of hectares using groundwater piezometers. *Geophys. Res. Lett.* **24**(6): 719–722.
5. Todd, D.K. (1959). *Ground Water Hydrology*. John Wiley & Sons, New York.

COMBINED FREE AND POROUS FLOW IN THE SUBSURFACE

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INTRODUCTION

The presence of a fluid layer adjacent to a porous medium is common in many environmental, chemical, mechanical and petroleum engineering problems. The flow behavior in the fluid layer is determined by the properties of the fluid (e.g., viscosity and density), and surface (e.g., pressure and shear) and body (e.g., gravity and electric field) forces. However, flow in the porous medium depends additionally on the properties of the medium which include, among others, porosity and permeability.

In fluid dynamic analysis of groundwater systems, it is commonly found that water flows through combined free (nonporous) and porous pathways between surface and subsurface systems. Such coupled regimes may also be present due to construction of industrial utilities and structures in the ground. Important engineering processes that may involve combined free and porous flow domains are, for example, fluid losses/leaks from underground pipes and storage tanks in old gas works sites; dig-and-treat, pump-and-treat, and permeable reactive barrier technologies for groundwater treatment; and drilling/extraction of oil from underground reservoirs. However, in most cases, the associated transport phenomena are determined by natural hydroenvironmental conditions, which include, for example, combined surface and subsurface flow, lake–groundwater interactions, seepage through preferential flow channels and macropores, circulatory flows and rise and fall of groundwater, glaciology, and multiple karstic regions interfaced with granular porous sections. The subdomains in coupled flow systems are generally distinguished by an interfacial surface, which represents the transitional zone for contaminants/fluid mobility from free to porous sections or vice versa. To gain on understanding of the combined flow behavior, it is necessary to develop realistic methodologies for evaluating mass and momentum transfer across the free/porous flow interfaces.

The construction of well-posed mathematical formulations for combining different flow regimes can present difficulties. Two general approaches have evolved for this purpose: (1) methodologies based on treating the combined flow domain as a single continuum and (2) formulations in which the flow domain is considered as a combination of discrete sections corresponding to different flow regimes. In the former, the porous section is effectively regarded as a pseudofluid layer, and the whole domain is analyzed as a whole. As such, a suitably formulated momentum equation for the entire domain in conjunction with mass conservation equations is solved. The mathematical model identifies fluid and porous domains based on spatially varying permeability. Such a single-domain approach is usually applied where the flow transition from free to porous flow zones is not distinct and properties of the porous domain change progressively (e.g., metal solidification problems involving mushy zones). However, if the permeability of the porous medium is constant and remains above a relatively high level, then at defined interfaces between adjacent zones, transitions between free/porous regimes occur. Under these conditions, the domain should be viewed as a combination of adjacent flow fields rather than a geometric continuum. In these situations, the second approach should be used where appropriate equations of motion describing the flow in different subdomains are

solved. In general, a groundwater system corresponds to this case.

GOVERNING MODEL EQUATION

The main aim of this article is to present a general methodology that can be used to simulate hydrodynamic behavior in combined free (nonporous sections) and porous flow zones in the subsurface based on the assumption of discrete flow domains, which involves selecting governing model equations for each subdomain and the matching conditions at the interface for linking them. Although fluid mobility in combined free and porous flow on the surface has been the focus of intense research for more than two decades, analyses of subsurface flow have not treated the possible interactions between free and porous flow regimes efficiently. Addressing these issues, the hydrodynamic conditions in underground zones of coupled fluid and porous domains have been analyzed on a 3-D spatial scale by Das et al. (1). This methodology is based on the principles of mass and momentum conservation and primitive variable formulations (i.e., the equations are expressed in terms of the pressure and velocity). Conservative forms of the equations have also been adopted to enhance the accuracy of the numerical calculations. The model equations are presented below.

Free Flow Region

The momentum transfer for constant density and viscosity of a fluid at a reference temperature in a free flow region can be represented by the well known Navier–Stokes (N-S) equation,

$$\nabla P_f = -\rho \frac{dv_f}{dt} + \mu \nabla^2 v_f \tag{1}$$

where the subscript f refers to the free flowing fluid. P and v are the pressure and velocity terms, and ρ and μ are the constant density and viscosity of the fluid, respectively. In Eq. 1, the body forces are automatically incorporated in the pressure term as the resultant flow potential. The following continuity equation that describes the mass conservation for an incompressible fluid can be used for a free flow regime:

$$\nabla \cdot v_f = 0 \tag{2}$$

Porous Flow Region

The corresponding macroscopic equations representing the flow field in the porous section are more uncertain. The momentum equations have received considerable attention in the past. The two most suitable are the Darcy (2) and Brinkman (3) equations shown below in the transient form for anisotropic porous media where the body forces have been incorporated in the pressure terms to represent the driving flow potential:

$$\text{Darcy equation: } \nabla P_p = -\rho \frac{\partial v_p}{\partial t} - \mu K^{-1} \bullet v_p \tag{3}$$

$$\text{Brinkman equation: } \nabla P_p = -\rho \frac{\partial v_p}{\partial t} - \mu K^{-1} \bullet v_p \mu' \nabla^2 v_p \tag{4}$$

In these equations, the subscript p refers to the porous section; P is the interstitial averaged pressure, v is the volume averaged seepage velocity; and ρ and μ are the constant density and viscosity of the fluid, respectively. μ' is the effective viscosity which depends on the fluid viscosity, μ, and the porosity. For flow of an incompressible fluid in a continuum porous medium, the equation of continuity is

$$\nabla \cdot v_p = 0 \tag{5}$$

where v is the volume averaged seepage velocity of fluid.

Matching Boundary Condition for the Darcy Equation as a Porous Flow Equation. To couple the equations representing the two domains, it is necessary to specify the matching hydrodynamic conditions at the interfacial region separating the two subdomains. Keeping the three-dimensional (3-D) subsurface problem in mind, the matching conditions for pressure (continuous or discontinuous) and velocity components (normal and tangential) must be specified at the interface. The Darcy equation is a first-order differential equation with respect to velocity and pressure, so it is not possible to describe the velocity components fully at the free/porous domain interface, which makes it impossible to link the Darcy and the N-S equations directly because the latter requires specifying all velocity components to solve them. Special techniques have been invoked, henceforth, for this purpose. Addressing this issue, Beavers and Joseph (4) performed their well-known experiment on the measurement of mass efflux of a Poiseulle fluid flowing over a permeable block. They hypothesized the existence of a slip velocity, commonly known as the Darcy slip phenomenon, at the interface and a shear velocity in the porous boundary layer. Consequently, an ad hoc boundary condition was proposed based on the assumption that the slip velocity is proportional to the shear effects. It allowed jumps in the tangential velocities and gave a much-needed relationship between the flow within and outside porous media. The Beavers and Joseph (4) formulation was represented as

$$\left(\frac{\partial u}{\partial y}\right)_f = \frac{\gamma}{\sqrt{K}}(u_f - u_p) \tag{6}$$

where the x direction was taken as parallel and the y direction as perpendicular to the interface. K is the direction-independent geometric permeability of the porous medium (isotropic), and γ is a slip coefficient that depends only on the properties of the porous medium and is independent of the fluid. The Beavers and Joseph condition has now been modified for cases where the flow and the interface are perpendicular rather than parallel, as in the original formulation. Jones (5) derived the following expression for the interfacial condition, assuming that the Darcy slip phenomenon is due to shear stress at the interface rather than a simple shear velocity:

$$\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right)_f = \frac{\gamma}{\sqrt{K}}(u_f - u_p) \tag{7}$$

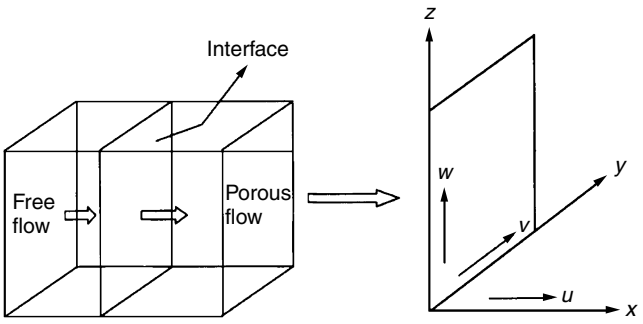


Figure 1. Model of combined free and porous flow domain for extending the Beavers and Joseph (1967) formulation to the 3-D subsurface region.

Direct extension of the above formulations to 3-D cases poses further challenges. However, by resolving the 3-D framework into two planes (x–y and x–z), it is possible to use the Beavers and Joseph formulation for three-dimensional modeling of combined flow in the subsurface (1,2). The extension can be done based on Fig. 1 where the x component of the velocity is normal to the interfacial plane and the y and z components are tangential (parallel). For the 3-D situation in Fig. 1, postulating that the Darcy slip phenomenon takes place at both x–y and x–z planes, the following relationships can be obtained heuristically based on the Jones (5) modification of Beavers and Joseph's original formulation (1,2). The velocity components that are parallel to the interface can be calculated by using these expressions:

$$\text{Velocity slip at } x\text{–}y \text{ plane: } \left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right)_f = \frac{\gamma}{\sqrt{K_{yy}}}(v_f - v_p) \tag{8}$$

$$\text{Velocity slip at } x\text{–}z \text{ plane: } \left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)_f = \frac{\gamma}{\sqrt{K_{zz}}}(w_f - w_p) \tag{9}$$

The slip coefficient is represented in Eqs. 8 and 9 by γ_{yz} to indicate the plane on which it is active. Equation 8 is used to simulate the jump in the transverse (y) velocity component across the interface, and Eq. 9 is used for the vertical (z) velocity component. K_{yy} and K_{zz} are the permeability in the y and z directions, respectively. The above equations, therefore, represent the slip-flow phenomena at the permeable interface with respect to directional geometric permeability. Also, the velocity component normal to the interface, the longitudinal component, can be taken as continuous across the interface:

$$u_f = u_p \tag{10}$$

However, the pressure does not necessarily remain continuous across the interface and only under static conditions, can it be said to be strictly continuous. If the pressure is to be modeled as discontinuous at the y–z interfacial plane during flow, the following relationship is used:

$$\left(-P + 2\mu\frac{\partial u}{\partial x}\right)_f = -P_p \tag{12}$$

This interfacial condition for pressure jump arises from the fact that stress in the porous side is carried by the porous materials, whereas in the free flow domain, the stress is borne by the fluid medium, which causes a discontinuity in stress, and hence fluid pressure, across the fluid/porous interface.

Matching Boundary Condition for the Brinkman Equation as a Porous Flow Equation. The use of the Brinkman equation for mathematically describing the flow in porous flow zones apparently does not cause any mathematical difficulty. The second-order derivatives of the N-S equations and the Brinkman equation with respect to velocity enable specifying all flow properties as continuous across the interface, which facilitates the task of coupling the equations of motion for the free and permeable domains. The continuity of the flow variables across the interface yields the following matching boundary conditions:

$$u_f = u_p \tag{13a}$$

$$v_f = v_p \tag{13b}$$

$$w_f = w_p \tag{13c}$$

$$P_f = P_p \tag{13d}$$

DISCUSSION AND CONCLUSIONS

Although there are superficial similarities in mathematical formulations of different coupled free and porous flow problems, Das et al. (1) clearly demonstrated that combined flow behavior in the subsurface may differ significantly from other combined flow processes encountered in chemical, petroleum and mechanical engineering applications. Therefore, models to represent specific scenarios need to be developed. In the above studies by Das et al., natural flow behavior has been defined at the exit of the domain by imposing stress-free boundary conditions. Das et al. demonstrated that at the open end (exit) of the domain, coexisting inflow and outflow might take place. In other words, fluid from the surrounding media might come inside the domain through the open end in addition to the defined inlet. For the particular domain investigated, Das et al. observed that although flow in the fluid domain is mostly unidirectional toward the free/porous interface and appears similar to pipe flow, it might become circulatory on the porous side and reverse its direction. Evidence of flow circulation, consistent with the simulated results of Das et al., can also be found in the literature dealing with various scenarios of subsurface flow (6). However, fluid circulation is a complex transient process often involving a moving center of circulation and shifts of the flow reversal front to or from the interface. After a certain time interval, the circulation may disappear, and the porous flow may become unidirectional toward the exit of the porous section. The main cause of such flow behavior has been attributed to complex/variable pressure distributions within the porous domain. The effects of a partially impermeable interface between the free and porous domains has

been explored by Das and Nassehi (7). It has been demonstrated that due to the impermeable interface, there is a possibility of buildup of fluid in the free flow region. The influence of having a the multiple number of fluid/porous interfaces in a flow domain has been demonstrated by Das and Nassehi (8). This study showed that, in general, the presence of a multiple number of interfaces in the free flow domain has a minimal effect on flow behavior. However, the flow patterns on the porous side may vary depending on the direction of the free/porous interfaces. Das and Nassehi (8) also examined concentration profiles of a conservative pollutant in associated free flow and porous domains. The effects of different aspect ratios of the subdomains on the hydrodynamic behavior of free/porous regimes have been investigated by Das and Nassehi (9). This study shows the influence of the extent of free and porous domains, which govern the entire flow behavior.

The study of combined free and porous flow in the subsurface using different methodologies is still relatively new in scientific literature. Although a number of issues have been studied, future research aimed at better understanding of combined flow behavior must be continued. For example, investigations into the effects of heterogeneity in porous media and multiphase flow (e.g., oil and water) in combined domains should be carried out. A general methodology, which is not restricted to systems where free/porous interfaces are aligned to coordinate axes, also needs to be developed.

BIBLIOGRAPHY

1. Das, D.B., Nassehi, V., and Wakeman, R.J. (2002). A finite volume model for the hydrodynamics of combined free and porous flow in sub-surface regions. *Adv. Environ. Res.* **7**(1): 35–58.
2. Darcy, H.P.G. (1856). *Les Fontaines Publiques de la Ville de Dijon, Exposition et Application des Principes à Suivre et des Furmules à Employer dans les Questions de Distribution d'Eau*. Victor Dalmont, Paris.
3. Brinkman, H.C. (1947). A calculation of the viscous force exerted by a flowing fluid on a dense swarm of particles. *Appl. Sci. Res.* **A1**: 27–34.
4. Beavers, G.S. and Joseph, D.D. (1967). Boundary conditions at naturally permeable wall. *J. Fluid Mech.* **30**(1): 197–207.
5. Jones, I.P. (1973). Low Reynolds number flow past a porous spherical shell. *Proc. Cambridge Philos. Soc.* **73**: 231–238.
6. Devito, K.J., Waddington, J.M., and Branfireun, B.A. (1997). Flow reversal in peatlands influenced by local groundwater systems. *Hydrological Processes* **11**: 103–110.
7. Das, D.B. and Nassehi, V. (2001). LANDFLOW: A finite volume model of combined free and porous flow of water in contaminated land sites. *Water Sci. Technol.* **43**(7): 55–64.
8. Das, D.B. and Nassehi, V. (2003). Modelling of contaminant mobility in underground domains with multiple free/porous interfaces. *Water Resour. Res.* **39**(3), doi: 10. 1029/2002 WR001506.
9. Das, D.B. and Nassehi, V. (2002). Development of a new mathematical model for subsurface water quality management. *Water Sci. Technol.* **45**(9): 301–307.

READING LIST

Das, D.B. (2001). *Computer Modelling of Contaminant Mobility in Subsurface Regions*. Ph.D. Thesis, Chemical Engineering Department, Loughborough University, Loughborough, UK.

GROUNDWATER TRACING

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INTRODUCTION

Groundwater tracing is now a major field in groundwater hydrology aiming mainly at demonstrating the direction of groundwater flow and secondly, at giving as much information on the hydrologic setting as possible. It has been used for several decades to study flow conditions, for groundwater reconnaissance, and for managing water resources. During the last decades, water protection has been one of the main issues due to strong pollution of the environment. A groundwater tracer is a substance or a sort of energy conveyed by water to be detected at a sampling point and to be used in analyzing the temporal and spatial distribution of water and the pollutant. Artificial and natural tracers can help in various ways to assess and to predict contaminant transport in surface and groundwater.

Groundwater tracing can be a component of a large hydrogeological program, or it can be a hydrogeological program by itself. Nowadays, new field methods, new tracers, and new measurement techniques are being developed to make hydrogeologists more satisfied with results.

The advantage of groundwater tracing is that it provides the possibility of a direct view of a groundwater system, so the results can be relied on with assurance. In a groundwater tracing program, depending on the question and technical problem, both "natural" (those existing in the water cycle) and "artificial" (those to be introduced into groundwater system) tracers can be selected. The main group of artificial tracers, is soluble tracers, such as fluorescent dyes that are highly detectable, as well as different salts. Another group of artificial tracers includes drift bodies, such as spores, bacteria, or phages. The applicability of each tracer depends on its properties and on the condition of the flow environment. The use of certain tracers, especially for groundwater flow, is strongly restricted due to hydrogeologic conditions and aquifer properties.

For artificial tracers, the methodology comprises introducing the tracer into the groundwater system, letting it travel together with the water, sampling, and finally analyzing the water samples. For natural tracers, the natural physical, chemical, or biological composition of water is traced. For example, the natural temperature of cold water from a spring could be a guide to identifying snowmelt as the main water source and differentiating it from local groundwater.

THE HISTORICAL BACKGROUND

The groundwater tracing method is as old as the interest of humans in nature. It was used while people were curious about finding the source of undiscovered or unknown caves or springs and used chaff, wood bits, or other drifts to reveal the route of the water. The way to perform the test is now almost as simple as it was in the past, at least in most cases. But the way to analyze samples and the results evolved into complicated analytical methods. The development of new tracers and new analytical methods during the last 10 years has led to more accuracy in the results and also more ability to cover longer distances in tracing tests. While using the method during the last decades, it was aimed to find the direction of groundwater flow and its velocity; now, its major application is in studying groundwater pollution problems and protecting the environment.

GOALS OF GROUNDWATER TRACING

The most important goals to be achieved in a tracing program can be categorized into two groups:

Quantitative goals: To determine

- groundwater recharge amount
- groundwater discharge amount
- components of groundwater recharge
- age of groundwater
- elevation of recharge
- groundwater velocity
- volume of aquifer dynamic storage
- dispersion coefficient
- travel time

Quantitative goals: To determine

- origin of water
- hydraulic connection between different surface water and groundwater bodies
- hydraulic connection between different basins
- spring catchment area
- aquifer recharge areas
- aquifer discharge areas
- aquifer boundaries
- groundwater flow direction and path
- flow regime
- role of structural features in groundwater flow
- saline water–freshwater interface
- source of pollution
- pollution distribution pattern
- degree of karstification
- seepage/leakage zones in dams and reservoirs

CHARACTERISTICS OF IDEAL TRACERS

Among the characteristics for selecting a tracer as an ideal applicable tracer are the following:

The tracer

1. should be detectable in low concentrations. In most cases, the tracer material is to be diluted in a big volume of groundwater storage, so it must be easily detectable at low concentrations in water samples. The tracer concentration should be easily differentiated from background values in sampled water.
2. should be applicable as a nontoxic additive to water. It is compulsory for the tracer material not to harm flora and fauna.
3. should not be an absorptive material. The tracer substance should not be easily adsorbed to aquifer material; otherwise, it is possible that a considerable portion of the injected tracer is lost during the test, and it may be a major source of error in interpreting the results. The tracer should move in the same manner as water, and should not interact with aquifer material.
4. should be economically available. In some tracing experiments, the cost of tracer is a decisive factor.
5. should not change the hydraulic conductivity of the medium under investigation.
6. should be stable enough during the test period from injection until detection.

It is obvious that one could not find an ideal tracer that meets all of these specifications. Although there are some tracers developed specifically for groundwater tracing, selecting a suitable tracer, as well as applying a suitable amount of the tracer, is a state-of-the-art task and cannot be done without sufficient experience, favorable expertise, and knowledge about the medium under study.

GROUNDWATER TRACER TYPES

Groundwater tracers can be categorized into two main groups of artificial (to be introduced into the system) and natural (environmental or preexisting in the system) tracers (Fig. 1). Natural tracers are those present in water molecules or accompany water molecules naturally along their path, such as deuterium (^{2}H), carbon-13, or water temperature. Discharge pulses are often good tracers for water especially in the response of springs to flash rainfalls. Artificial tracers are much more diverse in type, and there are many more tracers not mentioned.

Natural (Environmental) Tracers

Natural or environmental tracers are those that already exist in the natural environment, the hydrologic cycle. They could be substances or some kinds of energy.

Environmental Isotopes. Environmental isotopes used as groundwater tracers are isotopes of hydrogen, oxygen, and carbon. They could be part of a water molecule (^{2}H or deuterium, ^{18}O, and ^{3}H or tritium), or they might enter the hydrologic cycle and move together with water molecules (^{13}C, ^{14}C, ^{14}N, ^{15}N, ^{32}S, ^{34}S, ^{36}S ...).

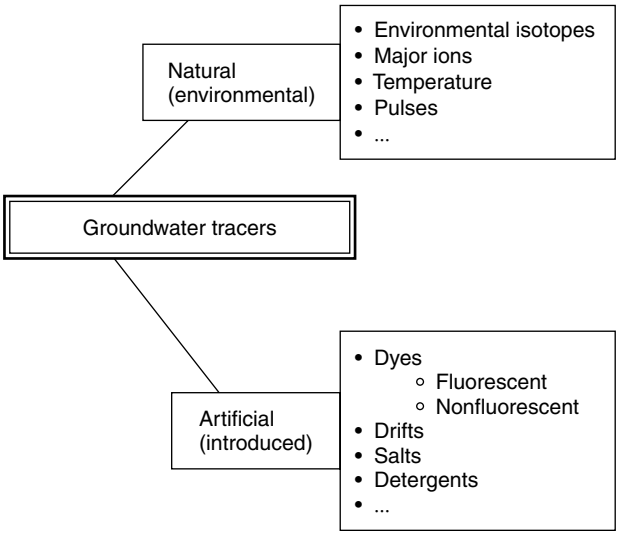


Figure 1. Groundwater tracer types.

Stable Isotopes

Hydrogen and Oxygen Isotopes. Analysis of the natural concentration of these isotopes in water has helped in understanding groundwater flow. Because of the large differences in mass between the two hydrogen isotopes, they tend to fractionate whenever evaporation or condensation takes place. Other factors being equal, waters of higher deuterium content are found near coastlines, at low elevations, in warm rains, and where partial evaporation occurs, as in saline lakes. The variations in oxygen isotope almost follow those of deuterium. The most common use of studies of ^{2}H and ^{18}O has been to trace the regional movement of groundwater and to locate recharge areas.

Nitrogen. The two abundant isotopes of nitrogen (^{14}N and ^{15}N) can vary significantly in nature. Ammonia escaping as vapor from decomposing animal wastes, for example, tends to remove the lighter nitrogen (^{14}N) and leaves behind a residue rich in nitrogen. In contrast, many fertilizers that have an ammonia base are isotopically light. Natural soil nitrate is somewhat between these two extremes. As a consequence, nitrogen isotopes have been useful in helping to determine the origin of unusually high amounts of nitrate in groundwater.

Most nitrogen in groundwater is in the form of nitrate anion (NO_3^-) or dissolved nitrogen gas (N_2) from the atmosphere. Locally, in zones devoid of dissolved oxygen, the chemically reduced form (NH_4^+) may predominate. In general, nitrate moves as a conservative tracer and is an important indicator of pollution. If nitrate concentrations exceed about 10 mg/L, the health of infant mammals including humans may be adversely affected. Also the presence of more than about 5 mg/L of nitrate commonly is an indirect indication of other forms of contamination, including those from fertilizers and sewage.

Sulfur. Most dissolved sulfur within shallow groundwater is bound within the sulfate ion (SO_4^{2-}). The stable sulfur isotopes (^{32}S, ^{34}S and ^{36}S) found in the sulfate ion vary quite widely and, under certain circumstances, can be useful indicators of the origin of the sulfate, which is particularly true if, for example, one wishes to distinguish sulfate originating from natural dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) from sulfate originating from an industrial spill of sulfuric acid.

Active Isotopes

Tritium. Tritium (^{3}H) is an unstable isotope of hydrogen whose half-life is 12.32 years. It enters the hydrologic cycle in the same manner as stable hydrogen in the H_2O molecule. This isotope is naturally produced at low levels in the atmosphere. During and after the nuclear tests in the Northern Hemisphere in the 1960s, the tritium concentration (referred to as TU: Tritium Unit) in the atmosphere increased from a level of 5–15 TU to up to 4000 TU. ^{3}H can be used qualitatively to date groundwater groundwater that has less than 2 to 4 TU is dated prior to 1953; if the amount is significantly greater than 10 to 20 TU, it has been in contact with the atmosphere since 1953. Tritium analysis in groundwater studies is mainly for absolute groundwater dating for ages up to 40 years.

Carbon-14. ^{14}C is the radioactive isotope of carbon. It has a half-life of 5730 years and is mainly used to date groundwaters up to 30,000 years of age. Most ^{14}C in potable groundwater is contained in the HCO_3^- ion in water. As a first approximation, the initial number of ^{14}C nuclei per total carbon nuclei, or X_0 in Eq. 1, in a water sample is considered to have been constant prior to 1950 due to the almost constant natural production of ^{14}C in the atmosphere by cosmic radiation interacting with the atmosphere.

$$X_t = X_0 e^{-\lambda t} \tag{1}$$

where λ = decay constant
t = time
X_0 = number of nuclei at zero time
X_t = number of nuclei at time t

If the only source of ^{14}C in water is originally from the active biosphere, then the ^{14}C that is measured in carbon from a water sample can be considered X_t in the equation because λ is known from experimental work, the age of the sample (t) can be determined directly. Due to some complexities, the use of ^{14}C in age determination is not so simple. The existence of carbon from carbonate formations, or formation of CH_4 gas, are factors that affect the results of age determination. But despite that, ^{14}C dating is highly useful in determining the approximate residence time of old groundwater.

Major ions. The chemical composition of groundwater is in most cases a good indicator of the environment through which the water has passed. In almost all groundwater tracing and isotopic hydrologic programs, water is analyzed for calcium, sodium, magnesium, potassium (major cations), chloride, sulfur, carbonate, bicarbonate, and nitrate (major anions).

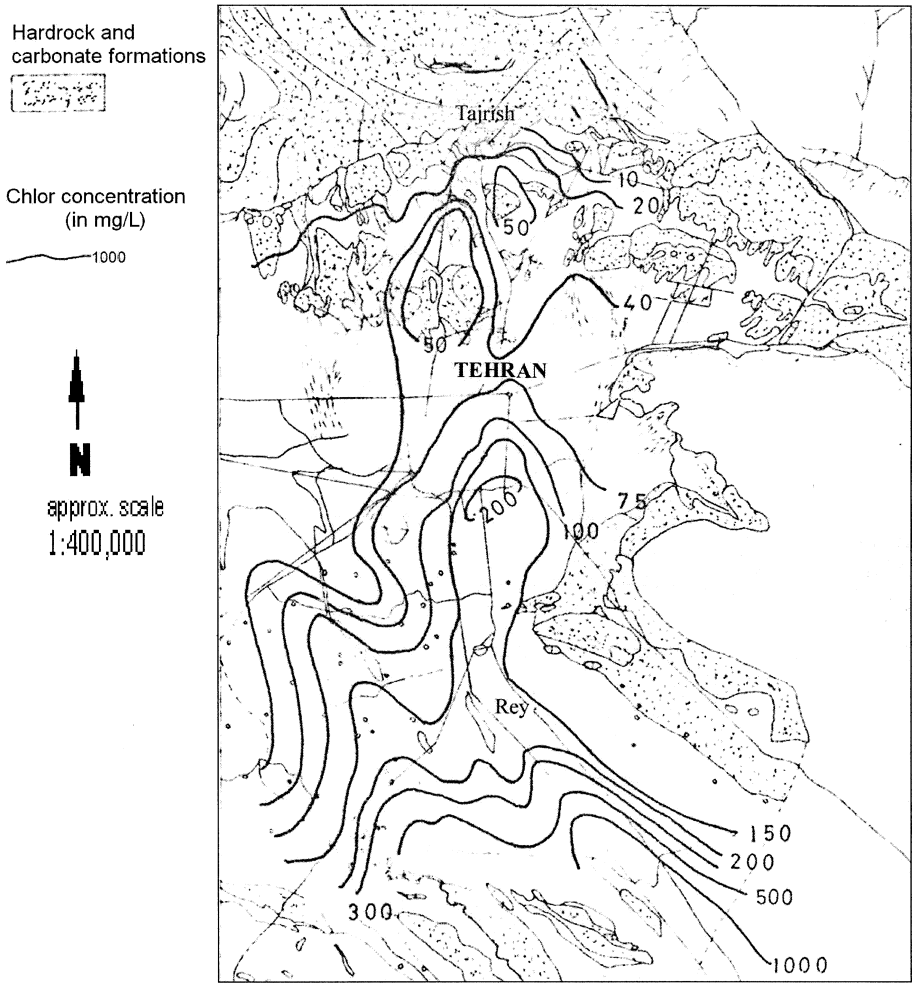


Figure 2. Isochlor map for Tehran plain, 1977, Tehran, Iran. The general groundwater flow direction is southward. As can be seen, groundwater gets richer in ions (specifically in chlor) as it flows downstream.

Typically, if we follow a recharge event and track the water down-gradient in the flow path, it can be seen that the ionic concentration in the water increases as it migrates down-gradient (Fig. 2). Generally, groundwater is the bicarbonate type in recharge areas the sulfate type midway, and the chloride type in terminal zones (e.g., basin outlet). The chemical composition of groundwater would finally be demonstrated on specific presentation charts such as Piper, Durov, Schuler, ... and different groundwater types could be easily recognized.

Temperature. Water temperature is almost a good indicator or tracer where there is an abrupt difference in the physical properties of the aquifer (e.g., a change in hydraulic conductivity, fracture properties ...) or where there is a significant temperature gradient (Fig. 3) Thermometry is a study tool for investigating changes in rock properties in a borehole column. It comprises a heat sensor that goes down through the borehole and records the water temperature along the borehole column. The record is called a temperature log.

Pulses. Pulses are sudden changes in the amount of a specific parameter that can be easily seen as a peak in a graph of the parameter versus time. It could be the graph of a spring discharge, electrical conductivity, turbidity, etc. A pulse is normally an indicator of a hydrologic event upstream. For example, a sudden rise in the amount of turbidity in a spring could be an indication of a storm in a spring recharge area. It could also be a sign of a hydraulic connection between the storm area and the spring.

Artificial Tracers

Artificial tracers are those that are introduced intentionally into groundwater. So an "injection point" is necessary in artificial tracing in addition to a sampling network.[1] While in environmental tracing, the study is performed only through a sampling network. Normally, artificial tracing and natural tracing are complementary, and sometimes both methods are applied to the same area to achieve more reliable results. Among all artificial tracers, the most applicable are fluorescent dye tracers which are discussed at the end for more emphasis.

Drifts. In areas such as karstified limestone terrains or highly faulted volcanic rocks where groundwater flow follows a turbulent pattern, drifts usually are good choices to be selected as tracers. Signal-emitting floats, yeasts,

[1]Sometimes the injection point and sampling point are the same. This is the case in the so-called single-well tracing method.

bacteria, viruses, and spores have reportedly been used as tracers in many cases.

Salts. Most tracers that have already been used extensively are common salts. This category of tracers includes those compounds that ionize in water, resulting in separation into charged elements possessing a positive charge (cations) or a negative charge (anions). The most common ionic tracers are chloride (Cl^-), bromide (Br^-), lithium (Li^+), and potassium (K^+). These tracers have been successfully used to determine flow paths, residence time, and aquifer properties. The most important factors that should be considered before applying such tracers are aquifer material texture and natural background concentrations in the aquifer.

The advantages of salt tracers are their availability, low cost, and stability, but they must be injected in large amounts, hundreds of kilograms or tons, and this causes problems in handling and transportation. As they are injected in huge amounts, they make water denser around the injection point, and it may affect the hydrodynamic behavior of the water.

Fluorescent Dyes. For many reasons, fluorescent dyes have become very important as tracers in hydrology and hydrogeology. They can be used in hydrology to measure transit times in streams and rivers, to measure discharge in open channels by the tracer dilution method, and to investigate dispersion processes in rivers, lakes, and seas. Of course their main application is in hydrogeologic studies for estimating hydrodynamic parameters as well as studying sources of pollution.

Application of fluorescent tracers has some great advantages and a few disadvantages:

- They are visible without the use of any instrument at higher concentrations (say more than 10 ppb). This property can be useful for qualitative experiments.
- The limit of detection for the dyes is in the sub-ppb range and therefore much better (up to a factor of 1000 to 10000) than salt tracers. So a small amount of tracer is enough.
- Instrument detection is quick and easy without time-consuming sample preparation.
- The chemical properties of the dyes are in some cases better because salts (particularly the cationic part) are influenced by ion exchange in clayey sediments.
- Fluorescent dyes do not influence the density of water near the injection point.
- Depending on the type of analytical instrumentation, the costs to determine fluorescent dyes are cheaper (using an ordinary photometer) or comparable to a flame photometer which can be used to analyze salt tracers. The detection of salts by electrical conductivity measurement is obviously cheaper but cannot distinguish between different types of salt tracers.
- A disadvantage is the relatively high cost of fluorescent dyes, but, on the other hand, up to 1000 times less dye than salt is necessary for a tracing experiment.

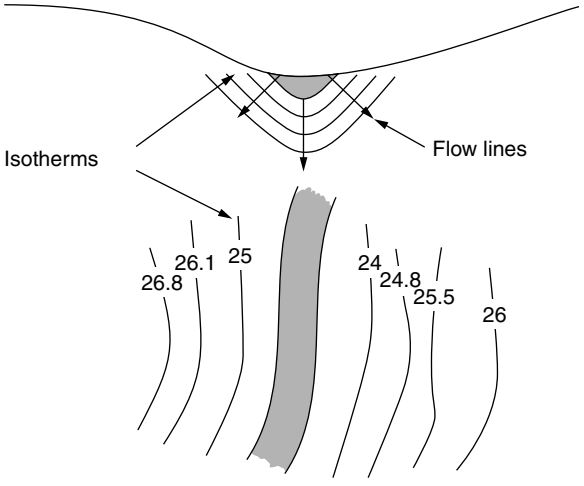


Figure 3. Sketch showing a section of a temperature gradient due to freshwater recharged from the river (up) and the plan of isotherms at both sides of the river (down).

These are the most commonly used fluorescent dyes:

Uranine. For hydrologic or hydrogeologic purposes, uranine ($C_{20}H_{10}O_5Na_2$, Color index name: Acid Yellow 73) is the most important tracer (Fig. 4). It is also the most sensitive of all. The dye is supplied as a hygroscopic orange-red powder: it is very soluble in water and has a yellowish-red color and an intense yellowish green fluorescence. In solutions at concentrations higher than 1 g/m^3 (equal to 1 ppm), the color is orange-red. The fluorescence is visible without any instrument above concentrations of 50 mg/m^3 (50 ppb) and approximately above 10 mg/m^3 (10 ppb) using a UV lamp, depending on the quality of the dye. It has no specific odor. At high concentrations, the fluorescent light is absorbed by the sample itself. The intensity of the fluorescence can be measured exactly only if the concentration is much lower (less than 100 ppb); otherwise, the solution has to be diluted.

The solubility of Uranine is 500 mg/L, and its detection limit is 0.001 mg/m^3. Its fluorescence intensity in solution is very much dependent on the pH. At pH lower than 6, the intensity tends to zero. Uranine is an anionic tracer, and it is adsorbed by clay minerals only to a minor extent. It has also good temperature stability which is important for analytics (a temperature increase in the instrument) and for injection, for example, into thermal systems. From

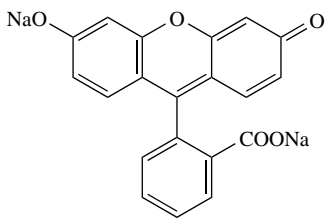


Figure 4. Molecular structure of uranine.

the view point of toxicity, it is not dangerous to humans or animals, in particular, at concentrations normally used in tracing experiments.

Eosin. Eosin ($C_{20}H_6Br_4Na_2O_5$, Acid Red 87) (Fig. 5) is a powder made of red crystals of a bluish tinge. A concentrated aqueous solution is deep brownish-red, dilute solutions are yellowish-red with a greenish fluorescence. The fluorescence is visible in more concentrated solutions (above 10 ppb).

It is very soluble in water, less in alcohol, and insoluble in ether. At high concentrations, fluorescent light is absorbed by the sample itself. For an exact analysis, the concentration should not be higher than 100 ppb, otherwise, dilution is recommended. Its solubility is 300 g/L and the detection limit is 0.01 mg/m^3. The pH effect for eosin is not as significant as that for uranine. Eosin is an anionic tracer and is generally little adsorbed by clay minerals. It can be used in karstic systems as well as in porous groundwater aquifers. It is not dangerous to humans or animals.

Among other fluorescent dyes, sulforhodamine G, Sulforhodamine B, rhodamine WT, rhodamine B, and pyranine are used most groundwater tracing.

Tracing Experiment

While planning a tracing test, there are some factors that must be considered. First, the objectives of the study should be defined well because they affect other study components such as selecting the tracer. Then all available resources (labor, money, time,) should be considered to facilitate formatting the program. Third, all relevant information and data (maps, reports, well logs) should be available so that a good idea of the geology and hydrogeology of the site is gained.

The general direction of groundwater flow and also its velocity should be estimated before starting the test, which will allow configuring the injection and sampling network effectively.

Different Phases of the Test

Planning and General Assessment. Before starting a tracing test, the test site should be visited and examined carefully, which is to schedule the program activities and other components of the work such as selecting the injection and sampling points, selecting the tracer (which is among the most important and critical components of the work), designing the sampling program, transportation (equipment, tracers, personnel, etc.

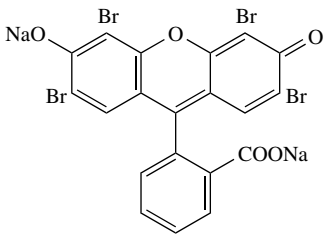


Figure 5. Molecular structure of eosin.

Tracer Injection. By injecting the tracer into the aquifer, it will enter the hydrologic cycle and (it is assumed that) will travel in the same manner as water. The injection method varies with the type of tracer, study purpose, site conditions, etc.

Sampling. Sampling is done for the purpose of analyzing water to find if there is tracer in it. Actually the sampling work starts before injecting the tracer because there might be some background concentration of the tracer in the water; this is called background sampling.

Because of the very high dissemination potential of fluorescent tracers, it is very important to avoid any contact between injecting personnel/equipment and sampling. The sampling time interval for each sampling point should be scheduled according to the hydrogeologic factors and distance to the injection point.

Analysis. All samples should be carefully packed and sent to the lab to be analyzed as soon as possible. The analytical method and the instrumentation for measuring the fluorescence of the samples are discussed following. As mentioned before, concentrations higher than 10 ppb of most fluorescent dyes may be visible and can be detected without any instrument.

Detection with a Two Monochromator Spectrofluorometer. To analyze for tracers, the best method is to use a spectrofluorometer with monochromators for excitation and emission (Fig 6). The light of the excitation source is transmitted through a filter of maximum transmittance near or at the absorption maximum of the dye. The dye molecules in the solution will be excited, and the fluorescence can then be dispersed by a secondary filter or a monochromator (prism or grating). Table 1 is a summary of spectral data of some fluorescent dyes, and Table 2 is a summary of their approximate detection limits in water. The final result of an analysis is a time–concentration (or breakthrough) curve, which presents the temporal evolution of the sampling point tracer concentration (Fig. 7).

Interpretation of Results. With regard to the breakthrough curve plotted for each sampling point, one should

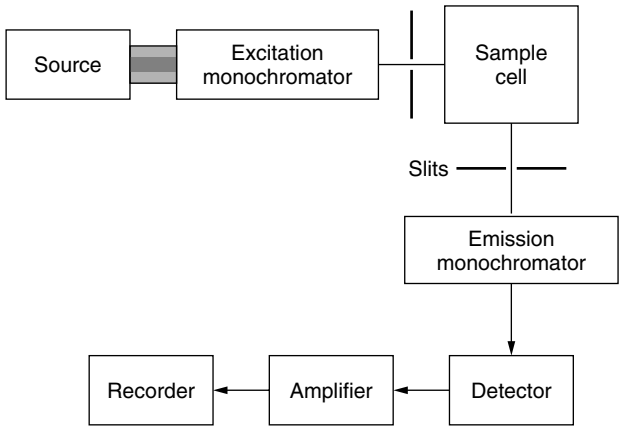


Figure 6. Scheme of a spectrofluorometer.

Table 1. Summary of Spectral Data of Some Fluorescent Dyes

Dye	Fluorescent Excitation	Fluorescent Emission	Wavelength Difference (nm)
Uranine	491.0	512.5	21.5
Eosin	515.5	536.0	20.5
RhodamineB	553.5	576.0	22.5
Pyranine	463.5	512.5	49.0

Table 2. Summary of Approximate Detection Limits for some Fluorescent Dyes

Dye	Limit of Detection (mg/m^3)
Uranine	0.001–0.025
Eosin	0.050–0.5
Rhodamine B	0.010–0.5
Pyranine	0.008–0.5

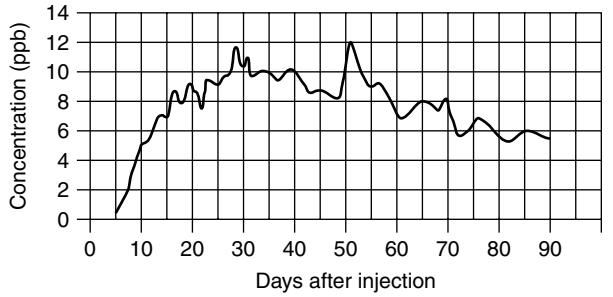


Figure 7. The breakthrough curve for a spring in the Tang-e Shemiran area, western Iran.

first of all focus on the first arrival time of the tracer. It reveals first, that there is an underground hydraulic connection between the injection point and the sampling point and, second, the maximum groundwater flow velocity in that zone. The peak concentration also leads to the average transit time. The shape of the curve is a guide to the approximate volume of water in which the tracer has been diluted. The area under the curve is equivalent to the total mass of tracer recovered from the sampling point (e.g., a spring). The summation of this figure for all sampling points should be close to the injected amount. Otherwise, there is another outlet for the aquifer which was unknown during planning.

READING LIST

Benischke, R. (2002). *Fluorescent Tracers in Hydrology*. Institute of Hydrogeology and Geothermics, Graz, Austria, p. 60.

Davis, S.N. (1985). *Groundwater Tracers*. National Groundwater Association, Westerville, OH, p. 200.

Ighanian, R. (1977). *Hydrochemical Studies of Tehran Plain*. Ministry of Energy, Tehran, Iran, p. 32.

Jahani, H.R. (2000). Groundwater Tracing in Tang-e Shemiran, *Western Iran*. Water Research Center, Tehran, Iran, p. 85.

Jahani, H.R. (1998). *Groundwater Tracing and Isotope Hydrological Studies in Rudbar-e Lorestan Area, Iran*. Water Research Center, Tehran, Iran, p. 83.

Standards Office. (2003). *Standard Guidelines on Groundwater Tracing in Karst and Hardrock Formations (Draft Edition-Farsi)*. Iranian Ministry of Energy, Tehran, Iran, p. 60.

HYDRAULIC CONDUCTIVITY/ TRANSMISSIBILITY

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Hydraulic conductivity is a fundamental parameter that governs the flow of liquids such as groundwater through aquifers and other porous media. Specifically, hydraulic conductivity is a quantitative measure of the capacity of a geologic formation or other porous media to transmit a specific fluid. It is determined by the characteristics of both the porous medium and the fluid of interest.

Transmissibility (or transmissivity) is a property closely related to hydraulic conductivity that describes the capacity of a specific water-bearing unit of a given thickness, such as an aquifer, to transmit water. Transmissibility is most simply defined as the effective hydraulic conductivity of an aquifer or other water-bearing unit multiplied by the thickness of that unit.

ORIGINS IN DARCY'S LAW

The concept of hydraulic conductivity dates back to Henry Darcy's famous 1856 paper regarding the water supply for the city of Dijon, France. In that paper, Darcy described the results of laboratory experiments that he had conducted to investigate the flow of water through sand. From the results of those experiments came the relationship now referred to as Darcy's law, it is valid for laminar flow conditions that occur in most groundwater systems and can be expressed as

$$Q = -K\frac{\partial h}{\partial l}A \tag{1}$$

where Q = volumetric flow rate (L^3/t)
K = hydraulic conductivity (L/t)
$\frac{\partial h}{\partial l}$ = hydraulic gradient (L/L)
A = Cross-sectional area perpendicular to the flow direction (L^2)

As evident from Eq. 1, the volumetric flow of a fluid through a porous medium is directly proportional to the coefficient K; Darcy recognized that it is dependent on the type of soil through which water flows. For this reason, the coefficient K has historically been referred to as Darcy's coefficient of proportionality. Today, the coefficient K is more commonly called hydraulic conductivity.

RELATIONSHIP TO PERMEABILITY

It is intuitive that the flow of a liquid through soil also depends on the characteristics of the liquid. For example, if all other factors are equal, the volumetric flow rate (Q in Darcy's equation above), and hence the hydraulic conductivity, will be greater for water than for a more viscous liquid such as a heavy oil.

The relationship of hydraulic conductivity (K) to permeability (k)[1] is useful in distinguishing the effects of the porous medium from the effects of the fluid:

$$K = \frac{k\rho g}{\mu} \tag{2}$$

where ρ = density of fluid;
μ = dynamic viscosity of fluid; and
g = gravitational acceleration constant.

Permeability k is a function only of the medium and is commonly used in petroleum studies where various fluids of differing characteristics such as oil, water, and natural gas may be present together in multiphase flow systems.

From Eq. 2, it is clear that hydraulic conductivity is a function of the characteristics of the fluid as well as the permeability of the medium (k).[2] Specifically, a soil with a given permeability will exhibit relatively greater hydraulic conductivity to fluids of lower viscosities and/or greater densities.

Rearranging Eq. 2 also allows determining the hydraulic conductivity to one fluid if the hydraulic conductivity to another is known:

$$K_1 = K_2 \frac{\mu_2}{\mu_1} \frac{\rho_1}{\rho_2} \tag{3}$$

where K_1, μ_1, and ρ_1 are properties of fluid 1 and K_2, μ_2, and ρ_2 are properties of fluid 2.

UNITS OF MEASUREMENT

The units of hydraulic conductivity are (L/t), and the units of permeability are (L^2). In the context of groundwater flow, the units of permeability are sometimes expressed as "darcys"; one darcy approximately equals 1×10^8 cm^2. Conversion factors for commonly used units of hydraulic conductivity and permeability are provided in Table 1. For most applications, the viscosity and density of water vary over a narrow range, and permeability values can be converted to hydraulic conductivity (of water), assuming standard temperature and pressure, without introducing significant error.

[1]In older publications, K was sometimes referred to as the coefficient of permeability and, therefore, k become known as "specific" permeability or "intrinsic" permeability to differentiate it from K. More recently, it has become conventional to refer to K as hydraulic conductivity, allowing k to be referred to simply as permeability.

[2]It is common practice in groundwater hydrology publications to use the term hydraulic conductivity as it relates to water, unless a different fluid is specified.

Because transmissibility is defined as hydraulic conductivity multiplied by aquifer thickness, its units are (L^2/t), often expressed as volume per unit width of the aquifer per unit time (e.g., gallons per day per foot or gpd/ft).

REPRESENTATIVE HYDRAULIC CONDUCTIVITY VALUES

Local hydraulic conductivity values can vary over an extremely wide range. Ranges in representative values of hydraulic conductivity for various geologic media are summarized below.

Figure 1 illustrates that hydraulic conductivity values may range over approximately 12 orders of magnitude, depending on the type of soil or rock. Even for specific types of geologic deposits, variations over several orders of magnitude are not uncommon.

In general, geologic deposits that exhibit the lowest hydraulic conductivity values are fine-grained unconsolidated materials (e.g., clays) and unfractured sedimentary and crystalline rocks. The presence of fractures in either consolidated or unconsolidated materials of otherwise low permeability can significantly increase the hydraulic conductivity of these materials.

Geologic deposits that exhibit the highest hydraulic conductivity values are typically coarse-grained unconsolidated materials (e.g., coarse sands and gravels) and rocks that are highly fractured or otherwise exhibit significant secondary permeability (e.g., solution-enhanced void space in carbonate formations or basalt shrinkage cracks).

GEOLOGIC FACTORS INFLUENCING HYDRAULIC CONDUCTIVITY

For unconsolidated materials, the factors that have the greatest influence on hydraulic conductivity are generally particle size and particle sorting. It can be theoretically shown that hydraulic conductivity is proportional to the square of the particle diameter for a uniform, porous medium, that is, doubling the particle diameter results in quadrupling hydraulic conductivity. In practice, however, geologic formations are not uniform but contain particles of varying sizes, and the definition of a representative particle diameter is not clear-cut. In general, poorly sorted deposits (i.e., those with greater variation in particle sizes) will exhibit lesser relative hydraulic conductivity compared to that of well-sorted deposits, due to infilling of pore space by finer grained particles.

In consolidated crystalline and sedimentary rocks, the hydraulic conductivity of the rock matrix tends to be low to extremely low. Transmission of water through these rocks is generally via interconnected voids such as fractures, solution channels, shrinkage cracks or metamorphic (e.g., schist) foliations. Transmission of water through such voids is said to occur via "secondary permeability."

HETEROGENEITY AND ANISOTROPY

Geologic depositional environments typically exhibit significant variability across very short distances. As a result, hydraulic conductivity values generally exhibit

Table 1. Hydraulic Conductivity and Permeability Conversion Factors[a]

		Hydraulic Conductivity					Permeability	
	Multiply / To obtain	cm/s by	m/s by	ft/s by	ft/day by	US gal/day/ft^2 by	cm^2 by	Darcy by
Hydraulic Conductivity	cm/s	1	100	30.48	3.53E−04	4.72E−05	9.71E+04	9.66E−04
	m/s	0.01	1	0.305	3.52E−06	4.72E−07	9.71E−02	9.66E−06
	ft/s	3.28E−02	3.28	1	1.16E−05	1.55E−06	3.19E+03	3.17E−05
	ft/day	2.84E+03	2.84E+05	8.64E+04	1	0.134	2.75E+08	2.74
	US gal/day/ft^2	2.12E+04	2.12E+06	6.45E+05	7.48	1	2.06E+09	1.48E+01
Permeability	cm^2	1.03E−05	1.03E−03	3.14E−04	3.63E−09	2.71E−08	1	9.87E−09
	Darcy	1.04E+03	1.04E+05	3.15E+04	3.65E−01	2.72	1.01E+08	1

[a] Conversions between units of hydraulic conductivity (K) and permeability (k) assume the properties of water at approximately 15 °C.

spatial variation across several orders of magnitude within an area of hydrogeologic interest.

The terms *heterogeneity* and *anisotropy* are often employed to describe variability in hydraulic conductivity. Heterogeneity refers to variability in space, and anisotropy refers to variability in direction from a given point. Figure 2 illustrates the relationship between heterogeneity and anisotropy.

The distinction between anisotropy and heterogeneity often depends on scale and context. For example, on one scale, layered heterogeneity (see Fig. 4) may require consideration as a series of distinct geologic formations that have different representative hydraulic conductivity values. On another scale, it may be more convenient and appropriate to describe this system as one anisotropic layer.

Heterogeneity

A porous medium of uniform characteristics is said to be homogenous. In reality, no geologic system is truly homogenous with respect to hydraulic conductivity. Each system exhibits varying types and degrees of heterogeneity. An illustration of actual heterogeneity is shown in Fig. 3. This two-dimensional cross-section was created from more than 700 measurements within an area approximately 2 meters deep by 20 meters long within the intensely studied Borden aquifer, which is generally recognized as "mildly" heterogenous compared to most groundwater systems. Even in this small area of a relatively uniform aquifer, measured hydraulic conductivity values range across approximately three orders of magnitude.

In some cases, heterogeneity in hydraulic conductivity values may exhibit one or more measurable trends due to geologic conditions. Freeze and Cherry (2) identified three types of common heterogeneity patterns: trending, discontinuous, and layered.

Trending heterogeneity refers to spatial trends resulting from, for example, gradational coarsening or fining depositional sequences such as those that typically result from encroaching or receding seas. Trending heterogeneity may also result from postdepositional processes such as vertical trends in rock fracture frequency.

Discontinuous heterogeneity refers to an abrupt change in local hydraulic conductivity values, such as those across a geologic discontinuity, fault, or other sharp stratigraphic contact.

Layered heterogeneity is a commonly encountered type of heterogeneity, particularly for unconsolidated or consolidated sedimentary sequences formed in time-varying depositional environments. An idealized example of layered heterogeneity is illustrated in Fig. 4. A more realistic depiction of layered heterogeneity is illustrated in the Borden aquifer hydraulic conductivity plot depicted in Fig. 3.

In reality, distinguishing between types of heterogeneities is often difficult. For example, layered heterogeneity may be considered a series of discontinuous heterogeneities. In addition, multiple patterns in heterogeneity may be present at any given location.

Anisotropy

If hydraulic conductivity is independent of the direction of measurement, the medium is described as isotropic; if, however, the hydraulic conductivity value depends on the direction of measurement, it is considered anisotropic. Mathematically, hydraulic conductivity is represented as

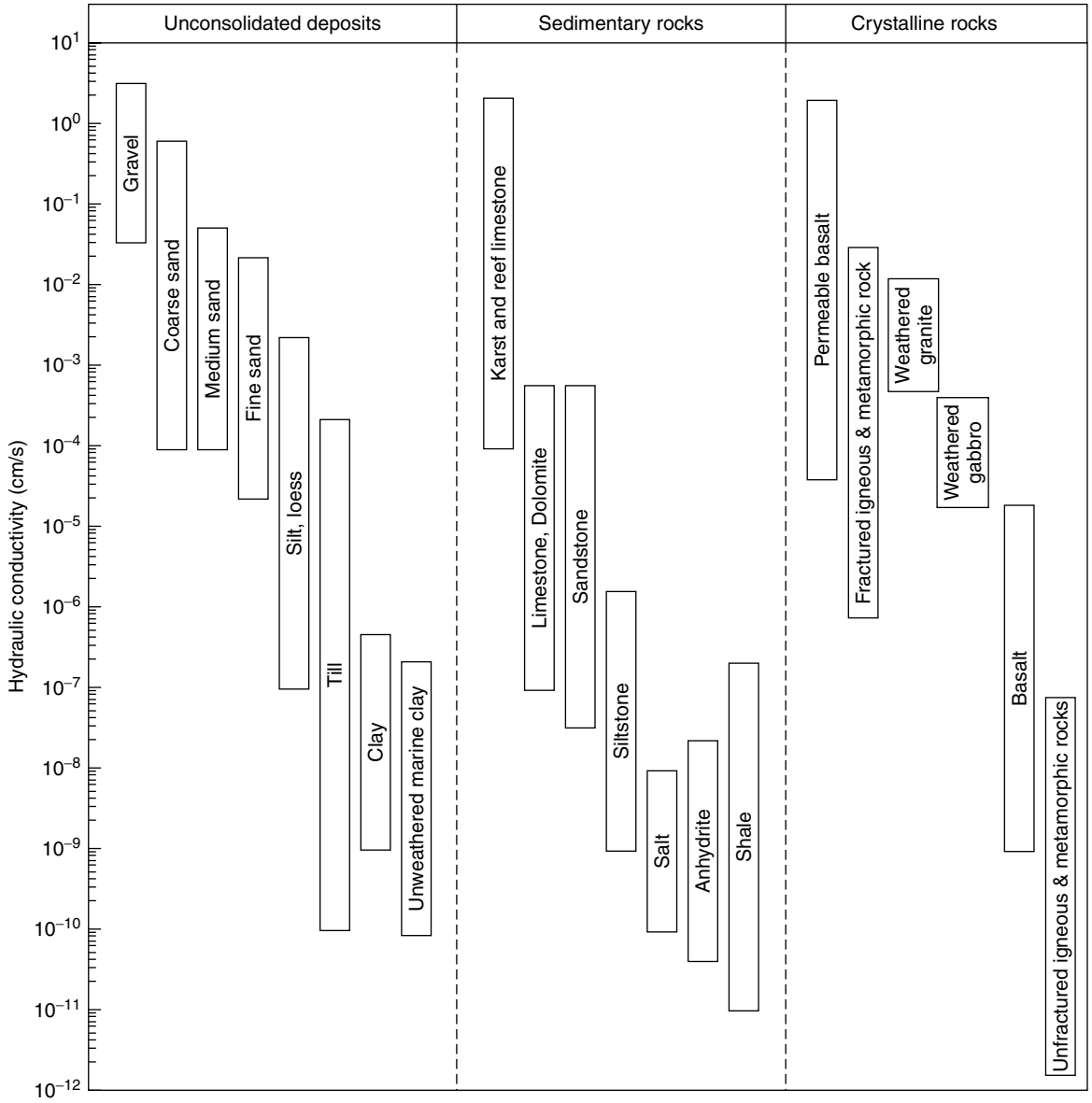


Figure 1. Representative values of hydraulic conductivity for various rock types (adapted from: Ref. 1).

a scalar (direction-independent) variable in the form of Darcy's law presented in Eq. 1 In anisotropic settings, hydraulic conductivity must be considered a tensor variable, leading to more complex forms of Darcy's law and other equations that describe the flow of groundwater and other fluids through porous media.

On a small scale, anisotropy can result from mineral grain orientation. On a larger scale, anisotropy can result from sedimentary bedding planes, metamorphic structure (e.g., shistocity) or directional fracturing of crystalline rocks resulting from postdepositional stresses.

In sedimentary deposits of horizontal or near-horizontal orientation, hydraulic conductivity is frequently greater in the lateral directions compared to the vertical direction. On a small scale, such anisotropy may be relatively modest. Freeze and Cherry (2) report ratios of horizontal hydraulic conductivity (K_h) to vertical hydraulic conductivity (K_v) between 3:1 and 10:1 for clays and shales due to mineral grain orientation. On a larger scale, however, K_h:K_v anisotropic ratios for sedimentary deposits may be extremely high due to stratified deposits of greatly different characteristics. High K_h:K_v anisotropic ratios for stratified deposits are not surprising, considering the large differences in typical hydraulic conductivities of coarse-grained and fine-grained deposits, which may differ by several orders of magnitude.

EFFECTIVE HYDRAULIC CONDUCTIVITY: STATISTICAL TREATMENT OF HYDRAULIC CONDUCTIVITY VALUES

Groundwater hydrologists have used a variety of techniques to characterize the spatial variability of hydraulic conductivity values and to assess groundwater flow in

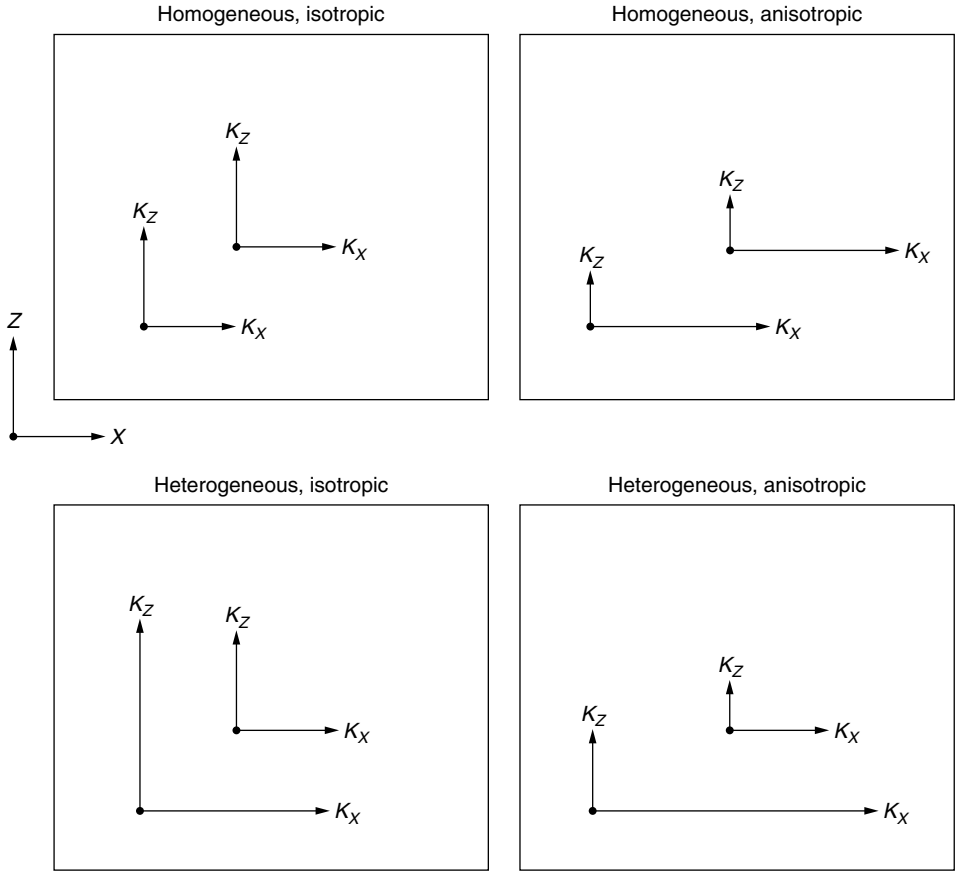


Figure 2. Four possible combinations of heterogeneity and anisotropy (adapted from Ref. 2).

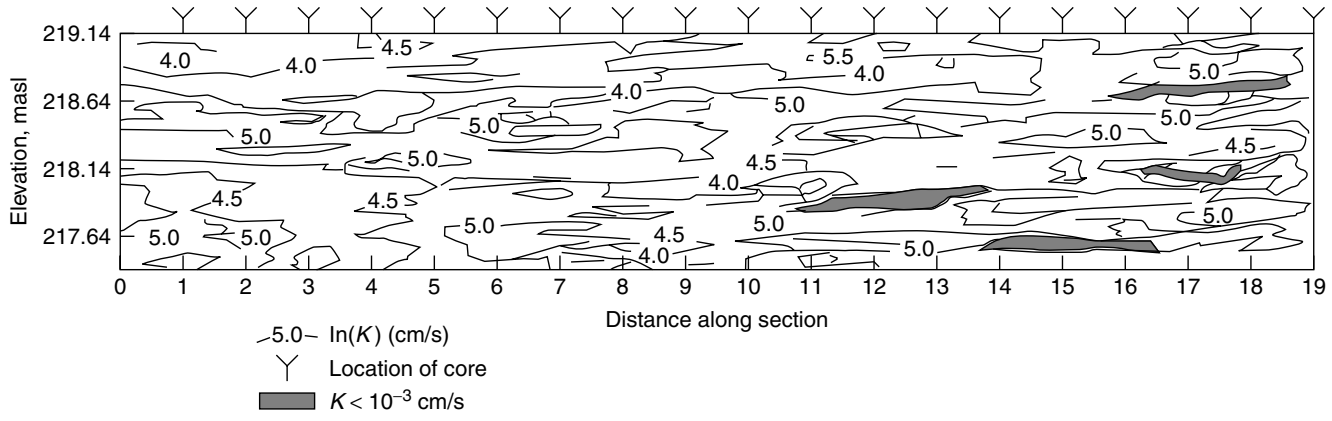


Figure 3. Hydraulic conductivity distribution at Canadian Forces Base Borden (from Ref. 3, v. 22, p. 2069–2082).

heterogenous geologic settings. One such approach is to identify an "effective" hydraulic conductivity that, applied to a heterogenous water-bearing geologic unit, will allow an accurate representation of its ability to transmit water as a whole.

Consider horizontal groundwater flow through an idealized layered geologic system such as that shown in Fig. 4 where the a number of layers equals n. The total flow through the system (Q) is equal to the sum of the flow in all layers (ΣQ_i). From Darcy's law, this can be expressed as

$$Q = \sum Q_i = \sum K_i \frac{dh}{dx} D_i W \tag{4}$$

where

K_i = hydraulic conductivity of layer i,
dh/dx = horizontal hydraulic gradient (assumed uniform in all layers),
D_i = thickness of layer i, and
W = unit width.

For combined flow through the layered system, an effective horizontal hydraulic conductivity ($K_{\text{H-EFF}}$) can be defined for groundwater flow such that

$$Q = K_{\text{H-EFF}} \frac{dh}{dx} DW \tag{5}$$

From Eqs. 4 and 5, the following relationship for $K_{\text{H-EFF}}$ is obtained:

$$K_{\text{H-EFF}} = \frac{\sum K_i D_i}{D} \tag{6}$$

This shows that, for flow parallel to the idealized layered system shown in Fig. 4, $K_{\text{H-EFF}}$ is equivalent to the arithmetic mean of K_i weighted by the thickness of each layer D_i. If all layers are of the same thickness (or all K values are uniformly distributed), $K_{\text{H-EFF}}$ is equal to the arithmetic mean of the individual K_i values.

Consider, however, vertical groundwater flow through the same system. Using a similar analysis, it can be shown that the effective horizontal conductivity in the vertical direction ($K_{\text{V-EFF}}$) is equal to

$$K_{\text{V-EFF}} = \frac{D}{\sum D_i / K_i} \tag{7}$$

If all layers are of equal thickness (or are uniformly distributed), $K_{\text{V-EFF}}$ for the idealized layered system is equivalent to the harmonic mean of K_i values, which is always lower than or equal to the arithmetic mean.

These two simplified conceptual models represent two extreme possibilities of flow uniformly parallel to or perpendicular to geologic layers, respectively. Therefore, the arithmetic and harmonic means of a population of hydraulic conductivity values are generally considered to be upper and lower bounding values, respectively, for the effective hydraulic conductivity of a heterogenous geologic system with respect to groundwater flow through that system.

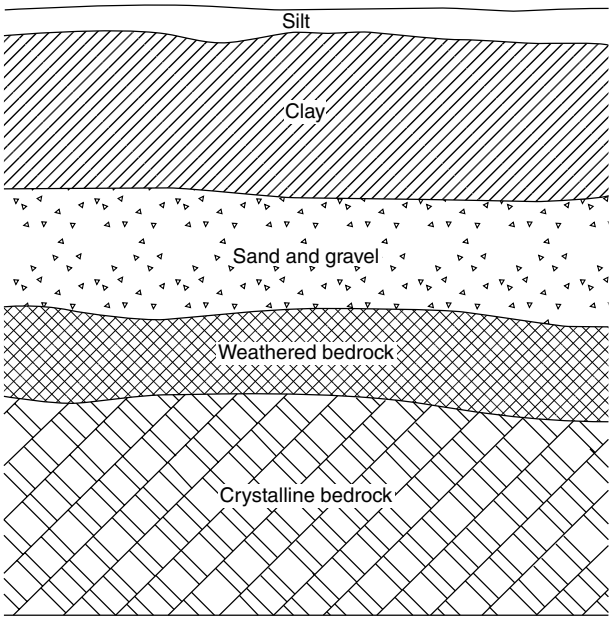


Figure 4. Example of layered heterogeneity.

Frequently, hydraulic conductivity values and well yields within a specific geologic setting are best characterized by a log-normal distribution. As such, the geometric mean is often preferred as a descriptive statistic for the central tendency (e.g., median and mode) of a population of log-normally distributed hydraulic conductivity values. Further, several studies have concluded that the geometric mean provides a better estimate of the effective hydraulic conductivity of a heterogenous groundwater system than the harmonic mean or arithmetic means, which are less than and greater than the geometric mean, respectively.

The preceding provides a simplified discussion of common statistical treatments for hydraulic conductivity values. In recent decades, much work has been conducted to apply more complex statistical models and stochastic techniques to characterize groundwater flow through heterogenous systems.

METHODS OF ESTIMATION AND MEASUREMENT

Empirical Relationships

Several efforts have been made over the years to correlate hydraulic conductivity and/or permeability empirically with characteristics of porous media through which water flows. Some of the more commonly used relationships are provided in Table 2.

Although such empirical relationships correlate hydraulic conductivity with various factors, nearly all can be simplified to the form

$$K = Cd^x \tag{8}$$

where C is a constant or shape factor that is a function of the fluid density and viscosity and may be correlated with properties of the porous medium such as porosity and d is some representative grain size (L). It has been mathematically shown (e.g., by Ref. 5) that for idealized systems of uniform grain size, $x = 2$. For all the empirical relationships shown in Table 2, x ranges between 1.5 and 2, which indicates a disproportionate increase in hydraulic conductivity as grain size increases, but suggests an exponent value of something less than 2 for many real-world situations.

Laboratory Testing

The hydraulic conductivity of geologic deposits can be measured in the laboratory by using a permeameter, a device similar to that originally devised by Darcy. Various configurations of permeameters have been used; the most common are the constant-head permeameter and the falling-head permeameter shown in Fig. 5.

Permeameters consist of a chamber to contain a sample of soil or rock and allow the application of a hydraulic gradient across the sample. Flow through the sample is measured, and hydraulic conductivity is calculated based on principles founded by Darcy. Careful consideration must be used in evaluating permeameter test data. For example, when testing unconsolidated material, was the

test conducted on an intact core or on a repacked sample? If the former, the test likely represents the vertical hydraulic conductivity, which may be much lower than the horizontal hydraulic conductivity. If the latter, the disturbance of the sample during repacking may result in a value that is neither representative of the horizontal nor the vertical hydraulic conductivity.

Field Measurements—Aquifer Tests

Hydraulic conductivity and transmissibility on a larger scale are estimated by evaluating data from aquifer tests. There are many different types of aquifer tests and methods for evaluating the test results, but the most common types of tests employed in groundwater studies are pumping tests and slug tests.

Pumping tests involve pumping water from a well at a known rate and measuring the changes in water level through time at the pumping well and/or nearby observation points. Slug tests involve rapid introduction or removal of a volume of water or other material into or out of a well and measuring the changes in water level through time at the well being tested.

Table 2. Examples of Empirical and Semiempirical Relationships for Estimating Hydraulic Conductivity and Permeability[a]

Source	Equation		Parameters
Hazen (1911)	$K = Cd_{10}{}^2$		K = hydraulic conductivity (cm/s) C = constant; 100 to 150 $(\text{cm/s})^{-1}$ for loose sand d_{10} = effective grain size (cm) (10% particles are finer, 90% coarser)
Harleman et al. (1963)	$k = (6.54 \times 10^{-4})\, d_{10}{}^2$		k = permeability, cm^2 d_{10} = effective grain size, cm (10% particles are finer, 90% coarser)
Krumbein and Monk (1943)	$k = 760\, d^2 e^{-1.31\sigma}$		k = permeability (Darcys) d = geometric mean grain diameter, mm σ = log standard deviation of the size distribution
Kozeny-Carmen Bear (1972)	$K = (\rho_w g/\mu) n^3/(1-n)^2 (d_m{}^2/180)$		K = hydraulic conductivity ρ_w = fluid density μ = fluid viscosity g = gravitational constant d_m = representative grain size n = porosity
Shepard (1989)	$K = 40{,}000\, d^2$	glass spheres	K = hydraulic conductivity, ft/day d = mean grain size, mm
	$K = 1{,}600\, d^{1.75}$	beach deposits	
	$K = 450\, d^{1.65}$	channel deposits texturally immature	
	$K = 100\, d^{1.5}$	consolidated sediments	

[a] Adapted from Refs. 1 and 4.

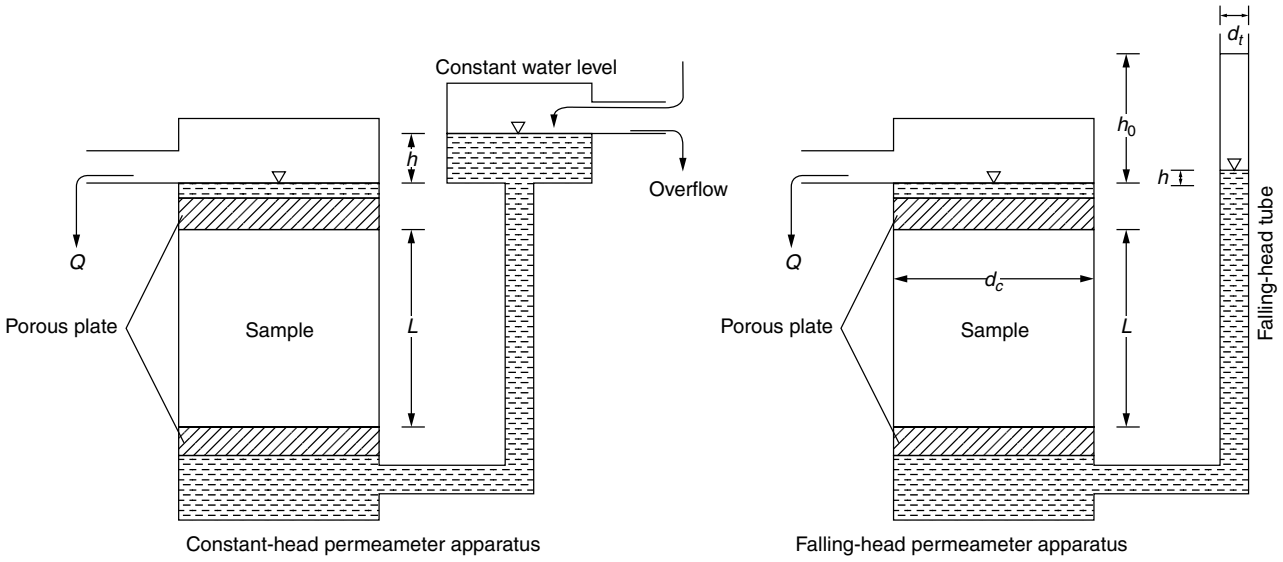


Figure 5. Permeameters (adapted from Ref. 4).

In general, pumping tests affect a significantly larger volume of the aquifer than slug tests, and the resulting hydraulic conductivity and transmissibility estimates are considered more representative of conditions across a broad area. Slug tests can be used to target specific zones and points within the aquifer but are generally considered "point estimates" of hydraulic conductivity and transmissibility.

BIBLIOGRAPHY

1. Domenico, P.A. and Schwartz, F.W. (1997). *Physical and Chemical Hydrogeology*. John Wiley & Sons, New York.
2. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
3. Sudicky, E.A. (1986). A natural gradient experiment on solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resour. Res*. **22**: 2069–2082.
4. Fetter, C.W. (1994). *Applied Hydrogeology*. Macmillan College Publishing Company, Inc., New York.
5. Hubbert, M.K. (1940). The theory of groundwater motion. *The Journal of Geology* **48**: 785–944.

GROUNDWATER FLOW AND TRANSPORT PROCESS

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INTRODUCTION

Groundwater is an important source of water for agriculture and domestic drinking water. Two-thirds of the world's freshwater is found in underground aquifers. Groundwater occurs mainly in the tiny spaces between soil particles that are called voids or pores. In its natural state, groundwater is perpetually moving. This movement is governed by conventional hydraulic principles such as Darcy's law, the concept of hydraulic gradient, and the permeability of the medium (1). With the increasing water demand due to population growth, management of water resources is becoming a challenging task. Management of groundwater resources must consider both sustainable development and prevention and control of groundwater contamination. Groundwater contamination is a critical issue because of the importance of groundwater supply and quality in sustainable development. In general, contaminants found in groundwater are associated with adverse health, social, environmental, and economic impacts (2). Exposure to contaminated groundwater may occur accidentally because contaminated water might be colorless, odorless, and tasteless. It is essential to understand groundwater flow and transport processes for the best management of groundwater resources, appraisal of the sustainable yield of aquifers, reliable evaluation of the extent of groundwater contamination, assessment of the corresponding hazards and risks, and design of effective remediation systems and protective alternatives.

This chapter provides an overview of the main principles of groundwater flow and transport processes, including the basic concepts, definitions and terms, physical governing equations, and mathematical modeling.

VERTICAL DISTRIBUTION OF SUBSURFACE WATER

The subsurface occurrence of water may be divided into zones of aeration and saturation (see Fig. 1). The zone of aeration is partially occupied by water and partially by air. In the zone of saturation, all pores are filled with water. The zone of aeration may be further subdivided into the soil–water zone, the intermediate vadose zone, and the capillary zone (see Fig. 1).

The saturated zone extends from the upper surface of saturation down to underlying impermeable rock. In the absence of an overlying impermeable formation, the water table forms the upper surface of the zone of saturation, which is defined as the surface of atmospheric pressure. Water in the soil–water zone exists at less than saturation except temporarily when excessive water reaches the ground surface from rainfall or irrigation. The zone extends from the ground surface down through the major root zone. The water content and distribution within this zone depends on soil texture, vegetation, and atmospheric conditions. The intermediate vadose zone extends from the lower edge of the soil–water zone to the upper limit of the capillary zone. The capillary zone extends from the

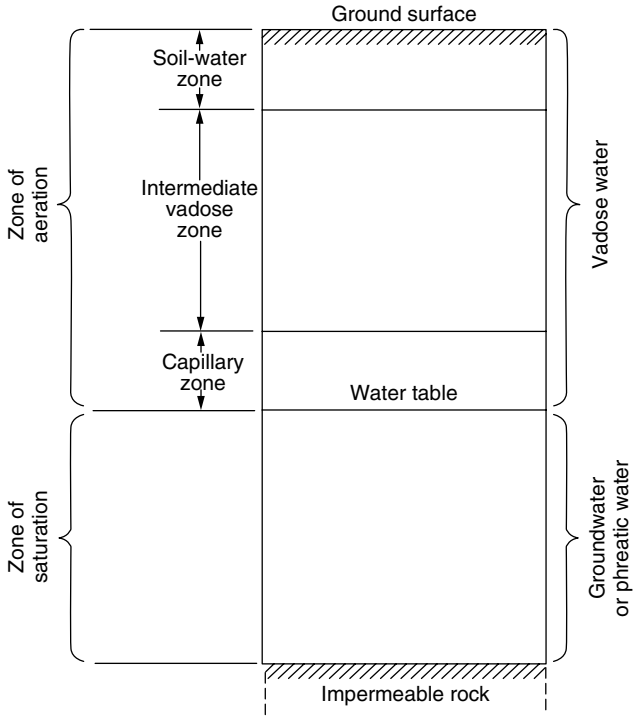


Figure 1. Illustration of saturated and unsaturated zones (1).

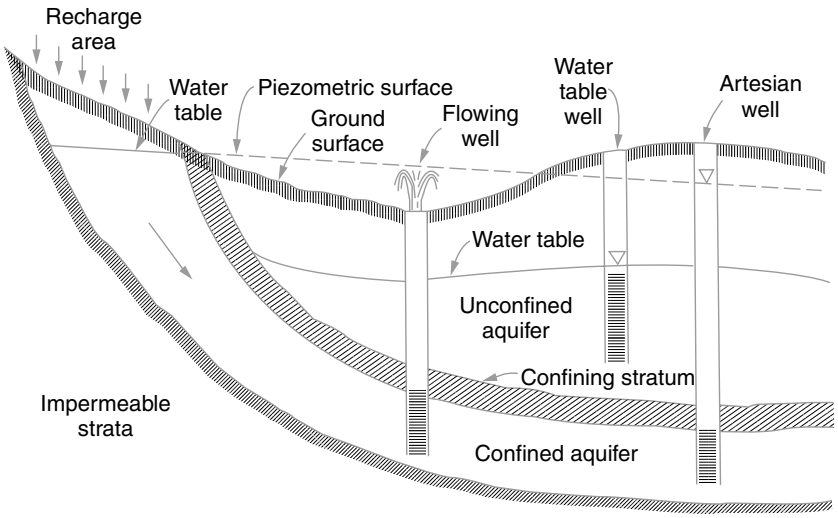


Figure 2. Schematic cross section of unconfined and confined aquifers (1).

water table up to the limit of capillary rise of water. The thickness of the capillary zone varies inversely with the pore size of a soil.

AQUIFER TYPES

An aquifer is a formation that contains sufficient saturated permeable material to yield significant quantities of water to wells and springs (3). Therefore, aquifers have the ability to store and transmit water. Aquifers might be bounded by confining beds that are relatively impermeable materials located adjacent to the aquifers. Confined aquifers occur where groundwater is confined under pressure greater than atmospheric by overlying relatively impermeable formations. In a well penetrating such an aquifer, the water level will rise above the bottom of the confining bed, as shown by the artesian and flowing wells of Fig. 2. Unconfined aquifers do not have confining beds above and the aquifer can be directly recharged by rainfall (see Fig. 2). An unconfined aquifer is one in which the water table varies in a rising and falling form.

DARCY'S LAW

In 1856, the French engineer, Henry Darcy, developed the principal equation in groundwater hydrology based on laboratory experiments he had carried out to analyze the flow of water through sand. Darcy's law can be written as

$$Q = -KA\frac{dh}{dl} \tag{1}$$

Q is the quantity of water per unit of time (L^3/T), A is the area perpendicular to flow (L^2), K is a constant of proportionality called the hydraulic conductivity (L/T), h is the hydraulic head (L), and dh/dl is the hydraulic gradient. The hydraulic conductivity expresses the ease by which water can pass through soil pores and openings and serves as a measure of the permeability of the porous medium. The hydraulic conductivity of a soil is a function of the properties of the porous medium and the fluid passing through it. In addition to hydraulic conductivity, the term transmissivity T (L^2T^{-1}) is widely employed in groundwater hydraulics. Transmissivity equals the hydraulic conductivity multiplied by the saturated thickness of the aquifer.

Darcy flux or specific discharge is given by the following relationship:

$$q = \frac{Q}{A} = -K\frac{dh}{dl} \tag{2}$$

The specific discharge q has the dimensions of velocity (L/T). Finally, the cross-sectional area of flow for a porous medium is actually much smaller than the dimensions of the aquifer. To find the velocity at which water is actually moving, the specific discharge is divided by the effective porosity to account for the actual open space available for flow. The result is the average velocity at which water moves between two points as in the following equation:

$$v = \frac{q}{n_e} = \frac{Q}{n_e A} = -\frac{Kdh}{n_e dl} \tag{3}$$

STORAGE IN CONFINED AND UNCONFINED AQUIFERS

Storage in confined aquifers is associated with the compressibility of water and the porous matrix. The change in the potentiometric head affects the arrangement of mineral grains as well as the density of water in the voids. If the water pressure increases, the mineral skeleton will expand; if it drops, the mineral skeleton will contract. Likewise, water will contract with an increase in pressure and expand if the pressure drops. The specific storage (S_s) is the amount of water per unit volume of a saturated formation that is stored or expelled from storage owing to compressibility of the mineral skeleton and the pore water per unit change in head. The value of specific storage is very small, generally 0.0001 ft^{-1} or less. In unconfined aquifers, pumpage causes drawdown in the water table itself, and the induced hydraulic gradient causes both a horizontal and vertical flow component. Thus, the drop in the water table creates a vertical hydraulic gradient which causes drainage of the porous medium (3–7).

The storativity (S) of a confined aquifer is the product of the specific storage S_s and the aquifer thickness. The value of the storativity of confined aquifers is of the order 0.005 or less. Storativity under unconfined conditions is referred to as the specific yield, defined as the ratio of the volume of water an unconfined aquifer drains by gravity due to the unit decline in the water table to the total volume of the aquifer. The coarser the material, the more closely the specific yield approaches the porosity. The volume of water drained from an aquifer as the head is lowered may be found from the formula,

$$V_w = S\,A\,\Delta h \tag{4}$$

where V_w is the volume of water drained or released (L^3), S is the storativity (L^0), A is the surface area overlying the drained aquifer (L^2), and Δh is the average decline in head (L). Note that Δh for a confined aquifer is the decline in the potentiometric head and for unconfined aquifers is the decline in the water table.

MATHEMATICAL MODEL OF GROUNDWATER FLOW

Groundwater flow is described using Darcy's law and the mass conservation equation. The governing equation, describing transient groundwater flow in a three-dimensional flow domain, is given as

$$\frac{\partial}{\partial x}\left(K_x\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_y\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_z\frac{\partial h}{\partial z}\right)+W'=S_s\frac{\partial h}{\partial t} \tag{5}$$

where K_x, K_y, K_z are the hydraulic conductivity values in the x, y, and z coordinates, respectively; S_s is the specific storage; t is time; h is the hydraulic head; and W' is the source or sink strength in units of volume/time/area. To solve Eq. 5, initial and boundary conditions should be specified for the study area. Solving this equation yields the head distribution in time and space. Computer codes can be used to solve Eq. 5 numerically. MODFLOW developed by the U.S. Geological Survey (8), is one of the most commonly used groundwater softwares for solving one-, two-, or three-dimensional groundwater flow problems. MODFLOW is divided into packages that deal with single simulation aspects. For example, the Well Package simulates the effects of injection and abstraction wells and the River Package simulates the effect of rivers, etc. The WWW address for MODFLOW model and documentation is: http://water.usgs.gov/sofware/ground_water.htm. A brief description of MODFLOW can also be found in Charbeneau (7).

SOURCES OF GROUNDWATER CONTAMINATION

There are three key features that differentiate groundwater contamination sources: (1) degree of localization, (2) loading history, and (3) types of contaminants. Sources of groundwater contamination can be classified into point and nonpoint sources. Point sources include leaking underground pipelines or tanks, wastewater lagoons, septic systems, and leaking barrels of chemical wastes. These sources are identifiable, located at single locations, and have local impacts on groundwater quality. Conversely, nonpoint sources are diffuse, originating from many smaller sources, largely distributed, lack a well-defined single point of origin, and have a regional influence on groundwater quality. Examples of nonpoint sources are agricultural activities such as fertilizer and manure applications; and polluted atmospheric deposition, including dry fallout, precipitation, and runoff from roads and parking lots. The loading history defines how the concentration of a contaminant or its rate of application changed with time at the source location.

TRANSPORT PROCESSES

The physical processes that control contaminant flux into and out of a groundwater system are advection, mechanical dispersion, and molecular diffusion. In the following subsections, the basic concepts related to these physical processes are illustrated.

Advection

Transport by advection or convection entails movement and carrying contaminants with flowing groundwater (6). In advective transport, contaminants travel at a rate equal to the average linear velocity of the groundwater (5). Mathematically, advective flux is expressed by the following equation (6):

$$J = v_x n_e C \tag{6}$$

where J_x is the advective mass flux (ML^2T^{-1}) per unit area per unit time, v_x is the average linear velocity of groundwater(LT^{-1}), n_e is the effective porosity through which flow occurs, and C is the contaminant concentration (ML^{-3}). The average linear velocity can be determined from Eq. 3. The product of the average linear velocity and time since contaminants were introduced into the groundwater system defines the position of the advective front, as depicted in Fig. 3, where the vertical line represents the advective front without considering the effects of dispersion and diffusion (6).

Diffusion

The movement of contaminants from an area of high concentration to an area of lower concentration is called molecular diffusion or diffusion. This diffusive flux is

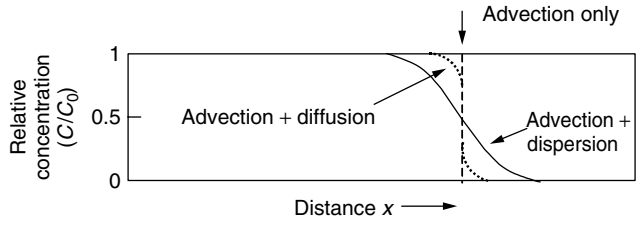


Figure 3. Advective transport and the influence of longitudinal dispersion and diffusion on the transport of a solute in one-dimensional flow.

directly proportional to the diffusion coefficient and the concentration gradient (9). This is known as Fick's first law and can be expressed in a one-dimensional system as in the following:

$$F_x = -D_d \frac{dC}{dx} \tag{7}$$

where F_x is the diffusive mass flux (ML^2T^{-1}), D_d is the diffusion coefficient for open water (L^2T^{-1}), C is the contaminant concentration (ML^{-3}); and dC/dx is the concentration gradient (ML^{-4}). The negative sign signifies that the diffusive flux is in the direction of decreasing contaminant concentration.

Mechanical Dispersion

Dispersion describes the gradual spreading of contaminants beyond the region they are expected to occupy when considering advection alone. The phenomenon of dispersion is attributed mainly to the discrepancy between contaminant velocities and the average linear velocity caused by subsurface heterogeneity (5,10,11). According to Fetter (3), this discrepancy is attributed to three key factors: (1) the velocity of groundwater flow is higher in the center of pores than at the edges, (2) the contaminants can pass through different flow paths to reach the same location, and (3) groundwater moves faster in large pores. Therefore, contaminants will dilute due to mixing with noncontaminated water. Mixing, called mechanical dispersion, may occur along the flow path, is called longitudinal dispersion, and is attributed to the aforementioned key factors. The groundwater flow path may diverge at the pore scale, so the contaminant will spread in directions normal to the flow path. This mixing is called *lateral* or *transverse dispersion* (3). The difference between the straight dashed line and the solid line in Fig. 3 depicts the influence of longitudinal dispersion on the transport of a contaminant. Molecular diffusion and mechanical dispersion contribute jointly to the dispersive process of contaminant transport. They are combined to define a coefficient called *hydrodynamic dispersion* as given in the following equations (6):

$$D_L = \alpha_L v_i + D^* \tag{8}$$

$$D_T = \alpha_T v_i + D^* \tag{9}$$

where D_L and D_T are the longitudinal and transverse hydrodynamic dispersion coefficients, respectively; and α_L and α_T are the longitudinal and transverse dispersivities, respectively.

Figure 4 illustrates the process of hydrodynamic dispersion in two-dimensional groundwater flow at a constant uniform velocity, V. A tracer was instantaneously injected into the aquifer at $t = 0$. The groundwater flow carries the tracer with it. Due to the effect of dispersion, the solute spreads out such that the maximum concentration decreases with time, as shown for times t_1 and t_2 when $t_2 > t_1$. The spread of the tracer results in an elliptically shaped concentration distribution that is normally distributed in both the longitudinal and transverse directions.

As mentioned earlier, longitudinal dispersivity or more specifically, dispersivity, is a scale-dependent property

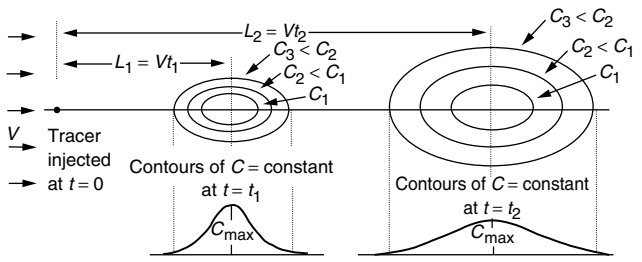


Figure 4. Longitudinal and transversal spreading of a tracer from an instantaneous point injection at $t = 0$.

that increases with the characteristic transport length distance of measurement. This phenomenon is attributed to the macroscale effects resulting from the heterogeneity of the subsurface on the field scale. Many researchers have developed relationships between longitudinal dispersivity and flow length (6,12–14). The ratio of longitudinal to transverse dispersivity (α_L/α_T) controls the shape of the contaminant plume. As the ratio decreases, the wider the plume will be (6). Bear (10) provided a range from 5 to 24 for α_L/α_T.

MATHEMATICAL MODEL OF CONTAMINANT TRANSPORT

The advection–dispersion–reaction partial differential equation that governs three-dimensional transport of a single chemical constituent in groundwater, considering advection, dispersion, fluid sinks/sources, equilibrium-controlled sorption, and first-order irreversible rate reactions, is given in the following (11):

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{n}C_s - \lambda\left(C + \frac{\rho_b}{n}S\right) \tag{10}$$

where the retardation factor is defined as

$$R = 1 + \frac{\rho_b}{n}\frac{\partial S}{\partial C} \tag{11}$$

and C is the dissolved concentration (ML^{-3}); S is the sorbed concentration (MM^{-1}) which is a function of the dissolved concentration, C, as defined by a sorption isotherm; t is time (T); D_{ij} is the dispersion coefficient tensor (L^2T^{-1}); v_i is the average linear groundwater velocity (LT^{-1}); q_s is the volumetric flow rate per unit volume of aquifer and represents fluid sources and sinks (T^{-1}); C_s is the concentration of the fluid source or sink flux (ML^{-3}); λ is the reaction rate constant (T^{-1}); R is the retardation factor (L^0); ρ_b is the bulk density of the porous medium (ML^{-3}); and n is the porosity (L^0). A complete derivation of this equation is provided in Freeze and Cherry (4) and Zheng and Bennett (11).

Solving time-dependent partial differential equations governing contaminant transport requires identification of the initial and boundary conditions. The initial condition describes the distribution of the contaminant in the groundwater within the domain at the beginning of simulation. The boundary conditions can be classified into three categories: (1) specified concentration boundary,

called the Dirichlet condition; (2) a specified concentration gradient boundary, called the Neuman condition; and (3) a variable flux boundary, called the Cauchy condition (5).

Solving the mathematical model yields the contaminant concentration as a function of space and time. The approach used in formulating and solving the mathematical model can be classified generally into numerical and analytical approaches. Analytical solutions of the advection–dispersion equations in one-, two-, and three-dimensional space can be found in Baetslé (14), Bear (10), Domenico (15), Domenico and Schwartz (5), and Fetter (6) among others.

Numerical methods provide an approximate solution of the mathematical model by solving a set of algebraic equations that replace the original partial differential equations. Numerical solutions are widely used and preferred because they have the capability to handle more general conditions. Numerical methods for solving the advection–dispersion–reaction equation divide the model domain into small cells, approximate the governing equation over each cell at time t, and then predict a new value at time $t + \Delta t$. This process continues forward in time for small Δt values. The most common numerical methods for solving the advection–dispersion–reaction equation include the finite-difference method, the finite-element method, and the random walk method. A detailed illustration of these methods can be found in Zheng and Bennett (11) and Sun (16). Bedient et al. (17) cited many references that provide detailed descriptions of these numerical methods. One of the common computer codes used in simulating the fate and transport of contaminants in groundwater is MT3D (18). MT3D is a three-dimensional contaminant transport model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems. MT3D is based on a modular structure to permit simulation of transport components independently or jointly with finite-difference groundwater flow models, such as MODFLOW. MT3D can be downloaded from http://hydro.geo.ua.edu. Further information on MT3D can be found in Zheng (18), Zheng and Bennett (11), and Zheng and Wang (19).

BIBLIOGRAPHY

1. Todd, D.K. (1980). *Groundwater Hydrology*. John Wiley & Sons, New York.
2. Office of Technology Assessment. (1984). Protecting the nation's groundwater from contamination, Office of Technology Assessment, OTA-0-233, Washington, DC.
3. Fetter, C.W. (1994). *Applied Hydrogeology*. Prentice-Hall, New York.
4. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, New York.
5. Domenico, P.A. and Schwartz, F.W. (1990). *Physical and Chemical Hydrology*. John Wiley & Sons, New York.
6. Fetter, C.W. (1999). *Contaminant Hydrogeology*. Prentice-Hall, New York.
7. Charbeneau, R.J. (2000). *Groundwater Hydraulics and Pollutant Transport*. Prentice-Hall, Upper Saddle River, NJ.
8. Harbaugh, A.W. and McDonald, M.G. (1996), User's documentation for MODFLOW-96, an update to the U.S. Geological Survey modular finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 96–485.
9. Ingebritsen, S.E. and Sanford, W.E. (1998). *Groundwater in Geologic Processes*. Cambridge University Press, Cambridge, UK.
10. Bear, J. (1979). *Hydraulics of Groundwater*. McGraw-Hill, New York.
11. Zheng, C. and Bennett, G.D. (1995). *Applied Contaminant Transport Modeling: Theory and Practice*. International Thomson Publishing, Stamford, CT.
12. Neuman, S.P. (1990). Universal scaling of hydraulic conductivities and dispersivities in geologic media. *Water Resour. Res.* **26**(8): 1749–1758.
13. Xu, M. and Eckstein, Y. (1995). Use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale. *Ground Water* **33**(6): 905–908.
14. Baestlé, L.H. (1999). Migration of radionuclides in porous media. *Progress in Nuclear Energy Series* XII, *Health Physics*. A.M.F. Duhamel (Ed.). Pergamon Press, Elmsford, NY, pp. 707–760.
15. Domenico, P.A. (1987). An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrolo.* **91**: 49–58.
16. Sun, N. (1996). *Mathematical Modeling of Ground Water Pollution*. Springer, New York.
17. Bedient, P.B., Rifai, H.S., and Newell, C.J. (1999). *Groundwater Contamination: Transport and Remediation*. Prentice-Hall, New York.
18. Zheng, C. (1990). MT3D, a modular three-dimensional transport model for simulation of advection, dispersion and chemical reactions of contaminants in ground water systems. Report to the US Environmental Protection Agency.
19. Zheng, C. and Wang, P.P. (1999). MT3DMS, a modular three-dimensional multi-species transport model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems; documentation and user's guide. U.S. Army Engineer Research and Development Center, Contract Report SERDP-99-1, Vicksburg, MS.

REACTIVE TRANSPORT IN THE SATURATED ZONE: CASE HISTORIES FOR PERMEABLE REACTIVE BARRIERS

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INTRODUCTION

The permeable reactive barrier (PRB) is an *in situ* remediation technology where contaminated groundwater is treated passively as it flows through a reactive medium. Most PRBs use granular zero valent iron (ZVI) to create redox conditions that result in degradation or immobilization of groundwater contaminants, such as chlorinated solvents and herbicides, heavy metals,

and radionuclides (1–5). These redox conditions promote precipitation of secondary minerals from ions typically in groundwater as well as some groundwater contaminants (2,6,7). The most common minerals formed in PRBs are magnetite, hematite, goethite, lepidocrocite, calcite, aragonite, siderite, green rust, ferrous hydroxide, ferrous sulfide, and marcasite (8). Calcium carbonates and siderite typically are found near the entrance face of a PRB, whereas magnetite, ferrous hydroxide, green rust, and iron oxyhydroxides form throughout a PRB (6,7). Accumulation of secondary minerals causes loss of pore space and reactive surface area of the medium in PRBs, which can alter flow paths, residence times, and the treatment effectiveness of a PRB (2,7,9).

Developing a general assessment of mineral precipitation in PRBs with field and/or laboratory data is complicated by site-specific geochemical and hydrogeological conditions (7), and the relatively long period over which mineral deposition occurs (9). An alternative approach is to conduct analyses with a reactive transport simulator that predicts mineral deposition and its effects on hydraulics (10–12). Li (12) developed a reactive transport simulator specifically for this purpose. This chapter describes a comparison between ion concentrations predicted with this model and concentrations measured in the field at three PRBs.

REACTIVE TRANSPORT SIMULATOR

Equilibrium and Kinetic Reactive Transport Models

Equilibrium and kinetic models have simulated geochemical processes and mineral formation in PRBs (10,11,13,14). Equilibrium models can estimate the aqueous species and solid phases that exist in a state of thermodynamic equilibrium, but they do not account for the rate at which reactions occur and generally do not involve the movement of groundwater. In contrast, kinetic models describe the rate at which geochemical reactions occur and predict aqueous and solid phase concentrations as a function of time. In kinetic models, the geochemical reactions usually are specified by the user along with reaction rate expressions and the rate coefficients. Thus, when a kinetic model is developed, an equilibrium model often defines the most important reactions to be included in the kinetic model (e.g., see Yabusaki et al. (10)).

Equilibrium models are appropriate when the reaction rate is fast compared with the flow rate, whereas kinetic models are appropriate when flow rates are not negligible relative to reaction rates. For most PRBs, flow rates are fast enough such that reaction kinetics must be considered when evaluating mineral precipitation (10). Reactive transport codes incorporating kinetic geochemical algorithms have been developed by Mayer et al. (11) and Yabusaki et al. (10) for simulating contaminant degradation and mineral precipitation in PRBs. The code developed by Li et al. (8) is similar to those developed by Mayer et al. (11) and Yabusaki et al. (10), but it focuses solely on geochemical reactions that result in mineral precipitation.

Conceptual Model

The conceptual model used by Li et al. (8) consists of a continuous-wall PRB containing ZVI that is placed orthogonal to the groundwater flow. Groundwater flowing into the PRB is assumed to contain dissolved oxygen, Fe^{2+}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, CO_3^{2-}, OH^-, HCO_3^-, and NO_3^-. These dissolved species are assumed to form $CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$, $Fe(OH)_2$ (am), FeS (am), and $Mg(OH)_2$ in response to the redox conditions induced by corrosion of the ZVI. In an actual PRB, additional ions may be present and minerals other than those included in the model may also form. However, the reactions in the model include the most common minerals observed in laboratory and field studies of PRBs (6,7,10,11). Contaminant transformation reactions were not included in the model because the volume of mineral precipitates formed as a consequence of contaminant treatment generally is negligible, even though the contaminant transformations are intrinsic to the remediation process (2,11).

Codes

The reactive transport simulator is created with the public domain codes MODFLOW and RT3D (15,16). MODFLOW simulated steady-state flow in the aquifer and PRB. Geochemical processes within the PRB were simulated with RT3D, a three-dimensional multicomponent model that describes advective–dispersive-reactive transport (16). Heads from MODLOW are input to RT3D. A detailed description of the codes that comprise the simulator can be found in Li (12) and Li et al. (8).

Li et al. (8) developed a geochemical module for RT3D that simulated the mineral-forming reactions. Geochemical reactions included in the module are summarized in Table 1. Three redox reactions are related to iron corrosion, along with six mineral precipitation reactions and one reaction for microbial sulfate reduction. A pseudo-first-order reaction rate was assumed for iron corrosion by oxygen or nitrate with the reaction rate proportional to the iron surface area and the concentration of oxygen or nitrate (11). For iron corrosion by water, the reaction rate was assumed to be proportional only to the iron surface area (10,11,17). The rate of degradation of sulfate to HS^- by sulfate-reducing bacteria was assumed to follow the Monod equation (11), and the kinetics of mineral precipitation were assumed to follow transition state theory (18). The kinetic rate expressions and solubility constants for the mineral reactions are summarized in Table 1. All geochemical reactions are assumed to occur in parallel and are solved simultaneously.

FIELD DATA SOURCES AND MODEL SETUP

Field data from three PRBs verified that the MODFLOW-RT3D simulator produces reasonable predictions of major ion concentrations. Comparisons were not made between measured and predicted solid phase concentrations at any of the sites because of a lack of field data. The selected PRBs are located at Moffett Federal Airfield in

Table 1. Geochemical Reactions and Solubility Constants

Reaction	Mineral Formed	Kinetic Rate Expression[a]	Solubility Constant Log(K_{eq})[b]
Iron Corrosion:			
$Fe^0 + H_2O + 0.5O_2(aq) \rightarrow Fe^{2+} + 2OH^-$	—	$k_{an,Fe}\ Sa_{DO}$	—
$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2(aq) + 2OH^-$	—	$k_{an,Fe}\ S$	—
$4Fe^0 + 7H_2O + NO_3^- \rightarrow 4Fe^{2+} + 10OH^- + NH_4^+$	—	$k_{NO3}Sa_{NO_3^-}$	—
Microbial Sulfate-Reduction:			
$SO_4^{2-} + 4H_2(aq) \rightarrow HS^- + OH^- + 3H_2O$	—	$k\left(\frac{[SO_4^{2-}]}{K_{SO_4^{2-}} + [SO_4^{2-}]}\right)\left(\frac{[H_2]}{K_{H_2} + [H_2]}\right)$	—
Secondary Mineral Precipitation-Dissolution:			
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	Aragonite/Calcite	$-k_{Ca}(1 - a_{Ca^{2+}}a_{CO_3^{2-}}/K_{eq})$	−8.1
$CaMg(CO_3)_2(s) \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	Dolomite	$-k_{CaMg}(1 - a_{Ca^{2+}}a_{Mg^{2+}}a^2_{CO_3^{2-}}/K_{eq})$	−17.7
$Mg(OH)_2(s) \leftrightarrow Mg^{2+} + 2OH^-$	Brucite	$-k_{Mg2}(1 - a_{Mg^{2+}}a^2_{OH^-}/K_{eq})$	−11.2
$FeCO_3(s) \leftrightarrow Fe^{2+} + CO_3^{2-}$	Siderite	$-k_{Fe1}(1 - a_{Fe^{2+}}a_{CO_3^{2-}}/K_{eq})$	−10.5
$Fe(OH)_2(am) \leftrightarrow Fe^{2+} + 2OH^-$	Ferrous hydroxide	$-k_{Fe}(1 - a_{Fe^{2+}}a^2_{OH^-}/K_{eq})$	−15.2
$FeS(am) + H_2O \leftrightarrow Fe^{2+} + HS^- + OH^-$	Ferrous sulfide	$-k_{FeS}(1 - a_{Fe^{2+}}a_{HS^-}a_{OH^-}/K_{eq})$	−18.4

[a] k is rate coefficient, S is reactive surface area of ZVI, a is activity of aqueous species, and K_{eq} is solubility constant. Activity coefficients were calculated with the extended Debye—Huckel equation.
[b] At 15 °C and 101 kPa.

Mountain View, CA; Monticello, UT; and Copenhagen, Denmark. These PRBs were selected because hydrological and geochemical data were sufficiently well defined for each PRB to permit an assessment of the simulator.

For all sites, the simulations were set up assuming homogeneous hydraulic conductivity in each medium (i.e., aquifer, reactive zone, etc.). Constant-head boundaries were applied along the upstream and downstream faces of the domain to establish a hydraulic gradient orthogonal to the PRB. No flow conditions were imposed at the other boundaries. Each species in the PRBs was assumed to have an initial concentration of zero. A constant concentration boundary was applied at the upstream face of the PRBs, and other boundaries were assigned the Cauchy boundary condition with no dispersive flux. Influent groundwater concentrations entering the PRB were set at values measured in the field.

Moffett Federal Airfield

A pilot-scale funnel-and-gate PRB consisting of ZVI was installed in 1996 at Moffett Federal Airfield to remove TCE and DCE from groundwater (10). The gate is 3.0 m long (orthogonal to flow direction), 3.0 m wide (along the flow direction), and 5.5 m deep. The gate consists of a 1.8-m-thick barrier of granular ZVI sandwiched between two 0.6-m-thick layers of pea gravel (up gradient and down gradient). Groundwater samples collected within the PRB between April 1996 (installation) and October 1997 were analyzed for target contaminants, pH, major cations and anions, and indicator parameters (10). Analysis of core samples showed that magnetite, hematite, aragonite, and marcasite formed in the iron media. No direct measurements were made of siderite, FeS, $Fe(OH)_2$ (am), $Fe(OH)_3$, brucite, or green rust.

The MODFLOW-RT3D simulator simulated the nearly one-dimensional conditions in the gate at the Moffett Federal Airfield site. The input was based on data provided in Yabusaki et al. (10). MODFLOW simulated steady-state flow in the pea gravel zones and iron media zone. The initial hydraulic conductivity in the PRB was 186 m/d, and the porosity was 0.66. The hydraulic conductivity in the pea gravel zones was 86.4 m/d. A hydraulic gradient of 0.0003 was applied across the PRB to yield the Darcy velocity (0.04 m/d) reported in Yabusaki et al. (10). Five minerals reported by Yabusaki et al. (10) were included in the model: $CaCO_3$, $FeCO_3$, $Fe(OH)_2$ (am), $Mg(OH)_2$, and FeS (am). Composition of groundwater entering the PRB was based on information provided in Yabusaki et al. (10) (Table 2).

Monticello

A full-scale funnel and gate PRB containing granular iron was installed in 1999 to treat uranium in groundwater at a former uranium mill site near Monticello, UT (14). The gate is 30.0 m long, 2.4 m wide (along flow direction), and 4.5~6.0 m deep. A 1.2-m-thick reactive zone consisting of 100% granular ZVI was sandwiched between two 0.6-m-thick layers of pea gravel (up gradient and down gradient) in the gate. Samples of groundwater were collected from June 1999 (installation) to September 1999 and analyzed for target contaminants, pH, major cations and anions, and indicator parameters. Core samples showed that magnetite and $CaCO_3$ formed within the PRB.

Reactive transport in the gate at the Monticello PRB was simulated with the MODFLOW-RT3D simulator using a one-dimensional model similar to that employed for the PRB at Moffett Federal Airfield (see previous section). A one-dimensional model was selected because flow through the pea gravel zones and ZVI was nearly one-dimensional and steady state. Hydraulic conductivities of the ZVI and pea gravel zones were set at 30.9 m/d and 8.64 m/d. Based on data in Morrison et al. (14), the porosity was set at 0.50 in the ZVI and 0.30 in the pea gravel and the hydraulic gradient was set at 0.142 to yield a

Table 2. Concentrations of Aqueous Species in Influent Ground Water

Aqueous Species in Influent Ground Water	Aqueous Species Concentrations (M)		
	Moffett Federal Airfield, Mountain View, California[a]	Former Mill Site, Monticello, Utah[b]	Copenhagen Freight Yard, Copenhagen, Denmark[c]
Fe^{2+}	1.0×10^{-10}	1.0×10^{-10}	1.0×10^{-10}
Ca^{2+}	3.9×10^{-3}	8.5×10^{-3}	3.3×10^{-3}
Mg^{2+}	2.7×10^{-3}	3.6×10^{-3}	1.2×10^{-3}
OH^-	1.3×10^{-7}	5.2×10^{-8}	5.0×10^{-7}
HCO_3^-	4.7×10^{-3}	2.5×10^{-3}	1.0×10^{-2}
CO_3^{2-}	1.4×10^{-6}	1.0×10^{-6}	1.0×10^{-6}
$O_2(aq)$	1.0×10^{-10}	1.0×10^{-10}	1.0×10^{-10}
NO_3^-	3.9×10^{-5}	1.0×10^{-10}	1.0×10^{-10}
SO_4^{2-}	3.6×10^{-3}	1.2×10^{-2}	1.2×10^{-3}

[a] From Yabusaki et al. (10).
[b] From Morrison et al. (14).
[c] From Killerich et al. (19).

groundwater velocity of 3 m/d. Five minerals were included in the geochemical model: $CaCO_3$, $FeCO_3$, $Fe(OH)_2$ (am), $CaMg(CO_3)_2$, and FeS. Composition of the groundwater entering the PRB was defined based on data reported in Morrison et al. (14), as summarized in Table 2.

Copenhagen

A full-scale PRB containing granular ZVI was installed in 1998 at the Copenhagen Freight Yard in Copenhagen, Denmark to treat chlorinated solvents in ground water (19). The PRB is a continuous trench 15.0 m long, 1.3 m wide (along flow direction), and 6.0 m deep and consists of a 0.9-m-thick zone of 100% granular ZVI sandwiched between 0.2-m-thick layers of pea gravel. Samples of groundwater were collected from July 1998 (installation) to September 1999 and were analyzed for target contaminants, pH, and major cations and anions (19). No direct measurements were made of minerals forming within the PRB (19).

The MODFLOW-RT3D simulator was set up to simulate one-dimensional flow and reactive transport along the centerline of the Copenhagen PRB. The model predicted steady-state flow in the surrounding aquifer, pea gravel zones, and ZVI. Hydraulic conductivity of the ZVI, pea gravel, and aquifer were set at 6.1, 2.1, and 0.6 m/d, respectively, based on site conditions (19). The porosity was set at 0.60 for the ZVI, 0.40 for the pea gravel zones, and 0.3 in the aquifer (19). A hydraulic gradient of 0.011 was applied across the aquifer based on data reported in Killerich et al. (19). Five minerals were included in the model: $CaCO_3$, $FeCO_3$, $Fe(OH)_2$(am), $CaMg(CO_3)_2$, and FeS. Composition of the groundwater entering the PRB was defined based on data reported in Killerich et al. (19), as summarized in Table 2.

COMPARISON OF PREDICTED AND MEASURED CONCENTRATIONS

Moffett Federal Airfield

Comparisons of the predicted and measured pH and concentration profiles are shown in Fig. 1 for the PRB at Moffett Field after 12 months of operation. The reaction rate coefficients initially were estimated from data in the literature, but ultimately they were adjusted by trial-and-error to reproduce the measured pH, alkalinity, and concentrations of SO_4^{2-}, Ca^{2+}, and Mg^{2+}. A similar calibration procedure was used at the other two sites. The calibrated reaction rate coefficients are summarized in Table 3 along with typical ranges based on data reported in the literature.

The predicted pH is in general agreement with the observed pH [Fig. 1(a)], including the rapid jump near the entrance face and the leveling out in the interior. The drop in alkalinity just up gradient of the PRB is not captured [Fig. 1(b)], but the alkalinity predicted by RT3D inside the PRB is similar to that measured in the field. The sulfate concentration predicted by RT3D also is in general agreement with the trends observed in the field [Fig. 1(b)], as are the Ca^{2+} and Mg^{2+} concentrations [Fig. 1(c)]. However, the predicted Ca^{2+} concentrations in the PRB are near the upper bound of the measured concentrations [Fig. 1(c)]. The field data are also too sparse to evaluate whether the simulator accurately predicts the rapid changes in geochemical conditions occurring at the entrance face.

Monticello Mill Site

Comparisons of measured and predicted pH, alkalinity, and concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} for conditions at 3 months of operation are shown in Fig. 2. Calibrated rate coefficients for the PRB at Monticello are summarized in Table 3. As with the PRB at Moffett Field, insufficient data exist to determine whether the rapid changes predicted at the entrance face accurately replicate the conditions occurring in the PRB at Monticello.

The measured and predicted pH, HCO_3^-, Mg^{2+}, and SO_4^{2-} concentrations in the Monticello PRB are in close agreement (Fig. 2). However, the predicted Ca^{2+} concentrations in the PRB are higher than are the measured concentrations [Fig. 2(b)]. One reason for this discrepancy may be that minerals other than $CaCO_3$ and $CaMg(CO_3)_2$ are precipitating (these minerals only account for 15%

Table 3. Calibrated Rate Coefficients in PRB Case Studies

Geochemical Reactions Terms	Units	Moffett Federal Airfield[c]	Former Mill Site[c]	Copenhagen Freight Yard[c]	Rate Coefficients Reported in Literature[d]
Oxygen Corrosion[a]	m^3/m^2-d	2.8×10^{-2}	2.8×10^{-2}	2.8×10^{-2}	$< 2.8 \times 10^{4}$
Water Corrosion[a]	mole/m^2-d	7.0×10^{-7}	1.5×10^{-5}	1.9×10^{-7}	$3.0 \times 10^{-8} - 5.4 \times 10^{-3}$
Nitrate Corrosion[a]	m^3/m^2-d	2.6×10^{-5}	—	2.8×10^{-5}	$1.8 \times 10^{-8} - 2.8 \times 10^{-5}$
Microbial sulfate reduction[b]	M/d	1.0×10^{-3}	1.0×10^{-3}	4.0×10^{-3}	$5.0 \times 10^{-6} - 5.0 \times 10^{-3}$
$CaCO_3$	M/d	1.0×10^{-4}	4.0×10^{-4}	1.0×10^{-5}	$2.7 \times 10^{-9} - 1.4 \times 10^{-4}$
$FeCO_3$	M/d	1.1×10^{-5}	2.1×10^{-5}	1.0×10^{-5}	$1.1 \times 10^{-5} - 2.7 \times 10^{-4}$
$Fe(OH)_2$ (am)	M/d	5.1×10^{-5}	5.1×10^{-5}	5.0×10^{-5}	$<2.2 \times 10^{-4}$
FeS (am)	M/d	1.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}	$1.1 \times 10^{-8} - 2.2 \times 10^{-5}$
$CaMg(CO_3)_2$	M/d	—	1.0×10^{-6}	1.0×10^{-9}	6.9×10^{-6}
$Mg(OH)_2$	M/d	2.0×10^{-3}	NA	NA	3.4×10^{-6}

[a] Reactive surface area of ZVI set at 3.9×10^6 m^2/m^3.
[b] Half-saturation constants for SO_4^{2-} and H_2 (aq) were $K_{SO4} = 1.0 \times 10^{-4}$ M, and $K_{H2} = 1.0 \times 10^{-7}$ M, respectively.
[c] After calibration with field measurements.
[d] Li et al. (8).

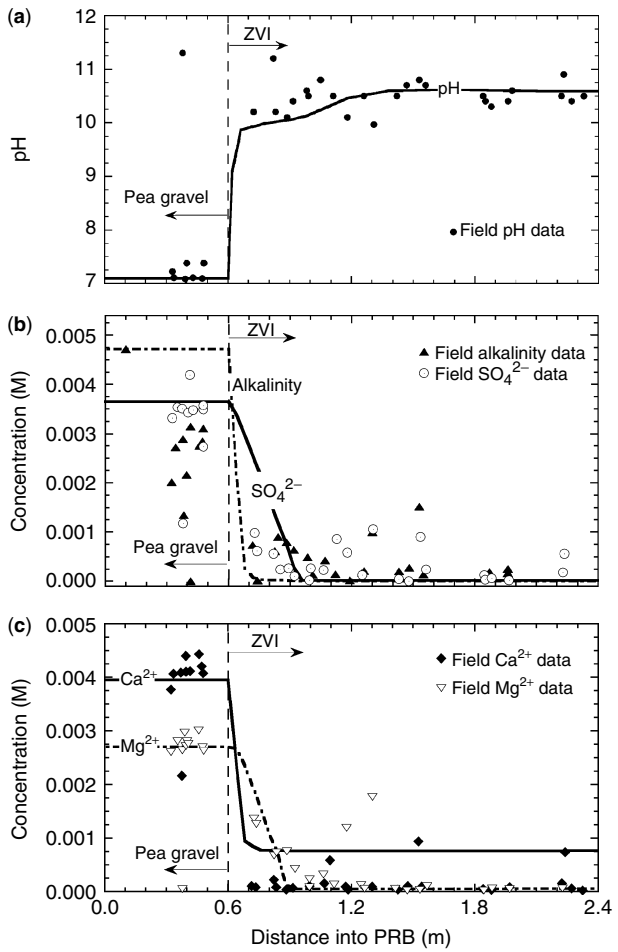


Figure 1. Measured and predicted concentrations for the PRB at Moffett Federal Airfield, Mountain View, CA, after 12 months of operation: (**a**) pH, (**b**) alkalinity and SO_4^{2-}, and (**c**) Ca^{2+} and Mg^{2+}.

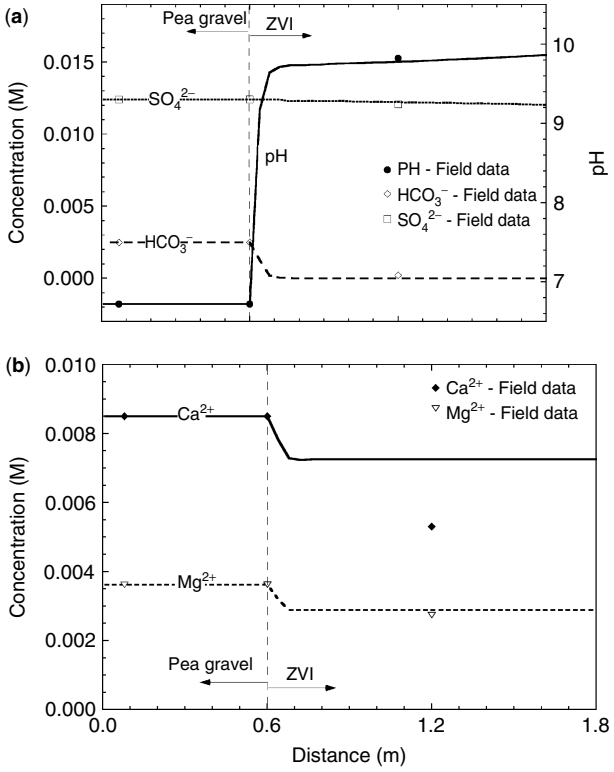


Figure 2. Measured and predicted concentrations for the PRB at the former Uranium Mill Site in Monticello, UT, after 3 months of operation: (**a**) pH, HCO_3^-, and SO_4^{2-} and (**b**) Ca^{2+} and Mg^{2+}.

of aqueous calcium). For example, Morrison et al. (14) included iron-rich calcite ($Fe_{0.4}Ca_{0.6}CO_3$) and gypsum ($CaSO_4$) in their equilibrium model to account for calcium removal in the ZVI. However, neither of these minerals has been observed in the core samples from the PRB at Monticello. The surface complexation of calcium on the ZVI and secondary minerals surfaces, neither of which are considered in the simulator, may also be removing calcium from the solution (10).

Copenhagen Site

Comparisons of measured and predicted pH and Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- concentrations after 15 month

of operation of the Copenhagen PRB are shown in Fig. 3. The calibrated rate coefficients corresponding to these predictions are summarized in Table 3.

Close agreement exists between the measured and predicted pH and the HCO_3^-, SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentrations in the ZVI of the Copenhagen PRB [Figs. 3(a) and (b)], but the field data are too sparse to evaluate whether the trends in geochemistry predicted by the model are accurate. In contrast to the PRBs at Moffett Field and Monticello, the predicted pH climbs gradually at the Copenhagen site. This more graduate change in pH may be caused by a lower rate of iron corrosion by water (1.9×10^{-7} mole/m^2-d, Table 3), which results in less OH^- released into solution.

Comparison of Calibrated Rate Coefficients and Literature Values

The calibrated rates coefficients for the three PRB case studies are summarized in Table 3. Most of the calibrated rate coefficients fall within the range of rate coefficients from the literature (Table 3). The exceptions are the rate coefficient for $Mg(OH)_2$ at the Moffett PRB and the rate coefficient for $CaCO_3$ at the Monticello PRB. Both rate coefficients are higher than are the maximum values reported in the literature. However, the rate coefficient for $CaCO_3$ is only slightly above the upper bound from the literature, and only one rate coefficient was available in the literature for $Mg(OH)_2$. Thus, these exceptions are not considered unusual.

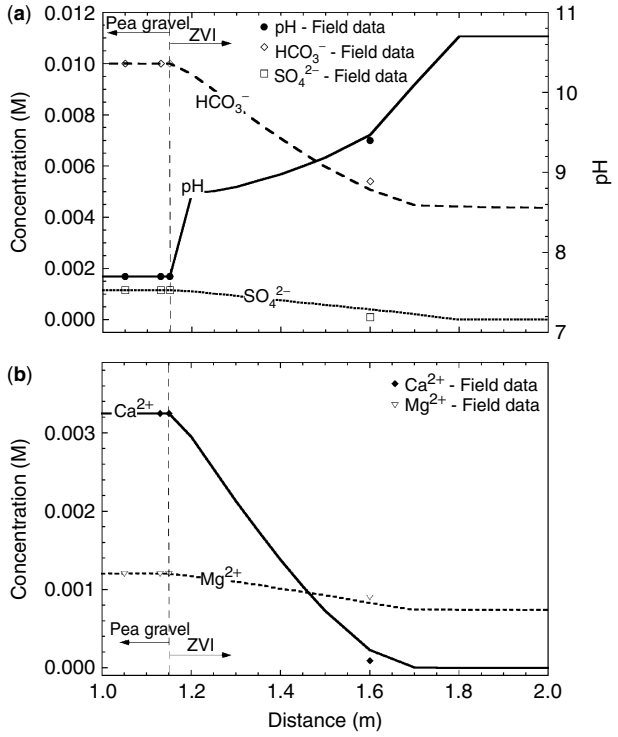


Figure 3. Measured and predicted concentrations at the centerline of the PRB at the Copenhagen Freight Yard, Copenhagen, Denmark, after 15 months of operation: (**a**) pH, HCO_3^-, and SO_4^{2-} and (**b**) Ca^{2+} and Mg^{2+}.

Although good agreement between measured and predicted concentrations has been shown in Figs. 1–3, the accuracy of the simulator when applied to other problems will depend greatly on the rate coefficients used as input. For example, the effect of varying the rate coefficient for iron corrosion by water (Table 1) within a reasonable range (1.0×10^{-7} to 1.0×10^{-5} mole/m^2-d) on pH is illustrated in Fig. 4 with the model for the PRB at Moffett Field. The influent concentrations used for the simulation are shown in Table 2, and the rate coefficients for the reactions other than iron corrosion by water are shown in Table 3. When the rate coefficient for iron corrosion by water is 10^{-7} mole/m^2-d, the predicted pH is much lower than the pH observed in the field, especially near the entrance. In contrast, when the rate coefficient for iron corrosion by water is 10^{-5} mole/m^2-d, the predicted pH increases too rapidly near the entrance and levels out approximately one pH unit higher than observed in the field.

In situ rate coefficients can vary considerably and depend on a variety of factors, and no method currently is available to predict rate coefficients accurately *a priori*. Thus, at the current time, simulators must be calibrated with field data if reliable predictions of mineral precipitation are to be obtained. Alternatively, parametric analyses can be conducted to evaluate the potential range of conditions that may be realized in the field.

SUMMARY

Comparisons between predicted and measured concentrations of common groundwater ions in PRBs have been described in this article. The simulator used for the predictions is based on the public domain codes MODFLOW and RT3D, the latter being augmented with a geochemical algorithm specifically for simulating geochemical reactions in PRBs. Field data from three PRBs were used for the comparison.

The comparisons showed that pH profiles and anion and cation concentrations in PRBs can be predicted accurately. The ability to predict solid phase concentrations has not been evaluated because of lack of field data. However,

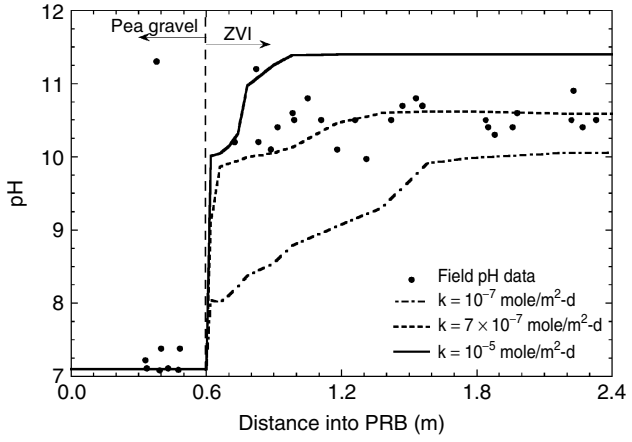


Figure 4. Measured and predicted pH for the PRB at Moffett Federal Airfield, Mountain View, CA, after 12 months of operation using various rate coefficients (k) for iron corrosion by water.

the accuracy of the predictions depends to a great extent on the reaction rate coefficients used as input. In this study, the rate coefficients were obtained by calibration because the actual *in situ* rate coefficients were unknown. Thus, predictions made *a priori* are prone to considerable uncertainty until methods are developed to accurately define reaction rate coefficients.

In many cases, the simulator predicted that the greatest changes in geochemistry generally occur at the entrance face of the PRB. However, the current field data sets contain insufficient detail to confirm that these changes in geochemistry are being predicted accurately. More detailed field observations are needed at the entrance face of the PRBs to more fully evaluate whether the simulator can accurately capture these rapid changes in geochemistry.

BIBLIOGRAPHY

1. Blowes, D.W. et al. (2000). Treatment of inorganic contaminants using permeable reactive barriers. *J. Contaminant Hydrol.* **45**: 123–137.
2. Wilkin, R.T., Puls, R., and Sewell, G.W. (2003). Long-term performance of permeable reactive barriers using zero-valent iron: geochemical and microbiological effects. *Ground Water* **41**: 493–503.
3. EPA. (1998). *Permeable Reactive Barrier Technologies for Contaminant Remediation*. United States Environmental Protection Agency, Washington, DC.
4. Lee, T. and Benson, C.H. (2004). Sorption and degradation of alachlor and metolachlor in ground water using green sands. *J. Environ. Quality* **33**: 1682–1693.
5. Lee, T., Benson, C.H., and Eykholt, G.R. (2004). Waste green sands as reactive media for groundwater contaminated with trichloroethylene (TCE). *J. Hazardous Materials* **B109**: 25–36.
6. Mackenzie, P.D., Horney, D.P., and Sivavec, T.M. (1999). Mineral precipitation and porosity losses in granular iron columns. *J. Hazardous Materials* **68**: 1–17.
7. Phillips, D.H. et al. (2003). Mineralogical characteristics and transformations during long-term operation of a zerovalent iron reactive barrier. *J. Environ. Quality* **32**: 2033–2045.
8. Li, L., Benson, C.H., and Mergener, E.A. (2004). Impact of mineral fouling on hydraulic behavior of permeable reactive barriers. *Ground Water*. In press.
9. Vikesland, P.J. et al. (2003). Longevity of granular iron in groundwater treatment processes: changes in solute transport properties over time. *J. Contaminant Hydrol.* **64**: 3–33.
10. Yabusaki, S. et al. (2001). Multicomponent reactive transport in an *in situ* zero-valent iron cell. *Environ. Sci. Technol.* **35**: 1493–1503.
11. Mayer, K.U., Blowes, D.W., and Frind, E.O. (2001). Reactive transport modeling of an *in situ* reactive barrier for the treatment of hexavalent chromium and trichloroethylene in groundwater. *Water Resour. Res.* **37**: 3091–3103.
12. Li, L. (2004). Fouling and the Long-Term Performance of Permeable Reactive Barriers. Ph.D. Dissertation, University of Wisconsin-Madison, Madison, WI.
13. Liang, L. et al. (2002). *Integration of Geochemical Data and Hydraulic Changes at Permeable Reactive Barriers Sites*. Oak Ridge National Laboratory, Oak Ridge, TN.
14. Morrison, S.J., Metzler, D.R., and Carpenter, C.E. (2001). Uranium precipitation in a permeable reactive barrier by progressive irreversible dissolution of zerovalent iron. *Environ. Sci. Technol.* **35**: 385–390.
15. McDonald, M.G. and Harbaugh, A.W. (1988). *MODFLOW: A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model*. U.S. Geological Survey Techniques of Water-Resources Investigations, Washington, DC, book 6, chap. A1.
16. Clement, T.P. (1997). *RT3D: A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers, PNNL-SA-11720*. Pacific Northwest National Laboratory, Richland, WA.
17. Reardon, E.J. (1995). Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evolution rates. *Environ. Sci. Technol.* **29**: 2936–2945.
18. Lasaga, A.C. (1998). *Kinetic Theory in the Earth Sciences*. Princeton series in geochemistry. Princeton University Press, Princeton, NJ.
19. Killerich, O., Larsen, J.W., and Nielsen, C. (2000). Field results from the use of a permeable reactive wall. *Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA.

TRANSPORT OF REACTIVE SOLUTE IN SOIL AND GROUNDWATER

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INTRODUCTION

Remediation of contaminated aquifers, both vadose zone (unsaturated portion of an aquifer) soils and groundwater, has proven to be a challenging environmental endeavor. Groundwater is the source of about 60% of the United States' water usage and, with contaminant plumes impacting many states, associated human health concerns of great importance exist. Groundwater can become polluted both directly by leaking underground storage tanks and indirectly by leakage of contaminants on the soil surface that leach to the groundwater. Common pollutants include agricultural chemicals applied to crops, industrial spills, landfill leachate, disposal sites, and waste ponds. Subsurface remediation is complicated by not only the behavior of the contaminants themselves but by the heterogeneities found in typical aquifer formations. The processes that govern the fate and transport of solute in aquifer systems generally fall into the categories of hydrodynamic, abiotic, and biotic.

The universal process that impacts all forms of solute include the hydrodynamic processes, which affect contaminant transport by impacting the flow paths of groundwater in the subsurface, including both the vadose zone and the saturated aquifer. Abiotic processes affect contaminant transport physically by causing interactions between the contaminant and the stationary subsurface materials (i.e., sorption) or by affecting the form of the contaminant (i.e., through hydrolysis and redox reactions). Biotic processes are driven by microbial activities and can affect contaminant transport by metabolizing or

mineralizing the contaminant (i.e., organic contaminants), or possibly by using the contaminant in the metabolic process (i.e., nitrate under denitrifying conditions).

PHYSICAL MECHANISMS OF SOLUTE TRANSPORT

The three basic hydrodynamic processes affecting contaminant transport in saturated and unsaturated porous media are advection, diffusion, and hydrodynamic dispersion. Advection represents the movement of a contaminant with the flowing groundwater according to the seepage velocity in the pore space. Advection is the most important process driving the down gradient migration of dissolved contaminants in the saturated subsurface (1). If advection was the only process acting on a tracer, a sharp interface would exist continuously as the tracer flushes out the solute-free water. In essence, the tracer would behave as a plug. A breakthrough curve, illustrating the relative effluent concentration (C/Co) vs. time in a continuous tracer input, would appear as a step function (Fig. 1a). The average velocity of advective transport is described by the amended Darcy equation:

$$v_x = -\frac{K}{n}\frac{dh}{dL} \tag{1}$$

where v_x is the average linear groundwater velocity [L/t], K is the hydraulic conductivity (a measure of a porous media's ability to transmit water) [L/t], n is the effective porosity [unit less], and dh/dL is the hydraulic gradient [L/L].

The average linear velocity or seepage velocity, v_x, equals the Darcy velocity divided by effective porosity, n, associated with the pore space through which water can actually flow. The average linear velocity is less than the microscopic velocities of water molecules moving along individual flowpaths, because of tortuosity. The one-dimensional (1-D) mass flux (F_x) because of advection equals the product of water flow and concentration (C) of solute, or $F_x = v_x nC$.

Darcy's law is also still valid for the macroscopic view (through the entire pore body) of unsaturated flow, except that hydraulic conductivity is now a function of moisture content. Darcy's law is then used with the unsaturated value for K and can be written as

$$v = -K(\theta)dh/dz \tag{2}$$

where v is Darcy velocity, z is depth below surface [L], $K(\theta)$ is unsaturated hydraulic conductivity [L/T], θ is volumetric moisture content, h is potential or head ($h = z + \psi$) [L/T], and ψ is tension or suction [L]. For saturated soils, the hydraulic conductivity was assumed to be constant; however, in unsaturated soil, it decreases sharply with decreasing water content, because as water drains from pores, the flow decreases (2).

Although advection is associated with bulk macroscopic groundwater movement, diffusion is a molecular-based phenomenon. The process involves spreading because of concentration gradients and random motion. Diffusion causes a solute in water to move from an area of higher concentration to an area of lower concentration. Diffusive transport can occur in the absence of velocity. Mass transport in the subsurface because of diffusion in one dimension can be described by Fick's first law of diffusion,

$$f_x = -D_d\frac{dC}{dx} \tag{3}$$

where f_x is the mass flux [M/L^2/T], D_d is the diffusion coefficient [L^2/T], and dC/dx is the concentration gradient [M/L^3/L].

Typical values of D_d are relatively constant and range from 10^{-4} to 10^{-5} cm^2/sec (3). In cases of very low velocities, such as in a tight soil or clay liner, or in the case of mass transport involving very long time periods, diffusion is the dominant hydrodynamic process. On the other hand, in areas of high groundwater velocity, molecular diffusion can actually be ignored compared with advection and other dispersion mechanisms.

Freeze and Cherry (4) defined hydrodynamic dispersion as the process in which solutes spread out and are diluted compared with simple advection alone. It is defined as the sum of molecular diffusion and mechanical dispersion, where diffusion is caused by concentration gradients alone and dispersion is generally caused by local variations in velocity around some mean velocity of flow. The net effect of the dispersive phenomena is to decrease the concentration gradient between two different solutions of the same solute. In essence, dispersion reduces the sharp interface between the two solutions. Mass transport because of dispersion can also occur normal to the direction of flow. This transverse dispersion, D_y, is caused by diverging flowpaths in the porous media and concentration gradients that cause mass to spread laterally from the main direction of flow. In most cases involving a two-dimensional plume of contamination, D_y is much less than D_x, and the shape of the plume tends to be elongated in the direction of flow (5). Many typical contaminant plumes in groundwater are represented by 2-D advective-dispersive mechanisms.

One-Dimensional Transport Equations

The governing mass transport equation is difficult to solve in field cases of practical interest because of boundary irregularities and variations in aquifer characteristics, so numerical methods must generally be employed (6). However, a limited number of relatively simple, 1-D analytical solutions exist. The simplifying assumptions include the following: (a) the tracer is ideal, with constant density and viscosity; (b) the fluid is incompressible; (c) the medium is homogeneous and isotropic; and (d) only saturated flow is considered. Initial conditions ($t = 0$) in a soil column are usually set to zero ($C(x, 0) = 0$) or to some constant background concentration. Boundary conditions must be specified at the two ends of the 1-D column. For a continuous source load at $x = 0$, the concentration is set to $C(0, t) = C_0$ for $t > 0$. The concentration at the other boundary, $x = \infty$ is set to zero $C(x, \infty) = 0$ for $t > 0$.

For an infinite 1-D column with background concentration of zero and a continuous input tracer concentration C_0 at $-\infty \leq x \leq 0$ for $t \geq 0$, Bear (7) solves the problem using

the Laplace transform at $x = L$, length of the column

$$\frac{C(x,t)}{C_0} = \frac{1}{2}\left(\text{erfc}\left[\frac{L - v_x t}{2\sqrt{D_x t}}\right] + \exp\left(\frac{v_x L}{D_x}\right)\text{erfc}\left[\frac{L + v_x t}{2\sqrt{D_x t}}\right]\right) \quad (4)$$

where erfc is the complementary error function, $\text{erfc}(x) = 1 - \text{erf}(x) = 1 - (2/\sqrt{\pi})\int_0^x e^{-u^2}du$, D_x is the coefficient of hydrodynamic dispersion, and v_x is the average seepage velocity. The center of mass ($C/C_0 = 0.5$) of the breakthrough curve travels with the average linear velocity, v_x, and corresponds to the point where $x = v_x t$. Note that the second term on the right-hand side of Eq. (4) can generally be neglected for most practical problems. The error functions erf (β) and erfc(β) are tabulated in Domenico and Schawartz (3).

The corresponding solution can be derived for the injection of a tracer pulse (instantaneous input) at $x = 0$ with background concentration equal to zero in the 1-D column. As the slug moves downstream with v_x in the $+x$ direction, it spreads out according to

$$C(x,t) = \frac{M}{(4\pi D_x t)^{1/2}}\exp\left[-\frac{(x - v_x t)^2}{4D_x t}\right] \quad (5)$$

where M is the injected mass per unit cross-sectional area. Figure 1b shows the resulting Gaussian distribution of concentration for the instantaneous pulse source in one dimension.

Plots comparing the shapes of Eqs. (4) and (5) are shown in Figs. 1a and 1b, respectively, at $x = L$ at the end of a soil column. The differences between instantaneous (spike) source and continuous source transport problems are obvious in one dimension. The continuous source produces a response or breakthrough curve, which starts at a low concentration and eventually levels off to the initial input concentration C_0 as a function of time. The spike source produces a normal or Gaussian distribution, which continues to decrease in maximum concentration because of spreading out with time in the direction of flow. For the spike source, the amount of mass under each curve is identical if the tracer is conservative.

Additional information can be found on transport equations in several sources (3–6,8), including three-dimensional derivations and those incorporating degradation.

Techniques for Determining Hydrodynamic Parameters

Tracers and tracer tests are valuable methods for estimating dispersion and advection below the water table. In a tracer test, a chemical species is introduced to the subsurface and monitored as it is carried by groundwater through the subsurface in the direction of flow. Average seepage velocity can be determined by analyzing the resulting curves in time and space, and hydraulic conductivity (K) values can be computed from Darcy's Law (Eq. 1). One of the most successful field sites for tracer studies has been the Borden landfill site in Canada, which resulted in a series of classic papers on dispersion and adsorption processes measured during a multiyear field experiment (9,10).

Other methods of determining hydraulic conductivity exist. Permeameters may be used in a laboratory setting to determine K, whereas slug tests and pump tests are recommended for field sites. A slug test involves suddenly adding or removing a volume of water (called a slug) from a well and monitoring the time it takes for the water level to return to normal. This test is convenient, but not as accurate as a tracer test to determine the speed with which a contaminant moves through an aquifer. The pump test involves the constant removal of water from a single well and the subsequent observation of drawdown in adjacent wells. This test gives the K value for a large part of an aquifer, but may produce a large volume of water that requires proper handling and treatment (if performed in a contaminated area) (3).

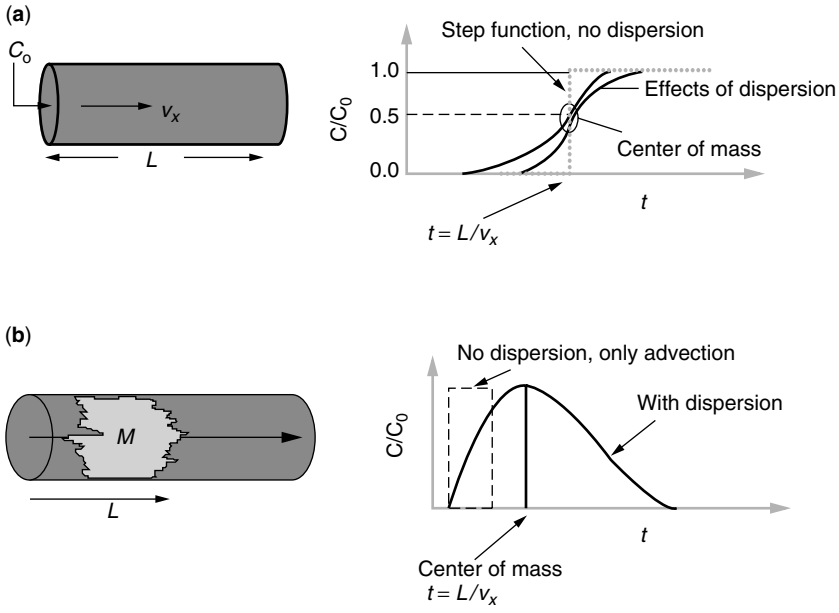


Figure 1. Breakthrough curves in one dimension for: (**a**) continuous and (**b**) instantaneous tracer inputs.

ABIOTIC SOLUTE TRANSPORT

Abiotic processes affect contaminant transport by causing interactions between the contaminant and the aquifer media or by changing the form of the contaminant that may subsequently interact with the subsurface material. The interfaces of most interest in subsurface fate and transport are liquid/solid interfaces and gas/solid interfaces. The processes that detail these interactions are discussed in this section.

Sorption

Sorption includes the phenomena of adsorption, absorption, and ion exchange. Weber (11) defines adsorption as the accumulation occurring at the interface, absorption as the partitioning between two phases (accumulation from groundwater into organic carbon), and sorption as including both adsorption and absorption. Often, the terms adsorption and sorption are interchangeable.

Many organic contaminants are removed from solution by sorption onto the aquifer matrix. Sorption of dissolved contaminants onto the aquifer matrix results in slowing (retardation) of the contaminant relative to the average groundwater seepage velocity and a reduction of dissolved organic concentrations in groundwater. In some cases, sorption is a reversible process; at a given solute concentration (steady state), some portion of the contaminant is partitioning out of solution onto the aquifer matrix and some portion is desorbing from the matrix back to solution; this process is called desorption.

The ability of chemicals to completely desorb from a solid is an area of current study (12–15). At high contaminant concentration, desorption patterns are generally predictable through equilibrium analysis. However, the phenomena of solid phase contaminant concentrations exceeding the predicted concentration, based on the surrounding aqueous phase concentrations, is observed in materials that have been contaminated for long time periods and contain low solid-phase contaminant concentrations (nominally less than 20 mg/kg). The importance of this observation is potentially enormous, because site remediation requirements include the removal of sorbed contamination. If a contaminant does not desorb as readily as it sorbed, the ability to meet cleanup levels may be seriously threatened (16).

Ion exchange is a specific category of sorption that occurs when the absorbent charge deficiency of a surface can be neutralized more efficiently by ions in solution than those ions currently absorbed (17). An example of ion exchange that is familiar is a home water softener. Home water softeners operate by accumulating the divalent cations from the groundwater onto the absorbent (ion exchange resin) while releasing monovalent ions, which reduces water hardness. In the subsurface, the resin would be natural minerals such as those found in clays. The most common ions occurring naturally are as follows (listed in order of occurrence from high to low): cations, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}; anions, $SO_4{}^{2-}$, Cl^{-}, $PO_4{}^{3-}$, and $NO_3{}^{-}$ (18).

Cosolvation and Ionization

Cosolvation and ionization are two examples of processes that act to increase the chemical solubility, by altering the solvent phase or by altering the chemical form, respectively. Cosolvation is the process by which the mobility of one contaminant is enhanced by the presence of a solvent (19), whereas ionization refers to the gaining or losing of protons as a function of pH and thus going from a neutral form to an ionic form. These processes are solvent motivated; when a contaminant is in the presence of a solvent, it will have decreased sorption and an increased solubility leading to elevated concentrations in the surrounding solute. Based on these assumptions, it would be expected that as the fraction of cosolvent increases in solution, the level of sorption will decrease.

These attributes of cosolvents lead to increased mobility of originally slow dissolving hydrophobic (lacking affinity for water) contaminants. An example of this is the affect of ethanol on petroleum hydrocarbons. The issue concerning an ethanol releases' potential to cosolubilize benzene and other aromatic compounds in groundwater (20) has been addressed in recent groundwater modeling studies (21,22) and in laboratory studies (23,24). The reason that tremendous efforts are being employed to understand this phenomenon is that benzene, which is known to increase cancer risks, has a maximum contaminant level of only 0.005 mg/L in drinking water as set by the U.S. EPA and ethanol is now being used as a fuel additive (an oxygenate).

Oxidation and Reduction

Oxidation and reduction (or redox) refer to the transfer of electrons and contaminant species change of ions or compounds. Oxidation refers to the loss of electrons and reduction refers to the gain of electrons in a reaction. The two processes often occur in tandem; electrons given by one compound must be gained by another compound. Inorganic compounds, such as reduced metals and reduced sulfur, are possible mediators of oxidation-reduction reactions (25–27). The presence or absence of inorganic species is often dependent on aquifer conditions. A common condition is that many anaerobic environments will contain elevated levels of Fe(II) or Fe^{2+}, H_2S/HS^{-}, and other reduced species that are capable of donating electrons and reducing certain contaminants. For example, the two half reaction equations for the oxidation-reduction of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) are:

$$4\,Fe^{2+} \Leftrightarrow 4\,Fe^{3+} + 4e^{-}\,[\text{oxidation}]$$

$$O_2 + 4H^{+} + 4e^{-} \Leftrightarrow 2H_2O\,[\text{reduction}]$$

Biologically mediated oxidation-reduction reactions are often more rapid than abiotic reactions for many contaminants of interest in groundwater systems, and thus abiotic oxidation-reduction are often neglected in transport calculations. In cases where they become important, oxidation-reduction processes are generally introduced as a first-order reaction (rate $= k^1X$) with respect to contaminant concentration, analogous to hydrolysis.

Hydrolysis

Hydrolysis refers to a chemical reaction between a contaminant molecule and water. Hydrolysis may function when direct biodegradation (microbially driven) of the contaminant cannot, and hydrolysis may produce a product that is susceptible to biodegradation, which can be significant in affecting fate and transport (17). With respect to organics, this process frequently results in the formation of alcohols and alkenes (28).

The rate that a chemical undergoes hydrolysis is strongly influenced by the temperature and pH of the system (27). As temperature increases, hydrolysis rates increase. As pH becomes either acidic or alkaline (e.g., greater than or less than 7.0), rates of acid-catalyzed or base-catalyzed hydrolysis can increase. Typically, hydrolysis is described with a first-order rate expression as shown in Eq. 6

$$\frac{C}{C_0} = e^{-k_{hyd}t} \tag{6}$$

where C is the concentration of the chemical species and k_{hyd} is a first-order hydrolysis rate coefficient. Knowing factors, such as pH and temperature, is important in determining the appropriate rate coefficient for a particular contaminant.

Volatilization

The transfer of a contaminant from the aqueous phase, nonaqueous phase liquid (NAPL), or sorbed phase directly to the gas phase is a process referred to as volatilization. The rate and extent to which volatilization occurs is strongly influenced by a number of parameters including the contaminant phase, the contaminant's vapor pressure, environmental factors (e.g., temperature and others), proximity in respect to the vadose zone, and other site-specific parameters (29,30). As a result of the range of factors, that play an important role in vapor transport, which include the physical transport processes of advection and dispersion, it is difficult to calculate the contribution of volatilization to the fate of chemicals in groundwater.

For the evaluation of volatilization, however, consider a closed bottle that contains water and air. If a contaminant is introduced to the bottle and allowed to equilibrate, some fraction of the contaminant added will reside in the gas phase. The distribution of a chemical between the water and the gas at equilibrium is described by the Henry's law coefficient (31,32). Mathematically, Henry's law is presented in Eq. (7), where P_c is the partial pressure of the contaminant, $[C]_{aq}$ is the aqueous phase concentration of the contaminant, and H_c is the Henry's constant.

$$H_c = \frac{P_c}{[C]_{aq}} \tag{7}$$

In groundwater systems that are isolated from the vadose zone, Henry's law can be applied to estimate the distribution of contaminants between the aqueous phase and the gas phase. If direct exchange is possible with the vadose zone, equilibrium may not be achieved and the calculation of gas phase concentrations is more difficult. Additionally, volatilization from NAPLs in the vadose zone or floating on the water table can yield high concentrations of contaminants in the gas phase (16).

BIOTIC PROCESSES AFFECTING SOLUTE TRANSPORT

Biotic processes include those biological phenomena that affect the transport and/or fate of compounds (organics, inorganics, or the microbes themselves) in the subsurface. Biodegradation of organics is one process that is of particular interest to minimize human health risks associated with the widespread contamination of chlorinated ethenes and hydrocarbons in the environment, because this process is able to achieve mineralization (endproducts CO_2,H_2O, etc.) and effectively render the contaminant innocuous (harmless). It has only been in the last two decades that the variety and magnitude of micro-organisms present in aquifers, and thus the ability of aquifers to support biodegradation, has been realized (33). Laboratory column studies (34) and improved field sampling methods are chiefly responsible for these advances.

Energy Flow and Metabolism

All living organisms require energy to survive, and the capture of usable energy through the process of catabolism is a significant part of an organism's overall metabolism. Bacteria that obtain energy from chemical forms are classified as chemotrophs. Chemotrophic organisms are further differentiated as either lithotrophs, which use inorganic sources of energy, or organotrophs, which use organic compounds. Examples of lithotrophic substrates include ammonia (NH_3), hydrogen (H_2), ferrous iron (Fe^{2+}), and sulfide (HS^-). Examples of common groundwater contaminants that serve as organotrophic substrates include fuel components and chlorinated solvents (35).

Biodegradation involves the process of extracting energy from organic chemicals via oxidation of the organic chemicals during catabolism. As a chemical is oxidized, it loses electrons. For this reason, chemotrophic substrates are often referred to as primary electron donors. Electrons lost during oxidation are coupled with the reduction of electron acceptors. Eventually, the complex sequence of oxidation-reduction reactions that occur during catabolism results in the reduction of a terminal electron acceptor. Common terminal electron acceptors in groundwater systems include oxygen (O_2), nitrate (NO_3^-), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). Aerobic catabolism occurs when oxygen is the terminal electron acceptor, and anaerobic conditions are in place when all other terminal electron acceptors are used. Typically, an individual bacterial strain is capable of using only one terminal electron acceptor. Facultative aerobes are the exception to this rule; these organisms can use nitrate as a terminal electron acceptor in the absence of the preferred oxygen. An important evaluation of contaminant biodegradation potential involves an analysis of the availability of primary electron donors and terminal electron acceptors, as their presence is required for organisms to obtain energy for survival and selects the types of organisms that will be present (16).

The metabolism of organic contaminants can be broadly differentiated by the ability of organisms to use the contaminant for catabolic processes. If the compound is a primary electron donor and provides the bacterium with energy for cell growth, the contaminant is referred to as a primary substrate, whereas secondary substrates are contaminants that provide the cell with energy, but are present at concentrations that are not sufficient to support the energy requirements of the organism. If a compound is metabolized fortuitously as the cell is obtaining energy from another primary electron donor, the transformation is referred to as cometabolic (36,37). However, cometabolism is generally a slow process and not all chlorinated solvents are susceptible (e.g., PCE and carbon tetrachloride). In the case of chlorinated ethenes, the contaminant serves as an anaerobic terminal electron acceptor in a process referred to as dehalorespiration, which is faster than cometabolism.

Metabolic Pathways of Common Contaminants

An overview of how bacteria are capable of metabolizing two of the primary groundwater contaminants (hydrocarbons and chlorinated solvents) is presented in this section. It is important to note that this continues to be an area of extensive research. Theoretical frameworks continue to change and it is difficult to assert definitive analysis regarding the totality of metabolic processes that may impact an individual contaminant's fate.

As a result of accidental spills and leaking underground storage tanks, hydrocarbon compounds consisting of gasoline, diesel, and jet fuels are common groundwater contaminants. Of particular concern are benzene, toluene, ethylbenzene, and xylene isomers (BTEX), which, under aerobic conditions, are rapidly biodegraded as primary substrates (38). Unfortunately, the oxygen demand resulting from the aerobic oxidation of these compounds can exceed the solubility of oxygen in water. Dissolved oxygen concentrations are rapidly depleted because of the biodegradation of these and other fuel constituents, yielding anaerobic conditions in contaminated aquifers (39).

Only recently have laboratory studies confirmed that the biodegradation of all BTEX compounds occurs under all anaerobic electron acceptor conditions (listed above). From these studies, it appears that toluene is the most degradable under all electron acceptor conditions and benzene is the least degradable. Certain modeling studies of certain well-characterized contaminated field sites infer that anaerobic benzene degradation may occur *in situ*. Only several recent laboratory studies conducted under anaerobic conditions have demonstrated that benzene may degrade in the absence of oxygen (40). Despite the possibility of anaerobic degradation of BTEX compounds, it is still generally slower than rates that are observed through aerobic processes.

Chlorinated methanes, ethanes, and ethenes comprise a group of compounds commonly referred to as chlorinated solvents. Chlorinated ethenes, particularly tetrachloroethene (PCE) and 1,1,2-trichloroethene (TCE), are commonly used as degreasers and cleaning solvents in the dry cleaning, aviation, and computer industries. Through accidental spills, improper storage, and disposal techniques, these chemicals have become major subsurface contaminants (41). The extensive impacts observed are primarily because of their widespread usage by industry, their general mobility and persistence in the environment, and the health risks associated with compound exposure.

The metabolism of chlorinated solvents is perhaps more diverse than any other group of environmental contaminants. Depending on the compound of interest, the electron acceptor condition, and the presence of inducing substrates, the metabolism of chlorinated solvents may occur through primary metabolism, secondary metabolism, cometabolism, or through terminal electron acceptor processes (16). Laboratory studies (34,36,37,42–44) have shown that, in the presence of a suitable substrate, certain microbes are capable of anaerobically metabolizing PCE by using it as an electron acceptor. In this process, known as reductive dechlorination, PCE may be dechlorinated to 1,1,2-trichloroethene (TCE), to typically cis-1,2 dichloroethene (DCE), to vinyl chloride, and eventually to ethene and ethane, an innocuous compound (45).

SUMMARY OF SOLUTE TRANSPORT PHENOMENA

Fate and transport of solutes in subsurface soils and groundwater is impacted by a combination of many processes that are difficult to quantify. No two field sites or aquifers have the exact same characteristics. Soil type, pH, temperature, groundwater flow velocity, the availability of electron donors for microbes, and the contaminant itself (among other parameters) all influence the path and lifetime of the pollution source. However, measurement techniques are improving, and understanding these processes is an area of on going research.

In summary, nonreactive (conservative) chemicals tend to move unimpeded through the subsurface and are subject to only hydrodynamic processes such as advection, dispersion, and diffusion. On the other hand, many actual contaminants (organic solvent and fuels, and inorganic metals) can be affected during groundwater transport by a number of subsurface mechanisms and chemical reactions. The processes that have the largest impact on contaminant fate and transport include advection, dispersion, sorption, cosolvation, volatilization, biological oxidation-reduction reactions, and cometabolism/mineralization. These processes are reviewed in Table 1, and Fig. 2 provides an illustration of these processes acting on a typical contaminant spill.

BIBLIOGRAPHY

1. Wiedemeier, T.H., Rifai, H.S., et al. (1999). *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, New York.
2. Wierenga, P.J. (1995). *Water and solute transport and storage, Handbook of Vadose Zone Characterization and Monitoring*. CRC Press, Boca Raton, FL, pp. 41–60.
3. Domenico, P.A. and Schwartz, F.W. (1998). *Physical and Chemical Hydrogeology*. 2nd Edn. John Wiley & Sons, New York.

Table 1. Subsurface Processes Affecting Solute Transport

Category	Process	Contaminant (Solute) Behavior
Hydrodynamic Solute Transport	Advection	Plug flow; movement with bulk fluid
	Diffusion	Movement from high to low concentration
	Dispersion	Spreads out and dilutes
Abiotic Solute Transport	Sorption	Decreased solubility
	Ion exchange	Neutralizes the charge and sorbs
	Cosolvation	Increased solubility by solvent
	Oxidation-Reduction	Transfer of electrons
	Hydrolysis	More susceptible to biodegradation
	Volatilization	Phase transfer from aqueous or sorbed to gas
Biotic Transport Influences	Cometabolism	Metabolized as cell obtains energy
	Mineralization	Broken down to benign products
	Oxidation-Reduction	Microbial driven transfer of electrons

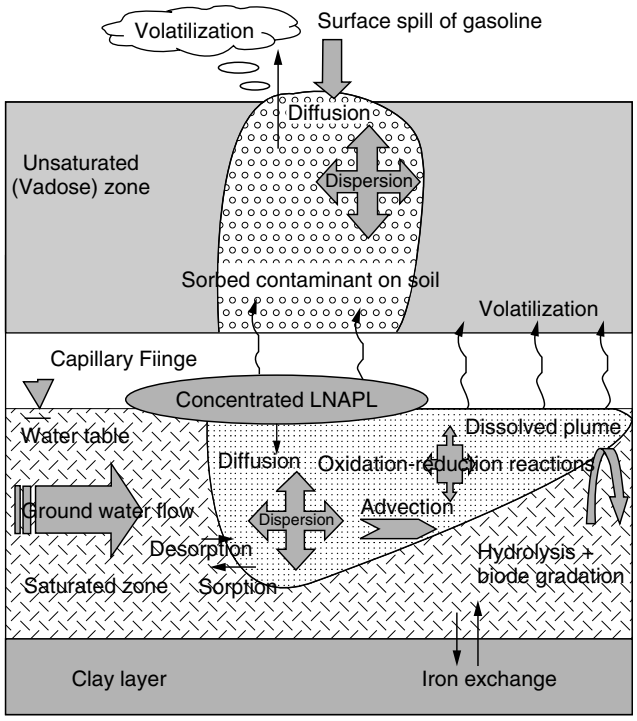


Figure 2. A typical scenario showing the processes impacting a surface gasoline spill, and its transport through the vadose zone to the groundwater.

4. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
5. Charbeneau, R.J. (2000). *Groundwater Hydraulic and Pollutant Transport*. Prentice-Hall, Upper Saddle River, NJ.
6. Bedient, P.B., Rifai, H.S., and Newell, C.J. (1999). *Ground Water Contamination, Transport and Remediation*. Prentice-Hall, Upper Saddle River, NJ.
7. Bear, J. (1979). *Hydraulics of Ground Water*. McGraw-Hill, New York.
8. Fetter, C.W. (1993). *Contaminant Hydrogeology*. Macmillian Publishing Company, New York.
9. Mackay, D.M., Freyberg, D.L., Roberts, P.V., and Cherry, J.A. (1986). *Water Resources Res.* **22**(13): 2017–2029.
10. Roberts, P.V., Goltz, M.N., and Mackay, D.M. (1986). *Water Resources Res.* **22**(13): 2047–2058.
11. Weber, W.J., Jr. (1972). *Physiochemical Process for Water Quality Control*. John Wiley & Sons, New York.
12. Fu, G., Kan, A.T., and Tomson, M.B. (1994). *Environ. Toxicol. Chem.* **13**(10): 1559–1567.
13. Kan, A.T., Fu, G., and Tomson, M.B. (1994). *Environ. Sci. Technol.* **28**: 859–867.
14. Kan, A.T., Fu, G., Hunter, M.A., and Tomson, M.B. (1997). *Environ. Sci. Technol.* **31**: 2176–2185.
15. Pignatello, J.P. and Xing, B. (1995). *Environ. Sci. Technol.* **10**: 1–11.
16. Hughes, J.B. (1999). *Ground Water Contamination, Transport and Remediation*. Prentice-Hall, Upper Saddle River, NJ, pp. 203–240.
17. Knox, R.C., Sabatini, D.A., and Canter, L.W. (1993). *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, FL.
18. Mitchell, J.K. (1976). *Fundamentals of Soil Behavior*. John Wiley & Sons, New York.
19. Gorelick, S.M., Freeze, R.A., Donohue, D., and Keely, J.F. (1993). *Groundwater Contamination: Optimal Capture and Containment*. Lewis Publishers, Boca Raton, FL.
20. Rice, D., Powers, S.E., and Alvarez, P.J.J. (1999). Potential scenarios for ethanol-containing gasoline released into surface and subsurface waters. In: *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*. Report to the California Environmental Policy Council in Response to Executive Order D-5-99. Vol. 4.
21. Molsen, J.W., Barker, J.F., Frind, E.O., and Schirmer, M. (2002). *Water. Res. Research* **38**(1).
22. Powers, S.E. et al. (2001). *Crit. Rev. Environ. Sci. Technol.* **31**: 79–123.
23. Heermann, S.E. and Powers, S.E. (1998). *J. Contam. Hydrol.* **34**: 315–341.
24. Rixey, W.G. and He, X. (2001). Dissolution characteristics of ethanol from NAPL sources and the impact on BTEX groundwater concentrations. In: *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*. November 14–16, Houston, TX, Ground Water Publishing Company, Dublin, OH, pp. 41–52.
25. Kleeka and Gonsior. (1984). *S.J. Chemosphere* **13**: 391–402.
26. Macalady, D.L. and Wolfe, N.L. (1984). *Abiotic hydrolysis of Sorbed Pesticides*. ASC Symposium Series, No. 259, pp. 221–244.
27. Schwartzenbach, R.P., Gschwend, P.M., and Imboden, D.M. (1993). *Environmental Organic Chemistry*. John Wiley & Sons, New York.

28. Johnson, R.L., Palmer, C.D., and Fish, W. (1989). *Transport and Fate of Contaminants in the Subsurface*. U.S. Environmental Protection Agency, Ada, OK, EPA/625/4-89-019.
29. Mackay, D. and Leinonen, P.J. (1975). *Environ. Sci. Technol.* **9**: 1178–1180.
30. Mackay, D. and Wolkoff, A.W. (1973). *Environ. Sci. Technol.* **7**: 611–614.
31. Mackay, D., Shiu, W.Y., and Sutherland, R.P. (1979). *Environ. Sci. Technol.* **13**: 333–337.
32. Thibodeaux, L.T. (1996). *Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil*. John Wiley & Sons, New York.
33. Young, L.Y. and Cerniglia, C.E. (1995). *Microbial Transformation and Degradation of Toxic Organic Chemicals*. John Wiley & Sons, New York.
34. Maymo-Gatell, X., Tandoi, V., Gossett, J.M., and Zinder, S.H. (1995). *Appl. Environ. Microbiol.* **61**: 3928–3933.
35. Rittman, B.E. and McCarty, P.L. (2001). *Environmental Biotechnology: Principles and Applications*. McGraw-Hill, New York.
36. Hollinger, C., Schraa, G., Stams, A.J.M., and Zehnder, A.B. (1993). *Appl. Environ. Microbiol.* **59**(9): 2991–2997.
37. Carr, C.S. and Hughes, J.B. (1998). *Environ. Sci. Technol.* **32**: 1817–1824.
38. Alvarez, P.J.J. and Vogel, T. (1991). *Appl. Environ. Microbiol.* **57**: 2981–2985.
39. Lee, M.D. et al. (1988). *CRC Cri. Rev. Environ. Control.* **18**: 29–89.
40. Lovely, D.R., Coates, J.D., Woodward, J.C., and Phillips, E.J.P. (1995). *Appl. Environ. Microbiol.* **61**: 953–958.
41. Pankow, J.F. and Cherry, J.A. (1996). *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*. Waterloo Press, Portland, OR.
42. DiStefano, T.D., Gossett, J.M., and Zinder, S.H. (1992). *Appl. Environ. Microbiol.* **58**(11): 3622–3629.
43. Smatlak, C.R., Gossett, J.M., and Zinder, S.H. (1996). *Environ. Sci. Technol.* **30**(9): 2850–2858.
44. Yang, Y. and McCarty, P.L. (2000). *Environ. Sci. Technol.* **34**: 2979–2984.
45. Freedman, D.L. and Gossett, J.M. (1989). *Appl. Environ. Microbiol.* **55**: 2144–2151.

WATER IN THE UNSATURATED ZONE

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The soil profile immediately below the land surface and above the water table is called the unsaturated zone, where the pores contain both water and air. Figure 1 shows a schematic diagram of the unsaturated zone. This zone differs from the saturated zone, where the pores are saturated with water. The unsaturated zone is sometimes called the vadose zone.

The thickness of an unsaturated zone can range from zero (e.g., when a lake or marsh is at the surface) to hundreds of meters, as is common in arid regions. It is a zone of natural and human-induced activity. It experiences physical phenomena such as thermodynamic interactions, transport processes of various kinds, and chemical reactions involving both natural and artificial substances. Several biological activities involving plant roots, rodents, worms, microbiota, and other organisms also take place in this zone. The zone is used for cultivating plants, constructing structures, and disposal of waste.

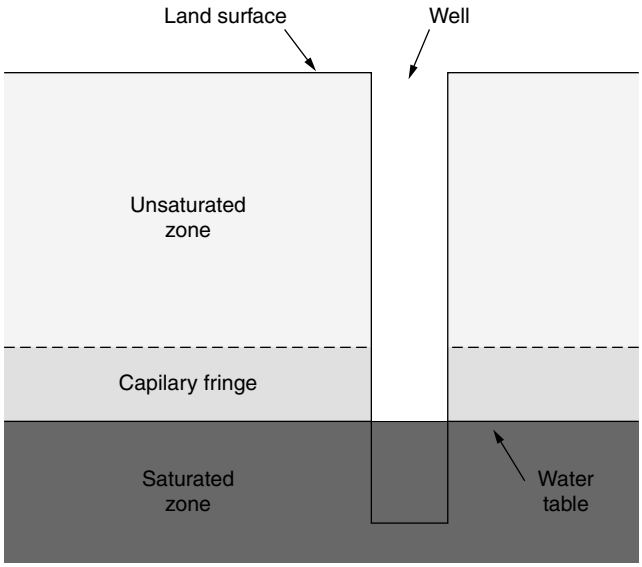


Figure 1. A schematic diagram of the unsaturated zone.

To a large degree, the unsaturated zone controls the transmission of water to aquifers (water bearing strata), as well as to the land surface, to water on the surface, and to the atmosphere. It also acts as a filter as it removes undesirable substances before they reach and affect aquifers. Figure 2 gives a pictorial representation of the unsaturated zone.

Though the unsaturated zone stores water, plant nutrients, and other substances, it is not always considered a major storage component of the hydrologic cycle because it holds only a tiny fraction of the earth's fresh water and this water is usually difficult to extract. But it is of great importance for storing water and nutrients in ways that are vital to the biosphere.

SOIL WATER

Soil water is normally considered to include both the water contained in the soil profile and the subsurface water in the unsaturated subsoil layers. Soil water may be present as gravity water in transit in larger pores, as capillary water in smaller pores, as hygroscopic water adhering

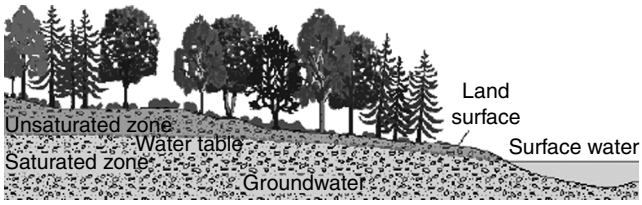


Figure 2. Unsaturated zone.

in a thin film to soil grains, and as water vapor. After a rain, gravitational water moves downward in larger pores, but it is dispersed into capillary pores or passes through the unsaturated zone to the groundwater or to a stream channel. Hygroscopic water is held very tightly to the soil surface by molecular attraction and is not normally removed from soil. Capillary water, therefore, is the important variable element of soil water.

SOIL WATER POTENTIAL

The most basic measure of the water in an unsaturated soil is water content or wetness, defined as the volume of water per bulk volume of the soil. Water is held in unsaturated soil by forces whose effect is expressed in terms of the energy state or pressure of the water. Like all matter, water can possess both kinetic and potential energy. However, in general, the flow of water in soils is too small to consider kinetic energy. Therefore, the energy state of soil water is represented by its equivalent potential energy. Potential energy is defined as the ability to do work. Work is done whenever an object is accelerated through a distance or heat is produced or transferred. Soil water potential thus measures the ability of soil water to move and/or produce heat. Water potential is important to any process in which soil water moves, such as infiltration and redistribution within the soil or removal of water from the soil by evaporation or plant uptake.

To define the soil water potential parameter, a reference body of water is defined, and the soil water potential of any other body of water is defined as the difference in potential energy concentration (potential energy per unit quantity of water) between the soil water and the reference body of water. The reference body of water is usually called the reference state, which is defined as "*pure* (no dissolved solutes), *free* (free of adsorptive forces) water at a specified temperature and *specified elevation* exposed to *atmospheric pressure*." The water potential of water in the reference state is zero.

Total soil water potential may formally be defined as the amount of work per unit quantity of pure water that must be done by external forces to transfer an infinitesimal amount of water reversibly and isothermally from the reference state to the soil at the point under consideration (1).

FACTORS AFFECTING WATER POTENTIAL

A change in the potential energy of the soil water brings about a change in the soil water potential. There are several factors that affect the potential energy of soil water, including adsorption of water onto soil particles, solutes dissolved in the soil water, the elevation of the soil water in the earth's gravitational field, and applied pressure (both positive and negative).

WATER POTENTIAL COMPONENTS

The total soil water potential can be broken into several components. A complete list of soil water potential components consists of gravitational potential, osmotic potential (also sometimes called solute potential), matric potential, vapor potential, hydrostatic pressure potential, and overburden pressure potential. The major potential components of interest in the unsaturated zone are gravitational potential, osmotic potential, and matric potential that give rise to the total potential as follows:

$$\Psi_t = \Psi_g + \Psi_o + \Psi_p + \dots \quad (1)$$

where Ψ_t is the total potential, Ψ_g is the gravitational potential, Ψ_o is the osmotic potential, and Ψ_p is the matric potential.

Gravitational potential is defined as the energy of water per unit volume that is required to move a specific amount of pure, free water from an arbitrary reference point to the soil-water elevation. It is independent of soil properties and solely dependent on the vertical distance between the arbitrary reference point and the interest point. Often, the soil surface is chosen as the point of reference, whereby the distance z (m) to each point of interest is negative by convention. Gravitational potential is given as

$$\Psi_g = \rho_l g z \quad (2)$$

where ρ_l is the density of the soil water, g is the acceleration due to gravity (m/s^2) and Ψ_g is the gravitational potential (J/m^3).

The osmotic potential component arises due to the salts in the soil water. It may be thought of more a suction than a pressure. In a dynamic soil–water–plant system, in the presence of a selective permeable membrane as found in the roots of plants, the pressure or energy potential (a suction) on the solution side is less than that of pure, free water. Water will pass through the membrane to the solution side until equilibrium is reached. The osmotic potential, Ψ_o, is given by

$$\Psi_o = -\frac{\Pi}{\rho_w} \quad (3)$$

where Π is the osmotic pressure and ρ_w is the density of water.

Soil is porous, so it acts as a semipermeable barrier to salt solutions. An individual particle has an electric field that causes a decrease in the concentration of the soil solution near the particle surface, which results in an increased cross-sectional area for water transport compared to the area available for transport of dissolved salts, causing water to move due to the osmotic difference. The amount of flow depends on the particle size of the soil and the gradient of the osmotic pressure. In coarse, saturated sand, soil pores are relatively larger than those in clays, and consequently, the thickness of fluid layer with decreased salt concentration is small compared to the total area available for transport. Thus, the semipermeability is small, and the transport of soil solution due to osmotic potential is negligible. In clays, with many more pores, the solutes in the soil solution can be completely repelled from the soil and restricted from flow. In such soils, water movement in response to an osmotic pressure gradient is significant.

The matric potential component results from the soil matrix. Water molecules can form hydrogen bonds with the surface of soil minerals that give rise to adsorption and with other water molecules that result in cohesion. In unsaturated soil, these forces of attraction between the soil mineral surfaces and the soil water exert a "pull" on the soil water reducing the free energy of the water. It is usual to deal with the combined effect of both capillary and adsorptive forces in the way in which water is held in the soil matrix. The matric potential is the potential of the water in a pore of the medium relative to the potential of the air that results primarily from the adsorptive and capillary forces of the soil matrix. When a medium is unsaturated, the water generally is at lower pressure than the air, so the matric potential is negative.

Moisture content increases as the matric potential increases. Zero matric potential is associated with high (saturated or nearly saturated) water content. As the matric potential decreases, the water content decreases. Figure 3 shows the relation between matric potential and water content, called a retention curve. It is a characteristic of a porous medium that depends on the nature of its pores. This relation strongly influences the movement of water and other substances in unsaturated media.

MEASUREMENT OF SOIL WATER

Soil water can be measured as either soil water content or soil water potential; conversion from one to the other uses the moisture retention curve. Their combined use provides a powerful approach to the study of soil fluxes in unsaturated soil.

The most commonly used method for measuring the water content of soil directly is the gravimetric method, which involves taking a number of soil samples of known volume and determining their weight loss when dried in an oven at 105 °C. The neutron probe is the most widely used indirect way of measuring soil water. In this method, a source of high-energy neutrons is used that is lowered into an aluminum access tube in the soil. Fast neutrons lose energy through collision with atoms of low atomic weight, such as the hydrogen in water, and are converted to slow neutrons. These slow neutrons are counted with a high count indicating high moisture content. Time-domain reflectometry (TDR) determines soil water content by measuring the dielectric constant of the soil. TDR has two significant advantages over the neutron probe method; it is nonradioactive and can be set up for an automatic, nonmanual operation. The satellite-mounted synthetic aperture radar (SAR) method has the potential for measuring soil moisture content on a drainage basin scale. It determines soil water content by monitoring changes in soil dielectric properties.

Tensiometers are the oldest and most widely used technique for measuring matric potential. They comprise a liquid-filled porous cup connected to a pressure-measuring device such as a mercury manometer or a pressure transducer. The cup is embedded in the soil, and water can flow between the soil and cup until the pressure potential inside the cup equalizes with that of the soil water. In fine-textured soils, the resistance block method may be useful. In this method, two electrodes are embedded in a porous block, which is buried in the soil. The matric potential in the block comes into equilibrium with that of the soil water, and the resistance across the electrodes varies with the resulting water content of the block. Gypsum resistance blocks can be used for measuring potentials as low as −15,000 cm (1500 kPa).

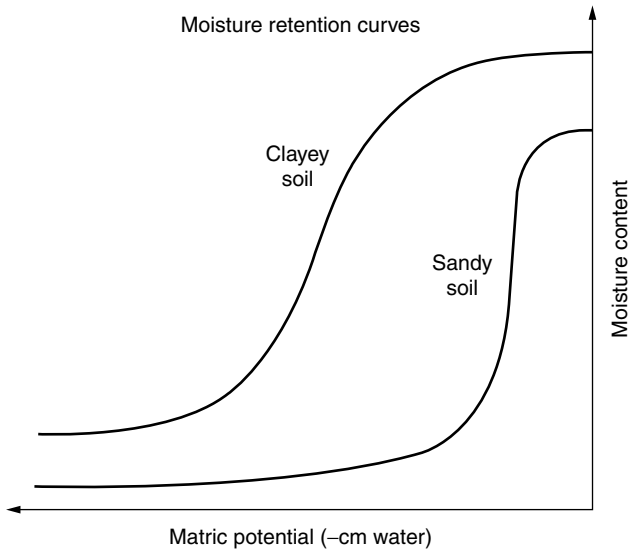


Figure 3. Moisture retention curves.

BIBLIOGRAPHY

1. Tindall, J.A. and Kunkel, J.R. (1999). *Unsaturated Zone Hydrology for Scientists and Engineers*. Prentice-Hall, Englewood, Cliffs, NJ.

GROUNDWATER AND VADOSE ZONE HYDROLOGY

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The vadose zone is the geologic media between the land surface and the regional water table.

The vadose zone

- is the foundation for most man-made structures;
- provides nutrients and water to all plant and animal life;
- protects drinking water reservoirs (aquifers);
- governs how much groundwater is replenished;
- provides the pathway for contaminants to penetrate into groundwater, and
- is one of the least understood media.

The latter point becomes evident when a definition for the vadose zone is needed. All publications include the unsaturated soil zone, but some publications include the capillary fringe; others do not. The term "vadose" is derived from the Latin noun *vadosu*s, which translates to "shallow".

The vadose zone includes the weathered soil horizon and the unconsolidated sediments and rocks below. The capillary fringe separates the water saturated zone from the unsaturated zone. The water saturated zone is often referred to as an aquifer if it allows significant amounts of water to be transmitted. Several processes take place in the vadose zone.

PROCESSES IN THE VADOSE ZONE

The processes, which influence the vadose zone and the recharge to groundwater include

- precipitation,
- evapotranspiration,
- surface water runoff, and
- infiltration and groundwater recharge.

Precipitation

Precipitation is the water that falls on the land surface as rain, snow, and other forms such as dew, frost, and irrigation water. It is measured as volume per time period (e.g., mm/a) or as volume per area and time (e.g., L/km^2 s), which is a relatively simple parameter to measure and is often available from meteorological stations. However, care should be exercised when using this parameter for climatic water balancing because there is great variability even between neighboring stations, due to the precipitation and wind characteristics as well as the various measuring devices.

Evapotranspiration

Evapotranspiration, the reverse of precipitation, represents the transport of water from the earth back to the atmosphere through evaporation and plant transpiration. This process depends on the microclimatic conditions at a given site. This parameter depends on many factors (air temperature and humidity, solar irradiation, vegetation, wind speed, etc.). It is more difficult to measure and therefore not available from all meteorological stations. Simple (1) and complex calculations (2–5) can estimate its range. Its units are generally reported as millimeter per time period. The vegetation type and cover greatly influence this parameter and are often neglected in standard formulas, which can lead to significant variations.

Surface Water Runoff

Surface water runoff is the amount of precipitation that does not immediately enter the subsurface and contributes to surface water discharge (e.g., into local creeks). A portion of this surface water runoff appears on the surface again after a short underground passage (interflow). The amount of surface water runoff depends on the size of the catchment, vegetative cover, relief [(slope or gradient) and depressions (pond formation)], soil cover and soil type, initial soil moisture content, and rainfall intensity. For instance, if the supply rate of water to the soil surface is greater than the soil's ability to allow the water to enter, excess water either accumulates on the soil surface or becomes runoff. Steep slopes cause greater runoff rates, allowing the water a shorter time to infiltrate. In contrast, gentle slopes have less impact on infiltration due to decreased runoff.

Surface water runoff is even more difficult to measure than any of the above parameters. Hydrological models aid in estimating it.

Effective Recharge or Infiltration

Both evapotranspiration and surface water runoff limit the amount of total precipitation that enters the subsurface, the effective recharge or infiltration into the vadose zone. The term infiltrability is generally used in soil physics and hydrology to define the maximum rate at which rain or irrigation water can be transmitted through a soil under a given condition.

As a general rule of thumb, a total of four water relevant zones exist in the vadose zone (after Reference 6):

1. a near-surface zone to shallow (<1 m) depths affected by episodic rain;
2. a zone below which shows signs of seasonal water infiltration;
3. a zone of virtually constant moisture content, in which the hydraulic gradient is unity (i.e., 1), and there is a predominantly downward flow toward the water table; and
4. a capillary zone above the water table, in which the water moves in the groundwater flow direction.

This simplified zoning is complicated by the fact that irregularities (heterogeneities) in the soil profile such as root channels, earthworm burrows, soil fissures or cracks, spatially varying sediment size therefore exhibiting variable hydraulic and physical characteristics

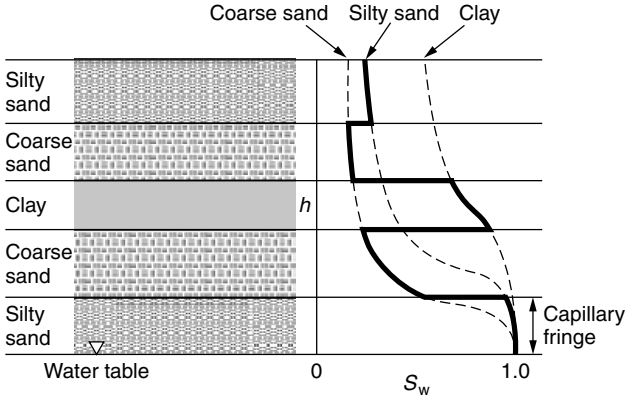


Figure 1. Saturated water content (S_w) above the water table for a layered sequence. Dashed lines represent water content for homogeneous sediments (from Reference 7, altered).

(see Fig. 1), and distinct layering allow preferential (i.e., faster) flow of water in selected areas. For instance, clay layers generally impede flow due to their lower saturated hydraulic conductivity, whereas sand layers have a lower tendency to retard the movement of infiltrating water. This process, which is also referred to as "fingering," can occur in less than a few percent and to up to 70% of the soil profile. Such layers generally retard water movement during infiltration. For the remainder of the soil profile, the entering moisture results in a semicontinuous wetting front, a zone of increased moisture content and a zone below of significantly lower moisture content. Beyond the wetting front, there is no visible penetration of water.

Infiltrating precipitation can appear as

1. retarded interflow discharging as surface runoff after a brief underground passage,
2. increased soil moisture, and
3. effective recharge.

The effective recharge can be measured by using lysimeters, but this requires a substantial effort. It is furthermore dynamic, changing constantly over time and space.

The measuring units are volume or m per time period. Infiltrating water also changes the moisture content of the soil. If rain infiltrates a previously dry soil (typical moisture content of less than 10% saturation), then the rainwater is first absorbed into the soil pores, increasing the moisture content. The soil gas in the soil profile needs to be replaced, and as a result the infiltration velocity is reduced initially. Later in the process when the soil gas dissolves gradually in the infiltrating water, the infiltration rate increases again before a renewed reduction occurs. This reduction is from increased solid particles washed into the soil profile from the rain and the growth of organisms near the soil surface. Additionally, the increase in soil moisture leads to a reduction in capillary pressure.

Snow and frost also impact the infiltration rate. In frost periods, soils of low initial water content may become porous, and the infiltration rate is increased. Soils of high initial water content may freeze and become nearly impermeable.

In detail, infiltration depends on material properties, such as

- grain size,
- porosity,
- capillary forces and soil suction,
- permeability, and
- fluid densities and viscosities.

MATERIAL DEPENDENCIES

Grain Size and Porosity

Unconsolidated materials are distinguished by their grain sizes. Various classifications exist, the grain sizes commonly decrease in the order block, cobble, gravel, sand, silt, clay, colloid, and ion. Clays are smaller than 2 μm, whereas colloids consist of particles less than 0.1 μm in size. On the other hand, gravels start at 2 mm. The distribution of soil grain size and bulk densities (often referred to as ρ) of soil and rock are commonly measured during geotechnical investigations.

With regard to water and contaminant transport, a critical parameter of vadose zone materials is the type and distribution of void spaces (pores). Loose materials contain widely distributed void spaces that typically are interconnected. These pores are usually individually very small, but numerous, and the total volume of pores usually varies from 30–50% of the total volume. However, not all of these pores are available for water circulation. A clay may exhibit a total porosity of >50%, however, only less than a few percent are available for water circulation. In contrast, in gravel sediments, almost all of the pore space (roughly 20% of the total volume) allows water transport.

As can be seen from Fig. 2, classifications exist for pore spaces. The largest pores are obviously present in the coarsest materials. Pores of the order of 60–1000 μm are present in sandy sediments. Small and smallest pores are present in clay grain size and below.

Also depicted in Fig. 2b is the approximate rate of water movement in meters per year. The coarser the sediments, the higher the rate of vertical water movement. It is, however, important to note that even in silts, the vertical water movement under unit gradient can be as high as 2 m per year.

Capillary Rise and Capillary Pressure

When water evaporates near the surface, it generates a low hydraulic potential, which is equilibrated by the capillary rise at the groundwater table. The rate at which this supply is determined is governed by the permeability (and size, respectively) of the sediments. Consequently, the height of the capillary fringe depends on the sediment's permeability, as Fig. 2a outlines. The water in the capillary fringe is held by capillary forces against gravity induced flow.

The capillary pressure (C_p, also named matrix or soil suction) for sands and silts can be estimated roughly from

$$C_p(\text{kPa}) = 0.3/\text{grain size (mm)} \quad (1)$$

The higher the soil suction, the higher the residual saturation of a sediment.

Soil–Water Characteristic Curve

The soil–water characteristic curve (also referred to as the water retention curve) for a soil is defined as the relationship between the water content and the capillary pressure. This curve is characteristic for each soil, it governs the rate at which water is taken up or released by the soil.

As can be seen from Fig. 3, when the water content decreases (i.e., the soil suction increases), the permeability of a sediment (here, a silty soil) decreases. The order of decrease depends on pore sizes. Sands have a much slighter decrease in permeability. Tight soils stay wet

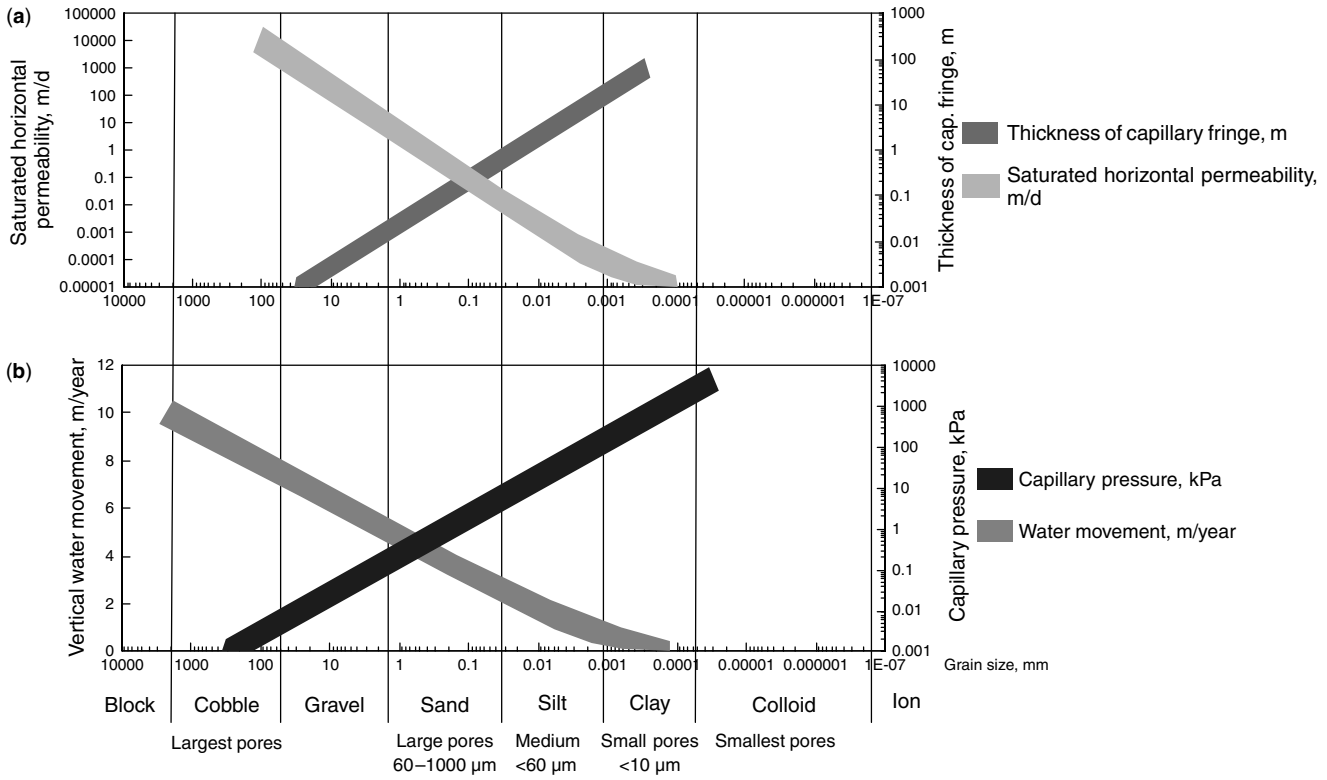


Figure 2. (**a**) Generalized diagram depicting the thickness of the capillary fringe and saturated horizontal permeability. (**b**) Generalized diagram depicting pore sizes, capillary pressure, and the vertical annual water movement rate of sediments.

for much longer, however, suffer much more from evaporative losses.

Figure 3 also introduces terms often used by soil scientists to describe the wetting and drying behavior of a soil. The term field capacity is used when the water content of a soil has reached a maximum (often referred to as Θ sat). Any further increase in soil moisture results in a water release (i.e., gravity induced flow). When the water content nearly equals its minimum, then the wilting point is reached. By definition, the wilting point equals a soil suction between 500 and 6000 kPa. A soil is referred to as "air dry" at or above a capillary pressure of 70,000 kPa. Furthermore, two terms are defined through this water retention curve: the air entry value and the residual water content. The air entry value is the meeting point of the two tangents shown in Fig. 3. The residual water content (referred to as Θ res) is defined similarly by using the lower tangent. Figure 3 further introduces a fundamental feature soils display when drying out or becoming wet (the hysteresis effect).

Hysteresis describes the effect of retardation of forces acting on a body to change (as if from viscosity or internal friction in magnetic induction and other physical phenomena). In soil science, when a soil is dried and then rewetted, the drying and wetting soil–water characteristic curves are not identical. The wetting curve is drier than the drying curve over a wide range of soil–water potentials. This hysteresis is caused by:

1. the drainage of an individual pore, which is controlled by the smallest radius. When the meniscus retreats under increasing tension, the pore's radius is decreasing. Rewetting (imbibition), on the other hand, is controlled by the pore's largest radius.
2. contact angle hysteresis. This is a well-recognized phenomenon, but it is only significant at relatively high flow rates. The slower the process, the less contact angle hysteresis. Because drainage and rewetting curves are generally measured at slow ("quasi-equilibrium") rates, this is not likely to be an important contributor.
3. Air entrapment effects. During imbibition, air can become trapped inside the larger soil pores. Given sufficient time, the entrapped air bubbles slowly dissolve in the water and cause hysteresis

Determining the Soil–Water Characteristic Curve. The most commonly used direct way to measure the soil–water potential is with a tensiometer. A body of pure water is hydraulically connected to the soil water via a permeable ceramic cup. If the soil water is under tension, then a small fraction of water in the tensiometer is pulled out, lowering the pressure inside. This negative pressure can then be measured by a gauge or pressure transducer.

Alternatively, mathematical models can help in determining the soil–water characteristics of a soil.

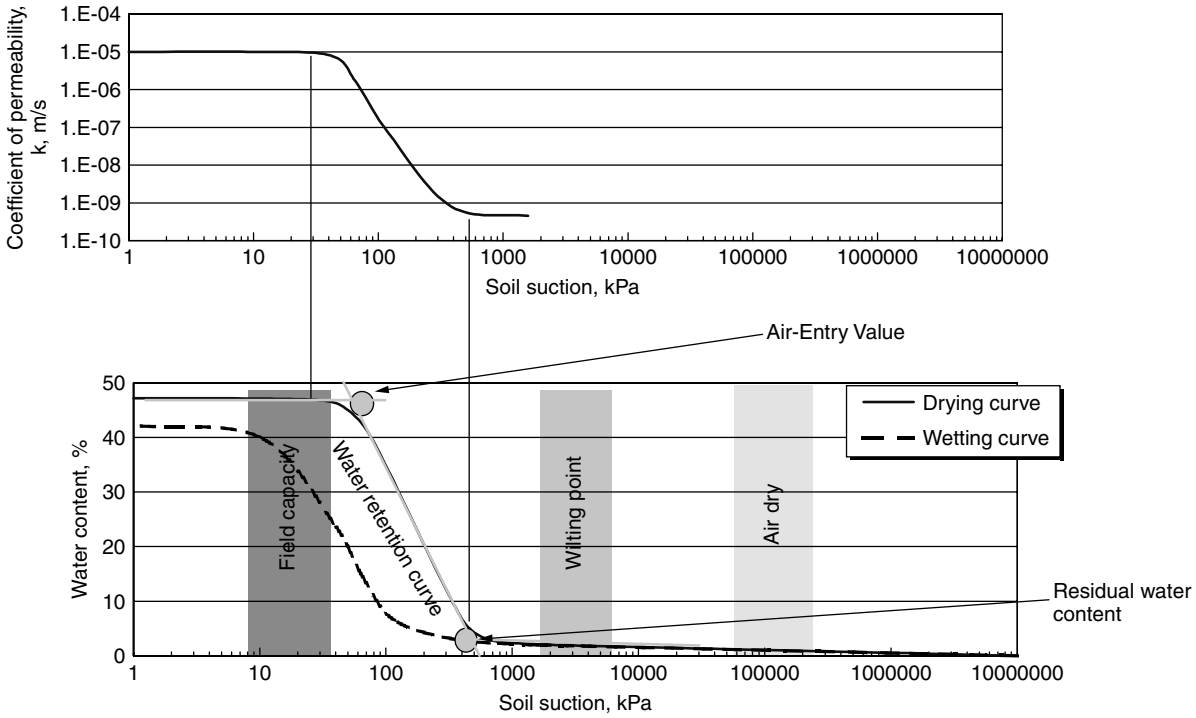


Figure 3. Visualization of the relationship between the permeability function and the soil water characteristic curve (from Reference 8, altered).

Hydraulic Conductivity

The basic formula to determine hydraulic conductivity was first developed by Henry Darcy in 1856 when he determined that the flux of water in sand columns depends on hydraulic conductivity and the hydraulic gradient. It can further be shown that hydraulic conductivity depends on both the water and the porous media properties according to

$$K = \frac{k\varphi g}{\mu} \tag{2}$$

where μ = viscosity,
ϕ = density
g = acceleration of gravity
k = intrinsic permeability of the soil (independent of fluid).

The intrinsic permeability is generally a function of the porous media, and it is proportional to the square of the grain diameter, $k \sim d^2$. Consequently, capillary pressure depends on the soil's conductivity:

$$Cp \sim 1/\sqrt{K} \tag{3}$$

This relationship is commonly used in numerical modeling studies to scale the magnitude of the capillary pressure curves in the absence of direct measurements of capillary pressure.

Measurements of Hydraulic Conductivity. The hydraulic conductivity of an aquifer with respect to water can be determined by a variety of field tests, including pumping tests from groundwater monitoring wells, slug tests, and other indirect measurements like grain-size distribution. In vadose zone studies, tensiometers are used for determining the field capacity of a soil.

FLOW PROCESSES IN THE VADOSE ZONE

Two processes control water in the vadose zone. The first is gravity, which moves water downward. The second is a capillary process that, similar to water dripped slowly on a sponge, moves water in all directions and stores and releases it. The capillary process is controlled by the nature of the sediment and rock and the pores and fractures within it. In most cases, capillary processes are dominant in fine-grained sediments (clay, silt, and the like), whereas gravity is dominant in coarse-grained sediment and large fractures. Pores and fractures can be completely filled with water in places within the vadose zone. These saturated portions of the vadose zone are typically referred to as "perched water" or "capillary fringe," depending on where they occur. At most sites, the water content is changing over time throughout the system representing a dynamic system.

Once saturation is continuous, this groundwater moves through the system from the highest potential to the lowest. Numerical modeling studies show that a range of infiltration patterns occur, which can be related to the ratio of infiltration rate to unsaturated hydraulic conductivity. A high value of this ratio reflects a prevailing hydraulic conductivity, which cannot readily redistribute the newly infiltrated moisture. Moisture accumulates in the near-surface region before advancing down through the soil as

a distinct wetting front. In contrast, low values of the ratio of rainfall to unsaturated hydraulic conductivity show minimal moisture accumulation, as the relatively small volumes of infiltrating moisture are readily redistributed through the soil profile.

MODELS

Accurate *in situ* measurement of unsaturated hydraulic conductivity is cumbersome and time-consuming. One alternative to direct measurement of unsaturated hydraulic conductivity is to use theoretical methods, which predict the conductivity from more easily measured soil water retention data. Methods of this type are generally based on statistical pore-size distribution models, a large number of which have appeared in the soil science and petroleum engineering literature during the past several decades (see Reference 9 for a review). Implementation of these predictive conductivity models still requires independently measured soil–water retention data. Measured input retention data may be given either in tabular form or by closed-form analytical expressions, which contain parameters that are fitted to the observed data.

Water flow in variably saturated soils is traditionally described by the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left\{K(\theta)\frac{\partial h}{\partial z}\right\} + \frac{\partial K(\theta)}{\partial z} \tag{4}$$

where h is the soil water pressure head (or fluid pressure with dimension L), θ is the moisture content [–], t is time (T), z is soil depth (L), and K is the hydraulic conductivity [LT−1]. The solution of the Richards equation requires knowledge of the unsaturated soil hydraulic functions $\theta(h)$ and $K(h)$ or $K(\theta)$.

Several equations have been proposed to describe the soil–water retention curve near saturation. Most of these functions are mathematically too complicated to be easily incorporated into predictive pore-size distribution models for hydraulic conductivity. A smooth function with attractive properties is the equation of van Genuchten (10):

$$S_{\text{eff}}(h) = [1 + (ah)^n]^{-m} \tag{5}$$

where a, n, and m are empirical constants affecting the shape of the retention curve (i.e., curve fitting parameters). Another mathematical solution is provided by Brooks and Corey (11).

Various computer programs exist to model unsaturated soil properties, including (but not limited to)

- Soil Vision: www.soilvision.com.
- Rosetta: U.S. Salinity Laboratory USDA; http://www.ussl.ars.usda.gov/models/rosetta/rosetta.
- RETC: Code for Quantifying the Hydraulic Functions of Unsaturated Soils, U.S. Salinity Laboratory USDA; http://www.ussl.ars.usda.gov/models/retc.
- SEEP/W: http://www.geo-slope.com/products/seepw.asp.
- Hydrus: http://www.ussl.ars.usda.gov/models/tutorials/hydrus2d/tutorial2d.htm.
- UnSat: Waterloo Hydrogeologic Inc;. http://www.flowpath.com.

BIBLIOGRAPHY

1. Linacre, E. (1993). A three-resistance model of crop and forest evaporation. *J. Theor. Appl. Climatology* **48**: 41–48.
2. Penman, H.L. (1948). Natural evaporation from open water, bare soil and grass. *Proc. R. Soc.London* **A193**: 120–146.
3. Thorntwaite, C.W. and Mather, J.R. (1955). *The water balance, Publication in Climat.* VIII, Nr.1. Drexel Inst. Laboratory of Climatology, Centerton, NJ.
4. Turc, L. (1954). Le bilan d'eau des sols, relations entre les precipitations, l'evaporation et l'ecoulement. *Trois Journée d'Hydraulique*. Alger.
5. Haude, W. (1955). Zur Bestimmung der Verdunstung auf möglichst einfache Weise. *Mitt. dt. Wetterd.* **2**: 11, Bad Kissingen.
6. Faybishenko, B. (2000). Vadose Zone Characterization and Monitoring—Current Technologies, Applications, and Future Developments. In: *Vadosc Zone Science and Technology Solutions*. Battelle Press, Columbus, OH.
7. Looney, B.B. and Falta, R.W. (Eds.). (2000). *Vadose Zone Science and Technology Solutions*. Battelle Press, Columbus, OH, pp. 1–1465.
8. Fredlund, M.D. (1988). Unsaturated seepage modelling made easy. *Geotechnical News* **June**.
9. Mualem, Y. (1986). Hydraulic conductivity of unsaturated soils: Prediction and formulas. In: *Methods of Soil Analysis*. A. Klute (Ed.), Part 1. *Physical and Mineralogical Methods*. Agron. Monogr. 9, 2nd Edn. American Society of Agronomy, Madison, WI, pp. 799–823.
10. van Genuchten, M.Th. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **44**.
11. Brooks, R.H. and Corey, A.T. (1964). *Hydraulic Properties of Porous Media*. Hydrology Papers, No. 3, Colorado State University, Fort Collins, CO.

VADOSE ZONE MONITORING TECHNIQUES

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INTRODUCTION

Monitoring fluids of the vadose zone has multiple motives, including detecting contaminants, measuring soil properties and water conditions for construction or monitoring geologic hazards, and determinations of water saturation that may be used for optimizing irrigation. Because fluids must move through the vadose zone to reach the water table, monitoring of the vadose zone allows predicting possible sources and processes of groundwater contamination. Geologic hazards such as landslides,

rising water tables, or land subsidence can be partially predetermined by monitoring the vadose zone. And in agriculture, monitoring soil water content to irrigate most efficiently has a long history.

Monitoring the temporal and spatial variance in the vadose zone is vitally important to engineers, geologists, meteorologists and other environmental scientists interested in studying water and contaminants. There are many techniques that directly or indirectly assess water content, sorbed mass, gaseous and liquid contaminants, flow direction, and other parameters that may be monitored. The methods discussed here are divided into two categories, direct and indirect monitoring techniques. Direct monitoring techniques require a degree of sampling or large-scale soil disturbances. Conversely, indirect techniques are analogous to remote sensing in which no disturbance to the soil or water is required, although a well may be required in some techniques. This section discusses in short detail some of the attributes and shortfalls of most of the currently used techniques for monitoring the three phases of the vadose zone: liquid, soil, and gas. For a more in-depth understanding, readers are directed to the references listed after each entry.

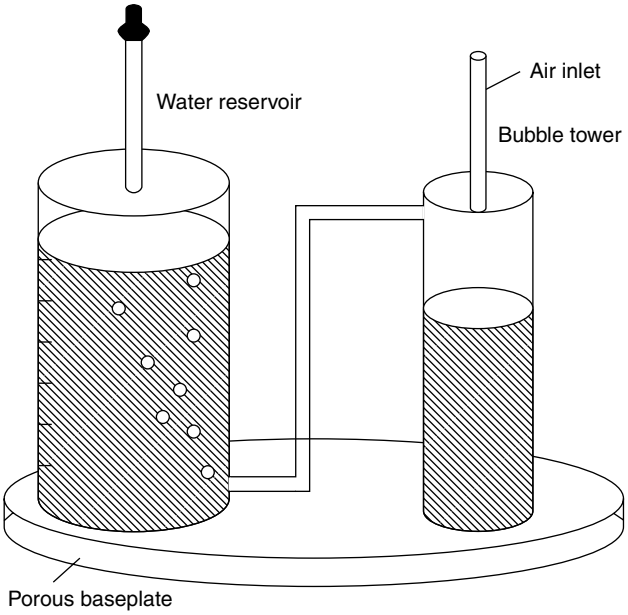


Figure 1. Tension infiltrometer. Tension measurements may be made using a handheld tensiometer on nongraduated models or on the side of graduated models (pictured).

INDIRECT MONITORING METHODS

Indirect methods for monitoring the vadose zone commonly have links to geophysical tools, principles, and techniques. Many vadose zone characteristics such as water content, the presence of contamination, and flow direction, among others may be determined without soil sampling. These techniques may also be used to determine the nature and extent of soil stratification for site delineation.

In practice, these methods are generally nonintrusive and do not require disturbing the soil, but some require well installation. When drilling or augering is necessitated, proper techniques must be ensured so that mud linings, drilling fluids, or other drilling by-products do not affect hydraulic conductivity, which may then affect measurements. It is also important to clean any grease or oil from drilling tools to avoid contamination and to clean tools between use.

Tension Infiltrometers

Tension infiltrometers are used to characterize hydraulic properties of saturated and partially saturated porous media, including saturated and unsaturated hydraulic conductivities. Infiltrometers are commonly used to measure hydraulic conductivity as a function of matrix potential in partially saturated porous media, sorptivity, steady-state volumetric flow rate (Q), and water content (Fig. 1).

There are variations of the disk infiltrometer and multiple methods of measuring hydraulic properties using infiltrometers, but all consist of three basic parts: the bubble tower, the reservoir, and a porous baseplate. The porous base plate lies flat on a wetted soil surface, and both the bubble tower and reservoir are connected perpendicularly to it. The purpose of the baseplate is to establish hydraulic contact between the soil and the reservoir. A thin layer of moist sand may be placed under the baseplate to ensure better hydraulic conductivity between it and the soil. The reservoir supplies water to the baseplate and the bubble tower; the latter consists of a series of tubes that relieve the vacuum in the reservoir when water infiltrates into the soil. Tension measurements correspond to the level of the water in the reservoir. An important point to note is that hydraulic conductivity must exist between the baseplate and the wet porous media for the device to operate.

The main advantage of disk infiltrometers is that *in situ* measurements of vadose zone hydraulic properties are rapid, reliable, and replicable and the devices are inexpensive and easy to operate. There exists, however, a limited range of tensions (generally 0 to 25 cm below the ground surface (BGS) in which the infiltrometers can operate, and measurements can be made only at the soil surface unless trenches are dug to the desired measurement level and the device used (1–3). Ideal soil properties are also assumed (soil is uniform, homogenous, and nonswelling), and pore closure may result from the weight of the device if used on freshly cultivated soils. There are other limitations that may be observed in Hussen and Warrick (4).

Neutron Moisture Probe

Initially designed for the agricultural industry, the neutron moisture probe has been adapted to environmental monitoring to obtain soil moisture levels. It is a nondestructive method of obtaining soil moisture levels when the probe is inserted in a well. The only restriction to depth of use is the length of the well used and the probe cord length.

Once lowered down a well, the probe begins to emit neutrons. The velocity at which neutrons return to the

probe is correlative to the substance by which they were reflected. Neutrons reflected by heavy atoms of the soil matrix return with higher velocities compared to those of neutrons reflected by lighter hydrogen atoms. Hydrogen may be found in organic matter or in mineral lattices, but water is the greatest source of hydrogen in the subsurface. Due to this, the counts of reflected low-velocity neutrons are correlative to soil moisture content. A complete moisture stratification along the length of a well may be obtained, given a well-calibrated instrument.

Attributes of the neutron probe include ease of use and high accuracy, given a well-calibrated probe. It may be operated by one person, and soil moisture changes of the order of 1–5 volume % may be measured. Water flow pathways may also be located with the instrument. The largest drawback of the neutron moisture probes lies with calibration difficulties that may be extreme. Improper neutron probe calibration nearly renders the probe useless. Ideally, the probe is calibrated using soils collected in a drum with a known quantity of water from the field site of interest. Another drawback is that neutron probes cannot distinguish between water and other substances with similar hydrogen densities in the subsurface, such as gasoline. Problems of applying single calibrations to multiple media types also arise, which is the case in heterogeneous soils. Inaccuracies may also be result from improper well packing and the presence of certain elements, such as migrating boron or chlorine. Finally, care should be taken to mitigate exposure to the neutron source (5–8).

Psychrometers

Psychrometers represent another tool adapted from the agricultural industry for environmental monitoring. Estimation of the hydraulic gradient using the matric suction, osmotic potential, and water vapor potential are possible.

The generic class of instruments used to measure relative humidity using both wet and dry bulb thermometers are called psychrometers; they may be used for both surface (agriculture) and subsurface (environmental) applications. For the latter, they are placed in a small diameter well and surrounded by silica flour or air-filled packers. A dry bulb thermometer is employed to measure the ambient temperature, and a wet bulb thermometer is then used to measure the temperature decrease resulting from fluid evaporation in the subsurface (evaporative cooling). Liquid-filled thermometers are not accurate enough for the precision required, however, and thus more precise thermocouple thermometers are employed. The junction of two wires, a thermocouple, generates an electrical current that is a function of the junction temperature. The temperature of the thermocouple determines the activity of the water surrounding it, which is then correlated with the evaporation rate.

The direction and magnitude of water and contaminant migration may be observed easily and inexpensively with psychrometers, but regular calibration and monitoring of the thermocouple are necessary as temperature deviations of $\pm 0.001\,^{\circ}\mathrm{C}$ between the thermocouple and the liquid phase can introduce significant errors. Regular calibration is necessary due to corrosion of metals and the accumulation of salts on the thermocouple junction. Also, psychrometer equations assume that water is the first liquid to condense, and, at a site containing volatile liquids, this may not always be true (9,10).

Tensiometry

Tensiometers measure the force which holds water to the soil, or the soil–water potential, at shallow depths (0 to 8 m BGS). Because water moves from areas of high potential energy to low, evaluation of water's energy may be used to estimate the direction of water flow and the direction of contaminant plume migration. Rapid measurements at different locations may be obtained with tensiometers, which may then be plotted to obtain a spatial distribution of water and an estimation of the water flow direction.

A tensiometer measures matric potential using a porous ceramic cup placed in the soil, a connecting tube, and a vacuum gauge. The cup and tube are filled with water to provide hydraulic contact from the tensiometer to the water in the soil. Once placed in the ground, water flows out of the cup and into the soil until equilibrium is reached. Because the device is sealed from the atmosphere, the drop of the water level in the tube creates a vacuum which is measured by a vacuum gauge or pressure transducer from the surface.

Tensiomenters represent a low-cost, simple, and accurate measurement of matric potential (11–13). It is one of the most widely used devices for monitoring soil moisture levels in the vadose zone, though tensiometry values are limited to tension values below 0.85 bar at atmospheric pressures near 1 bar. For field applications, air coming out of solution from water or air trapped in the tube are the major shortcomings. During installation, care must be taken to ensure good hydraulic contact between the cup and the soil.

Time-Domain Reflectometry

Time-domain reflectometry (TDR) allows shallow, rapid, *in situ* measurements of water content and electrical conductivity in porous media (14–17). It is commonly used to locate underground cables. It is a relatively new development in vadose zone monitoring that was first described by Topp et al. (18). Accuracy within 1–2% of volumetric water content is feasible with TDR.

TDR uses a probe that is inserted into the soil equipped with 2 or 3 metallic rods that transmit electromagnetic pulses. The travel time of these pulses across the rods through the soil is used to compute the soil's bulk dielectric constant from which the water content is inferred, which provides an average soil water content over the depth of probe insertion.

The main advantage of TDR is that simple and rapid accumulation of shallow soil moisture content with high volumetric accuracy is possible. Calibration requirements are minimal compared to other indirect monitoring methods, and measurements for spatial and temporal analyses are easily obtained. The drawbacks associated with TDR include temperature-dependent readings and probe insertion in rocky or hard substrates because

readings are limited to depth of insertion. Additionally, water molecules bound by interfacial forces in high surface area substances, for example, clays, result in lowered bulk dielectric constant compared to other soils at similar water content.

Ground-Penetrating Radar

Ground-penetrating radar (GPR) is an adaptation of seismic reflection for shallow use that images subsurface features by deploying radar waves. It may be used to image any homogeneity in the vadose zone, including contaminant plumes and soil stratification.

GPR is used to observe the electromagnetic impedance of soils using high-frequency radar waves to measure subsurface properties. It consists of an enclosed wave emitter and antenna unit that is dragged across the ground, generally in a grid pattern. Wave pulses are emitted and when an inhomogeneity is encountered, part of the incident energy is reflected back to the radar antenna within the unit. The reflected signal is amplified and transformed into a viewable image. The data are in visual form, not a quantified form, so results must be interpreted.

Any inhomogeneity in the vadose zone can be imaged with GPR. For vadose zone monitoring, contaminant plumes of both light nonaqueous phase liquids (LNAPLs) and dense nonaqueous phase liquids (DNAPLs), as well as buried utility lines and pipes may be imaged with GPR. Additionally, both underground storage tanks (UST) and leaking underground storage tanks (LUST) may be imaged and discerned. The most obvious drawback to GPR, however, is the fact that all data must be interpreted from visual images. Heterogeneities are viewed as anomalies in imaged data, which must be deciphered according to available information on subsurface conditions. Due to this fact, GPR benefits from use in combination with other vadose zone monitoring techniques to avoid misinterpretations (19,20).

Electrical Resistance Blocks

Electrical resistance blocks have been used in agriculture for more than 50 years to measure soil moisture in dry areas. In the environmental field, they are employed where other methods, including tensiometers, lysimeters, and manometers, are not operable due to low soil–water tension, generally between 0.5 and 15 bars.

The method consists of two or more electrodes that are placed in a porous block, commonly made of gypsum. The block is buried in the soil and allowed to remain until moisture equilibrium with the native soil is achieved. Changes in the electrical properties of the block, measured with the electrodes, reflect changes in the water content, which are measured with a wheatstone bridge resistance meter.

The benefits of this technique include low-cost, extensive historical use in agriculture research, and simplicity of use. It is generally useful for approximate soil moisture level changes. The disadvantages include limited historical use in the environmental industry and measurement and calibration difficulties at wet soil moisture potentials. Standard calibration curves exist, but as in many indirect techniques, soil-specific calibration of the instrument is recommended. Other limitations are associated with dissolution of the gypsum block and salinity changes in vadose zone water.

DIRECT MONITORING METHODS

Direct monitoring methods, in contrast to indirect monitoring methods, employ sampling of the vadose zone for liquid, soil, or gas. Obtaining liquid samples is fairly straightforward, using the most widely practiced method, suction lysimeters, but techniques for soil and gas sample acquisition are generally more complicated. Soil sampling commonly involves trenching or digging of some sort, which may be subject to Occupational Safety and Health Administration (OSHA) guidelines (24). Trenches deeper than 5 feet are subject to OSHA regulations and diggings deeper than 20 feet require the approval of a professional engineer. Soils are also subject to maximum allowable slope protocol, depending on their nature. In addition, certain cases may require confined space, heavy machinery, or decontamination permits. Readers are referred to OSHA literature for proper digging protocol. In gas sampling, problems stem from the nature of the phase being sampled, and, to a lesser extent, safety concerns. Vadose zone gas readily exchanges with any other gas with which it comes in contact, and thus samplers must be fully enclosed. Special safety procedures are required when considering volatile substances, such as methane.

Additionally, direct monitoring methods have a much higher risk of introducing contamination into the aquifer or exposing workers to contamination, and thus proper field procedures are absolutely necessary. In contaminated areas, all equipment must be constructed of nonreactive and low sorbing materials and be decontaminated between each use (25–27).

Direct Liquid Monitoring Techniques

Directly monitoring the liquid phase of the vadose zone involves obtaining a representative sample, whether in the form of water or NAPL. These may be important for soil–water chemistry analyses or contaminant plume delineation, among others. The primary method of collection is by using suction lysimeters placed into unconsolidated soil. As a suction device, lysimeters rely on applying a vacuum greater than the soil–water tension to draw a water sample up to the surface. A porous cup is inserted into the soil or in a shallow well, and a vacuum tube connects it to the surface. Once the vacuum is applied, water is drawn to the surface and a sample is obtained. Outside of lysimeters, other methods involve driving devices into unconsolidated sediment or lowering devices down wells above the water table to acquire liquid samples. Lysimeters have the advantage of being relatively cheap and simple to install. Virtually no maintenance is required, although sample volumes may be small.

Described by Gardner (28), wavelengths of light from gamma to X ray may be used to monitor the water content of the vadose zone by direct soil sampling. In practice,

however, only gamma rays are employed. In this method, a sample is collected and a narrow beam of gamma radiation is sent through it. A recorder on the opposite side of the sample records only those rays that passed freely through the sample with no reflection along the way. By this method, the volumetric water content can be measured (29).

Direct Soil Monitoring Techniques

Due to the sorbing nature of many contaminants, soil samples are used to monitor the spatial and temporal distributions of contaminants in the soil. For certain applications, undisturbed samples are desired, in which case special precautions must be taken, and certain sampling tools and techniques must be employed. Generally, soil sampling involves inserting a device into the ground to recover a soil sample, although more intensive methods may be necessary in certain situations. Hand-operated samplers are typically used for shallow sampling and mechanically powered devices for deeper sampling. There are five basic hand-operated samplers, as described by Dorrance et al. (30), that include screw augers, barrel augers, tube samplers, hand-powered augers, and bulk samplers (shovels, etc). Each type has its own pros and cons depending on cost, ease of use, availability, size of matrix grains, degree of sediment cohesiveness, and other factors. Due to these, sampler choice is often site specific. For deeper monitoring applications, mechanically powered tools such as a drill rig must be employed.

Direct Vadose Zone Gas Monitoring

Monitoring the gas phase of the vadose zone is important because many contaminants volatilize to a significant degree. Unlike liquid and soil phases, the gaseous component of the vadose zone is problematic because atmospheric air and foreign vadose zone gases readily exchange and react upon exposure. When sampling, all gaseous vadose zone samples must avoid exposure to foreign air, and all sampling methods must be designed to avoid it. *In situ* sampling and devices with internal liners designed to seal samples from the atmosphere are preferred (31).

Monitoring through sampling the gas phase typically involves hydraulically ramming a specially designed device into the soil where it collects samples via a vacuum and pumps them to the surface for collection. Passive gas sampling by an *in situ* absorbent, such as an activated carbon trap placed in the vadose zone, may be used, but less information is provided by this method. Direct sampling of gases is more desirable, but it is more difficult and costly. An alternative is monitoring gas advection by using groundwater tracers. A tracer that partitions to the gas phase is injected, samples are taken at other sites, typically at wells, and analyzed for the tracer concentration (32–35).

BIBLIOGRAPHY

1. Ankeny, M.M., Ahed, M., Kaspar, T.C., and Horton, R. (1991). Simple method for determining unsaturated hydraulic conductivity. *Soil Sci. Soc. Am. J.* **55**: 467–470.
2. Lin, H.S. and McInnes, K.J. (1995). Water-flow in clay soil beneath a tension infiltrometer. *Soil Sci.* **159**(6): 375–382.
3. Reynolds, W.D. and Elrick, D.E. (1991). Determination of hydraulic conductivity using a tension infiltrometer. *Soil Sci. Soc. Am. J.* **55**: 633–639.
4. Hussen, A.A. and Warrick, A.W. (1993). Algebraic models for disc tension permeameters. *Water Resour. Res.* **29**: 2779–2786.
5. Amoozegar, A., Martin, K.C., and Hoover, M.T. (1989). Effect of access hole properties on soil water content determination by neutron thermalization. *Soil Sci. Soc. Am. J.* **53**: 330–335.
6. Arslan, A., Razzouk, A.K., and Alain, F. (1997). The performance and radiation exposure of some neutron probes in measuring the water content of the topsoil layer. *Aust. J. Soil Res.* **35**(6): 1397–1407.
7. Dillel, D. (1982). *Introduction to Soil Physics*. Academic Press, London.
8. Grismer, M.E., Bali, K.M., and Robinson, F.E. (1995). Field scale neutron probe calibration and variable analysis for clay soil. *J. Irrig. Drainage Eng.—ASCE* **121**(5): 354–362.
9. Comstock, J.P. (2000). Correction of thermocouple psychrometer readings for the interaction of temperature and actual water potential. *Crop Sci.* **40**(3): 709–712.
10. Rawlins, S.L. and Campbell, G.S. (1986). Water potential: Thermocouple psychrometry. In: *Methods of Soil Analysis*. A. Klute (Ed.). Part 1, 2nd Edn. pp. 597–618.
11. Nyhan, J.W. and Drennon, B.J. (1990). Tensiometer data acquisition system for hydrologic studies requiring high temporal resolution. *Soil Sci. Soc. Am. J.* **54**(1): 293–296.
12. Williams, T.H.L. (1978). Automatic scanning and recording tensiometer system. *J. Hydrol.* **39**(1–2): 175–183.
13. Whalley, W.R., Leedsharrison, P.B., Joy, P., and Hoefsloot, P. (1994). Time-domain reflectometry and tensiometry combined in an integrated soil–water monitoring system. *J. Agric. Eng. Res.* **59**(2): 141–144.
14. Jones, S.B., Wraith, J.M., and Or., D. (2002). Time domain reflectometry measurement principles and applications. *Hydrologic Processes* **16**(1): 141–153.
15. Long, D.S., Wraith, J.M., and Kegel, G. (2002). A heavy-duty time domain reflectometry soil moisture probe for use in intensive field sampling. *Soil Sci. Soc. Am. J.* **66**(2): 396–401.
16. Lee, J., Horton, R., and Jaynes, D.B. (2002). The feasibility of shallow time domain reflectometry probes to describe solute transport through undisturbed soil cores. *Soil Sci. Soc. Am. J.* **66**(1): 53–57.
17. Noborio, K. (2001). Measurement of soil water content and electrical conductivity by time domain reflectometry: A review. *Comput. Electron. Agric.* **31**: 213–237.
18. Topp, G.C., Davis, J.L., and Annan, A.P. (1980). Electromagnetic determination of soil–water content: measurement in coaxial transmission lines. *Water Resour. Res.* **16**: 574.
19. Daniels, J.J., Roberts, R., and Vendl, M. (1995). Ground penetrating radar for detection of liquid contaminants. *Appl. Geophys.* **33**: 195–207.
20. Weil, G.J., Graf, R.J., and Leann, M.F. (1994). Investigations of hazardous waste sites using thermal IR and ground penetrating radar. *Photogrammetric Eng. Remote Sensing* **60**(8): 999–1005.
21. Everett, L.G., Wilson, G.G., and Hoylman, E.W. (1984). *Vadose Zone Monitoring for Hazardous Waste Sites*. Noyes, Park Ridge, NJ.
22. Fishback, P.E. (1977). Scheduling irrigations by electrical resistance blocks. *NebGuide* G 77–340, Institute of Agriculture and Natural Resources, University of Nebraska, Lincoln, NE.

23. Strangeways, I.C. (1983). Interfacing soil moisture gypsum blocks with a modern data-logging system using a simple, low cost, dc method. *Soil Sci.* **136**: 322.
24. http://www.osha.gov/ (Occupational Safety and Health Administration).
25. Fetter, C.W. (1999). *Contaminant Hydrogeology*, 2nd Edn. Prentice-Hall, Upper Saddle River, NJ.
26. Hudak, P.F. and Loaiciga, H.A. (1999). Conjunctive vadose and saturated zone monitoring for subsurface contamination. *Environ. Monitoring Assessment* **59**(1): 15–29.
27. Mickam, J.E., Bellandi, R., and Tifft, E.C., Jr. (1989). Equipment decontamination procedures for ground water and vadose zone monitoring programs: Status and prospects. *Ground Water Monitoring Rev.* **9**(2): 100–121.
28. Gardner, W.H. (1986). Water content. In: *Methods of Soil Analysis. Part 1.* A. Klute (Ed.). Monograph 9, American Society of Agronomy, Madison, WI.
29. Wilson, L.G. (1990). Methods for sampling fluids in the vadose zone. In: *Ground Water and Vadose Zone Monitoring*. ASTM STP 1053. D.M. Nielsen and Z.I. Johnson (Eds.) American Society for Testing and Materials, Philadelphia, PA, pp. 7–24.
30. Dorrance, D.W., Wilson, L.G., Everett, L.G., and Cullen, S.J. (1994). A compendium of soil samplers for the vadose zone. In: *Handbook of Vadose Zone Characterization and Monitoring*. L.G. Wilson, G.E. Lorne, and S.J. Cullen (Eds.). CRC Press, Boca Raton, FL, pp. 401–428.
31. Lewis, T.E., Crockett, A.B., Siegrist, R.L., and Zarrabi, K. (1991). Soil sampling and analysis for volatile organic compounds. E.P.A. *Ground Water Forum Issue*, EPA/540/4-91-001.
32. Fetter, C.W. (1999). *Contaminant Hydrogeology*, 2nd Edn. Prentice-Hall, Upper Saddle River, NJ.
33. Hubbell, J.M., Wood, T.R., Higgs, B., Wylie, A.H., and McElroy, D.L. (1998). Design, installation, and uses of combination groundwater and gas sampling wells. *Ground Water Monitoring and Remediation* **18**(3): 151–157.
34. Marrin, D.L. (1988). Soil-gas sampling and misinterpretation. *Ground Water Monitoring Rev.* **8**(2): 51–54.
35. Thompson, G. and Marrin, D. (1987). Soil gas contaminant investigations: A dynamic approach. *Ground Water Monitoring Rev.* **8**(4): 88–93.

VAPOR TRANSPORT IN THE UNSATURATED ZONE

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INTRODUCTION

The term "vapor" describes the gaseous phase of a substance that is normally a liquid or solid at standard atmospheric pressure and temperature. Examples of vapors that are important in environmental systems include humidity (water vapor), gasoline vapor, and solvent vapor. Soil and groundwater that are contaminated by organic solvents and fuel hydrocarbons may emit vapors that can move through the subsurface and reach the land surface. Human exposure to these harmful vapors has become an increasingly important topic in the evaluation and remediation of contaminated soil and groundwater. The potential for inhalation of vapors transported from a groundwater plume to the interior of buildings often controls the outcome of a risk based corrective action (RBCA) analysis (1). Additionally, vapors emanating from subsurface contamination contribute to the reduction of contaminant mass and may provide a beneficial mechanism of natural attenuation at sites where there are no human receptors. Subsurface processes affecting the transport of organic vapors through the soil above the water table (here defined as the unsaturated zone) may slow, reduce, or enhance the release of these vapors to potential receptors at the land surface. A careful investigation of organic vapor transport in the unsaturated zone is therefore important in assessing the potential for natural attenuation and the impact of even deep contamination on receptors at the land surface. This article describes potential sources, fate and transport, and measurement of organic vapors in the unsaturated zone. Although this article deals exclusively with organic vapors, many of the fate and transport properties discussed are also applicable to other vapors, including metals and moisture.

SOURCES OF ORGANIC VAPORS

Contaminants of concern in vapor transport in the unsaturated zone are typically volatile organic compounds (VOCs), although vapors emanating from inorganic sources such as mercury vapor may be of concern as well. A chemical is considered volatile if its Henry's law constant is 1×10^{-5} atm-m^3/mol or greater (2). Examples of VOCs that are important in impacted environmental systems include chlorinated solvents such as carbon tetrachloride, tetrachloroethylene, and trichloroethylene (and their degradation compounds), fuel hydrocarbons such as benzene, toluene, ethylbenzene, and *o*,*m*,*p*-xylenes as well as volatile pesticides such as chlordane, aldrin, and lindane. The U.S. Environmental Protection Agency lists 107 compounds whose toxicity and volatility produce a potentially unacceptable inhalation risk to receptors (2). These VOCs can be released into the subsurface environment from leaking landfill liners, improper disposal, accidental spillage, or leaking storage tanks (LSTs). Once in the subsurface, these compounds can become bound to the soil matrix, dissolved in groundwater (or soil water), and/or exist as a separate, residual phase known as a nonaqueous phase liquid (NAPL). Soil, aqueous, and NAPL-phase organics may all be sources of organic vapors in the subsurface. Therefore, organic vapor transport in the unsaturated zone requires understanding of interphase mass-transfer processes because the contaminant can be distributed among soil gas, water, soil, and NAPL phases. In modeling organic vapor transport, the equilibrium vapor concentration at the source of contamination is often estimated from the following relationships (3):

Soil contamination:

$$C_{\text{source}} = \frac{H_{\text{TS}} C_{\text{R}} \rho_{\text{b}}}{\theta_{\text{w}} + K_{\text{d}} \rho_{\text{b}} + H_{\text{TS}} \theta_{\text{a}}} \quad (4) \qquad (1)$$

Groundwater contamination:

$$C_{\text{source}} = H_{\text{TS}} C_{\text{w}} \qquad \text{Henry's Law} \qquad (2)$$

NAPL contamination:

$$C_{\text{source}} = \frac{x_i p_i \text{MW}_i}{RT} \qquad \text{Raoult's Law} \qquad (3)$$

where C_{source} is the vapor concentration at the source of contamination (ML^{-3}), H_{TS} is the dimensionless Henry's law constant at the system temperature (unitless), C_{R} is the soil concentration (MM^{-1}), ρ_{b} is the soil dry bulk density (ML^{-3}), θ_{w} is the soil water-filled porosity (L^3L^{-3}), θ_{a} is the soil air-filled porosity (L^3L^{-3}), K_{d} is the soil–water partition coefficient (L^3M^{-1}), C_{w} is concentration of the contaminant in the groundwater (ML^{-3}), x_i is the mole fraction of component i in the NAPL mixture (unitless), p_i is the vapor pressure of component i at the soil temperature ($\text{ML}^{-1}\text{T}^{-2}$), MW_i is the molecular weight of component i (M), R is the ideal gas constant ($\text{ML}^2\text{T}^{-2}\text{T}^{-1}\text{M}^{-1}$, e.g., 8.314570 $\text{J}^{\circ}\text{K}^{-1}$ mol^{-1}), and T is the soil temperature (T). Both Henry's law constant and vapor pressure rise with temperature for organic compounds of interest, so a higher source vapor concentration is expected from higher soil and groundwater temperature.

TRANSPORT AND FATE OF ORGANIC VAPORS IN THE UNSATURATED ZONE

Organic vapors emanating from contaminated soil or groundwater or from a residual phase such as gasoline floating on the water table may move through unsaturated zone soil gas by diffusion or soil-gas advection due to pressure or density gradients or a combination of these processes.

Diffusion

Molecular diffusion is the spreading out of compounds from random collisions resulting from thermal motion of atoms. These collisions may be between molecules themselves or between molecules and their surroundings. Under most environmental conditions, molecular diffusion in natural systems proceeds from locations of higher concentration toward locations of lower concentrations. In a typical scenario, organic vapors above a contaminated water table (high concentration) diffuse toward the land surface (lower concentration). The well-known relation describing the diffusion of a compound across a unit of cross-sectional area is Fick's first law:

$$F_{\text{x}} = -D^{\text{eff}} \frac{dC}{dx} \qquad (4)$$

where F_{x} is the mass flux [$\text{ML}^{-2}\text{T}^{-1}$], D^{eff} is the effective diffusion coefficient of the compound in the gas phase [L^2T^{-1}], and dC/dx is the concentration gradient of the compound in one dimension [$\text{ML}^{-3}\text{L}^{-1}$]. From this equation, it is apparent that the rate of molecular diffusion in the gas phase depends on the concentration gradient and the effective diffusion coefficient of the compound of interest. Several relations relate the effective diffusion coefficient to the free-air diffusion coefficient of the compound and the total and air-filled porosities of the diffusing media (5–14). An increase in diffusive flux is seen in soils with greater air passageways (i.e., greater porosities and air-filled porosities). Therefore, in a layered unsaturated zone, vapor diffusion from depth to the land surface is limited by the wettest, least porous soil layer. Because free-air diffusion coefficients are compound dependent, ranging from 2.5×10^{-3} $\text{cm}^2\,\text{s}^{-1}$ for hexachloroethane to 2.71×10^{-1} $\text{cm}^2\,\text{s}^{-1}$ for chloroethane among the 107 volatile compounds of concern to the U.S.EPA (2), different chemicals diffuse at different rates under the same concentration gradients. Increased temperature also produces an increased free-air diffusion coefficient, leading to a greater rate of diffusion relative to the same system at lower temperatures. Fick's First Law may not sufficiently describe vapor diffusion in systems where pore sizes are very small (Knudsen diffusion) and when volatile species constitute a substantial fraction of the total soil-gas concentration (nonequimolar diffusion) (15–17). In these situations, it may be necessary to employ the Stefan–Maxwell equation.

Advection

The flow of soil gas (advection) in the subsurface may be caused by gas-pressure gradients or, in certain cases, gas density gradients. Pressure-driven advection is produced when differences in soil-gas pressure form, causing soil gas to flow and carrying any vapors present with it. Air pressure gradients in the subsurface of natural systems may result from several phenomena. As diurnal or weather related atmospheric pressure cycles occur at the land surface, pressure waves are transmitted into the unsaturated zone and air may flow in response—a process known as "barometric pumping." Barometric pumping may cause soil gas to flow either toward the land surface carrying soil vapor or away from the land surface bringing in fresh atmospheric air (13,15,18–25). The underpressurization of an overlying building will produce gas pressure differences in subsurface soils. This underpressurization may be caused by thermal differences between indoor and outdoor air (stack effects), wind loading on the building superstructure, and unbalanced building ventilation (26,27). Soil-gas pressure gradients may also be produced by a rapidly rising or falling water table, as in coastal zones (28), or through the buildup of gas pressure from decomposing organic matter inside a landfill (29). Finally, natural temperature differences between warmer deep and cooler shallow soil gas will cause soil gas to rise (30,31). Density-driven flow of organic vapors may occur in the vicinity of residual-phase organic compounds whose saturation gas densities are greater than that of air. As organic liquids with high vapor pressures and molecular weights volatilize, the density of the soil gas surrounding the liquid changes. In almost all

cases, organic liquids have molecular weights that are greater than air, so the resulting density-driven flow is in a downward direction and is proportional to soil permeability and density differences between the vapor and air (32–34). Organic compounds for which density-driven advection may be significant include methylene chloride, 1,2-dichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and 1,1-dichloroethane, among others (32–34).

Sorption

As organic vapors move through the unsaturated zone by diffusion and advection, they come in contact with soil moisture, infiltrating rainwater, and the soil matrix itself. Each of these interactions may affect the concentration of the contaminant in the soil gas. Depending on the compound, organic vapors may adsorb to soil grain surfaces or partition into soil organic matter (35–40). Adsorption of relatively nonpolar organic vapors is suppressed by high humidity in the subsurface because as polar water molecules can effectively out-compete organic vapors for mineral-surface adsorption sites (41,42). For these high-humidity conditions, sorption may be limited to organic vapor partition into soil organic matter (41,42). Soil moisture trapped in unsaturated-zone pore space or infiltrating rain water may also sorb organic vapors to varying degrees (43,44). Finally, gas-phase organic compounds may adsorb to the air–water interface in unsaturated zones (45,46). Each of these sorption processes may act as both a source and a sink of organic vapors in the unsaturated zone.

Biodegradation

Under favorable conditions, organic vapors in the unsaturated zone that partition into soil moisture may be biodegraded by indigenous bacteria in oxidation/reduction reactions. The aerobic biodegradation of petroleum hydrocarbons requires an abundant oxygen supply as well as necessary nutrients of nitrogen and phosphorus (47–51). When oxygen is depleted, other possible electron acceptors for biodegradation of petroleum hydrocarbons include nitrate (NO_3^-), iron oxides (e.g., $Fe(OH)_3$), sulfate (SO_4^{2-}), and carbon dioxide (CO_2) (48). Lightly chlorinated compounds (e.g., chlorobenzene, dichlorobenzene) may be biodegraded under aerobic conditions. The more highly chlorinated hydrocarbons are recalcitrant to aerobic biodegradation but may undergo direct or cometabolic anaerobic reductive dechlorination. Reductive dechlorination has been observed to be most effective under sulfate-reducing and methanogenic conditions (52). In direct reductive dechlorination, the chlorinated hydrocarbon is used as an electron acceptor and the bacteria gain energy and grow as a result of the reaction (53). In cometabolic reductive dechlorination, enzymes produced during microbial metabolism of another hydrocarbon fortuitously reduce and dehalogenate the chlorinated contaminant. For either reductive dechlorination process to be successful, a primary substrate (electron donor) such as soil organic matter, lactate, acetate, methanol, or glucose is necessary (54).

VAPOR SAMPLING AND FLUX MEASUREMENT

Organic vapors in the unsaturated zone above contaminated soil or groundwater are typically sampled to provide evidence of biodegradation (49,55), calibrate vapor flow and transport models for estimating natural attenuation (23), or to estimate the region of contaminated groundwater (42,56,57). Soil gas is often sampled through low volume, inert pipe or tubing penetrating the subsurface to the desired sampling depth (42,44,49,56,58,59). This tubing can be installed with the help of a Geoprobe®-type device or inserted in a previously drilled borehole. The sampling portion of the tubing must be sealed from the atmosphere and other sampling depths to prevent preferential flow down the borehole during sampling. Samples may be collected from these vapor probes in various ways, including direct syringe withdrawal (49), pumping of soil gas into Tedlar® bags (57,60,61), or pumping of soil gas through adsorbent traps (58,62,63). Analyses of samples collected by syringe withdrawal require on-site analysis. Samples collected in Tedlar® bags or onto adsorbent traps may be transported to an off-site laboratory for analysis. Alternatively, there are field-portable gas detectors and gas chromatographs with flame-ionization and photoionization detectors capable of measuring real time hydrocarbon concentrations (47,57,64).

Efforts to measure the flux of VOCs from the unsaturated zone to the atmosphere at the land surface have included using the aerodynamic method, which necessitates the measurement of trace concentrations and atmospheric conditions such as wind speed, temperature and pressure (65); using groundsheets sampled through a nylon sampling tube (66); and several chamber designs (58,59,67–71). Surface measurements of vapor flux are important because they provide a direct measurement of total natural flux that can be used to estimate volatilization rates for a field site. This natural attenuation process for contaminants in soil and groundwater may be significant, and, at times, approach the removal rate of active remediation systems (58). Complexities involved in the measurement of vapor transport from the subsurface to the atmosphere include possible preferential flow paths (e.g., underground utilities, macropores, etc.) and spatial and temporal variability in vapor concentrations. Spatial variability may be produced by subsurface heterogeneities that are geologic as well as constructed barriers (e.g., storm drains, basement foundations). Temporal variability in vapor concentrations is produced by changing soil moisture content, temperature, and gas-pressure gradients.

SUMMARY

Analysis of the transport of organic vapors in the unsaturated zone is fundamental in evaluating potential human exposure to harmful compounds from a contaminated subsurface as well as determining a site's potential for natural attenuation. Analysis of soil gas vapors may also aid in estimating the areal extent of a contaminated plume. Soil, aqueous, and NAPL-phase organics may all be sources of organic vapors in the subsurface, and interphase mass transfer to and from soil, soil moisture, groundwater, and

soil gas all play a role in vapor transport in the unsaturated zone. Diffusion of the vapor phase contaminant proceeds from higher concentrations near the source toward lower concentrations at the land surface. Advection of soil gas results from pressure gradients in the subsurface and from density-driven flow for certain high molecular weight compounds. Under favorable conditions, organic vapors in the unsaturated zone may be biodegraded by indigenous bacteria in oxidation/reduction reactions. All biodegradation reactions of organic compounds require nutrients and electron acceptors in sufficient, usable quantities. Soil-gas concentrations may be quantified through the use of vapor probes, adsorbent traps, Tedlar® bags, direct syringe withdrawal with field-portable analytical equipment, and the use of gas chromatography. The total flux of contaminants from the subsurface to the land surface may be estimated by the aerodynamic method, through the use of ground sheets, or with flux chambers. Surface flux measurement is useful for estimating the total volatilization of contaminants from a site, but all vapor-phase measurements are complicated by spatial and temporal variability.

BIBLIOGRAPHY

1. Laubacher, R.C., Bartholomae, P., Velasco, P., and Reisinger, H.J. (1997). An evaluation of the vapor profile in the vadose zone above a gasoline plume. In: *Pet. Hydrocarbons Org. Chem. Ground Water: Prev. Detection Remediation Conf.*, Houston, TX, pp. 396–409.
2. Environmental Quality Management. (2003). *User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Durham, NC.
3. U.S. Environmental Protection Agency. (2002). *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater And Soils*. USEPA Office of Solid Waste and Emergency Response.
4. Johnson et al. (1990).
5. Buckingham, E. (1904). *Contribution to Our Knowledge of the Aeration of Soils*. USDA Bureau of Soils Bulletin No. 25.
6. Penman, H.L. (1940). Gas and vapor movements in soil I. The diffusion of vapours through porous solids. *J. Agric. Sci.* **30**: 463–462.
7. Van Bavel, C.H.M. (1952). Gaseous diffusion and porosity in porous media. *Soil Sci.* **73**: 91–105.
8. Rust, R.H., Klute, A., and Geiseking, G.E. (1957). Diffusion-porosity measurements using a non-steady state system. *Soil Sci.* **84**: 453–465.
9. Dye, R.F. and Dallavale, J.M. (1958). Diffusion of gases in porous media. *Ind. Eng. Chem.* **50**: 1195–1200.
10. Millington, R.J. (1959). Gas diffusion in porous media. *Science* **130**: 100–102.
11. Currie, J.A. (1970). Movement of gases in soil respiration. *Sorption and Transport Processes in Soils*. SCI Monogr. Ser. **37**: 152–171.
12. Nilson, R.H., Peterson, E.W., and Lie, K.H. (1991). Atmospheric pumping: A mechanism causing vertical transport of contaminated gases through fractured permeable media. *J. Geophys. Res.* **96**: 21933–21948.
13. Bartelt-Hunt, S.L. and Smith, J.A. (2002). Measurement of effective air diffusion coefficients for trichloroethylene in heterogeneous soil. *J. Contam. Hydrol.* **56**: 193–208.
14. Rolston, D.E. and Moldrup, P. (2002). Gas diffusivity. In: *Methods of Soil Analysis: Part 4-Physical Methods*. J.H. Dane and G.C. Topp (Eds.). Soil Science Society of America, Madison, WI, pp. 1113–1158.
15. Thorstenson, D.C. and Pollock, D.W. (1989). Gas transport in unsaturated zones: Multicomponent systems and the adequacy of Fick's laws. *Water Resour. Res.* **25**: 477–507.
16. Baehr, A.L. and Bruell, C.J. (1990). Application of the Stefan-Maxwell equations to determine limitations of Fick's law when modeling organic vapor transport in sand columns. *Water Resour. Res.* **26**: 1155–1163.
17. Partridge, G.P., McLeary, K.S., Showers, T.R., Huebner, R.S., and Elliott, H.A. (2002). Single and multicomponent gas phase diffusion in porous media: Modeling and laboratory measurements. *Soil Sediment Contam.* **11**: 555–581.
18. Sleep, B.E. and Sykes, J.F. (1989). Modeling the transport of volatile organics in variably saturated media. *Water Resour. Res.* **25**: 81–92.
19. Massmann, J. and Farrier, D.F. (1992). Effects of atmospheric pressures on gas transport in the vadose zone. *Water Resour. Res.* **28**: 777–791.
20. Auer, L.H., Rosenberg, N.D., Birdsell, K.H., and Whiteny, E.M. (1996). The effects of barometric pumping on contaminant transport. *J. Contam. Hydrol.* **24**: 145–166.
21. Elberling, B., Larsen, F., Christensen, S., and Postma, D. (1998). Gas transport in a confined unsaturated zone during atmospheric pressure cycles. *Water Resour. Res.* **34**: 2855–2862.
22. Tillman, F., Choi, J.C., Katchmark, W., Smith, J.A., and Wood, H.G.I. (2001). Unsaturated-zone airflow: Implications for natural remediation of ground water by contaminant transport through the subsurface. In: *Physicochemical Groundwater Remediation*. J.A. Smith and S.E. Burns (Eds.). Kluwer Academic/Plenum, New York, pp. 307–339.
23. Choi, J.W., Tillman, F.D., and Smith, J.A. (2002). Relative importance of gas-phase diffusive and advective trichloroethylene (TCE) fluxes in the unsaturated zone under natural conditions. *Environ. Sci. Technol.* **36**: 3157–3164.
24. Neeper, D.A. (2002). Investigation of the vadose zone using barometric pressure cycles. *J. Contam. Hydrol.* **54**: 59–80.
25. Rossabi, J. and Falta, R.W. (2002). Analytical solution for subsurface gas flow to a well induced by surface pressure fluctuations. *Ground Water* **40**: 67–75.
26. Nazaroff, W.W., Lewis, S.R., Doyle, S.M., Moed, B.A., and Nero, A.V. (1987). Experiments on pollutant transport from soil into residential basements by pressure-driven airflow. *Environ. Sci. Technol.* **21**: 459–466.
27. Garbesi, K. and Sextro, R.G. (1989). Modeling and field evidence of pressure-driven entry of soil gas into a house through permeable below-grade walls. *Environ. Sci. Technol.* **23**: 1481–1487.
28. Li, L., Dong, P., and Barry, D.A. (2002). Tide-induced water table fluctuations in coastal aquifers bounded by rhythmic shorelines. *J. Hydraul. Eng.* **128**: 925–933.
29. Little, J.C., Daisey, J.M., and Nazaroff, W.W. (1992). Transport of subsurface contaminants into buildings: An exposure pathway for volatile organics. *Environ. Sci. Technol.* **26**: 2058–2066.
30. Gustin, M.S., Taylor, G.E., and Maxey, R.A. (1997). Effect of temperature and air movement on the flux of elemental mercury from substrate to the atmosphere. *J. Geophys. Res.* **102**: 3891–3898.
31. Krylov, V.V. and Ferguson, C.C. (1998). Contamination of indoor air by toxic soil vapours: The effects of subfloor

ventilation and other protective measures. *Build. Environ.* **33**: 331–347.

32. Falta, R.W., Javandel, I., Pruess, K., and Witherspoon, P.A. (1989). Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds. *Water Resour. Res.* **25**: 2159–2169.
33. Mendoza, C.A. and Frind, E.O. (1990). Advective-dispersive transport of dense organic vapors in the unsaturated zone 1. Model development. *Water Resour. Res.* **26**: 379–387.
34. Mendoza, C.A. and Frind, E.O. (1990). Advective-dispersive transport of dense organic vapors in the unsaturated zone: 2. Sensitivity analysis. *Water Resour. Res.* **26**: 387–398.
35. Goss, K.U. (1994). Adsorption of organic vapors on polar mineral surfaces and on a bulk water surface: Development of an empirical predictive model. *Environ. Sci. Technol.* **28**: 640–645.
36. Goss, K.U. (1994). Effects of temperature and relative humidity on the sorption of vapors on quartz sand. *Environ. Sci. Technol.* **26**: 2287–2294.
37. Goss, K.-U. and Eisenreich, S.J. (1996). Adsorption of VOCs from the gas phase to different minerals and a mineral mixture. *Environ. Sci. Technol.* **30**: 2135–2142.
38. Popovicova, J. and Brusseau, M.L. (1998). Contaminant mass transfer during gas-phase transport in unsaturated porous media. *Water Resour. Res.* **34**: 83–92.
39. Ruiz, J., Bilbao, R., and Murillo, M. (1998). Adsorption of different VOC onto soil minerals from gas phase: Influence of mineral, type of VOC, and air humidity. *Environ. Sci. Technol.* **32**: 1079–1084.
40. Goss, K.-U., Buschmann, J., and Schwarzenbach, R.P. (2004). Adsorption of organic vapors to air-dry soils: Model predictions and experimental validation. *Environ. Sci. Technol.* **38**: 3667–3673.
41. Chiou, C.T. and Shoup, T.D. (1985). Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. *Environ. Sci. Technol.* **19**: 1196–1200.
42. Smith, J.A., Chiou, C.T., Kammer, J.A., and Kile, D.E. (1990). Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. *Environ. Sci. Technol.* **24**: 676–683.
43. Cho, H.J. and Jaffé, P.R. (1990). The volatilization of organic compounds in unsaturated porous media during infiltration. *J. Contam. Hydrol.* **6**: 387–410.
44. Cho, H.J., Jaffé, P.R., and Smith, J.A. (1993). Simulating the volatilization of solvents in unsaturated soils during laboratory and field infiltration experiments. *Water Resour. Res.* **29**: 3329–3342.
45. Kim, H., Rao, P.S., and Annable, M.D. (1997). Determination of effective air-water interfacial area in partially saturated porous media using surfactant adsorption. *Water Resour. Res.* **33**: 2705–2711.
46. Kim, H., Annable, M.D., and Rao, P.S.C. (1998). Influence of air-water interfacial adsorption and gas-phase partitioning on the transport of organic chemicals in unsaturated porous media. *Environ. Sci. Technol.* **32**: 1253–1259.
47. Ostendorf, D.W. and Kampbell, D.H. (1991). Biodegradation of hydrocarbon vapors in the unsaturated zone. *Water Resour. Res.* **27**: 453–462.
48. Norris, R.D., Hinchee, R.E., Brown, R., McCarty, P.L., Wilson, J.T., Reinhard, M., Bouwer, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and Ward, C.H. (1994). *Handbook of Bioremediation*. Lewis, Boca Raton, FL.
49. Lahvis, M.A. and Baehr, A.L. (1996). Estimation of rates of aerobic hydrocarbon biodegradation by simulation of gas transport in the unsaturated zone. *Water Resour. Res.* **32**: 2231–2249.
50. Lahvis, M.A., Baehr, A.L., and Baker, R.J. (1999). Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. *Water Resour. Res.* **35**: 753–765.
51. Hers, I., Atwater, J., Li, L., and Zapf-Gilje, R. (2000). Evaluation of vadose zone biodegradation of BTX vapours. *J. Contam. Hydrol.* **46**: 233–264.
52. U.S. Environmental Protection Agency. (2000). *Engineered approaches to in situ bioremediation of chlorinated solvents: Fundamentals and field applications*. EPA 542-R-00-008, Washington, DC.
53. McCarty, P.L. (1997). Breathing with chlorinated solvents. *Science* **276**: 1521–1522.
54. Vogel, T.M., Criddle, C.S., and McCarty, P.L. (1987). Transformations of halogenated aliphatic compounds. *Environ. Sci. Technol.* **21**: 722–736.
55. Roggemans, S., Bruce, C.L., Johnson, P.C., and Johnson, R.L. (2001). Vadose zone natural attenuation of hydrocarbon vapors: An empirical assessment of soil gas vertical profile data. *Am. Pet. Inst. Tech. Bull.* **15**: 12.
56. Kerfoot, H.B. (1987). Soil-gas measurement for detection of groundwater contamination by volatile organic compounds. *Environ. Sci. Technol.* **21**: 1022–1024.
57. Moseley, C.L. and Meyer, M.R. (1992). Petroleum Contamination of an elementary school: A case history involving air, soil-gas and groundwater monitoring. *Environ. Sci. Technol.* **26**: 185–192.
58. Smith, J.A., Tisdale, A.K., and Cho, H.J. (1996). Quantification of natural vapor fluxes of trichloroethene in the unsaturated zone at Picatinny Arsenal, New Jersey. *Environ. Sci. Technol.* **30**: 2243–2250.
59. Tillman, F., Choi, J.-W., and Smith, J.A. (2003). A comparison of direct measurement and model simulation of total flux of volatile organic compounds from the subsurface to the atmosphere under natural field conditions. *Water Resour. Res.* **39**: 1284–1294.
60. Fischer, M.L. et al. (1996). Factors affecting indoor air concentrations of volatile organic compounds at a site of subsurface gasoline contamination. *Environ. Sci. Technol.* **30**: 2948–2957.
61. Jeng, C.Y., Kremesec, V.J., and Primack, H.S. (1996). Models of hydrocarbon vapor diffusion through soil and transport into buildings. In: *Pet. Hydrocarbons Org. Chem. Ground Water: Prev. Detection Remediation Conf.* National Ground Water Association, Houston, TX, pp. 319–338.
62. Tillman, F. (2003). *Design and testing of a chamber device to measure total flux of volatile organic compounds from the unsaturated zone under natural conditions*. Ph.D. Dissertation. University of Virginia, Charlottesville, VA.
63. Hodgson, A.T., Garbesi, K., Sextro, R.G., and Daisey, J.M. (1992). Soil-gas contamination and entry of volatile organic compounds into a house near a landfill. *J. Air Waste Manage. Assoc.* **42**: 277–283.
64. Ririe, G.T., Sweeney, R.E., Daugherty, S.J., and Peuron, P.M. (1998). A vapor transport model that is consistent with field and laboratory data. *Pet. Hydrocarbons Org. Chem. Ground Water: Prev. Detection Remediation Conf.*, Ground Water Association, Houston, TX, pp. 299–309.
65. Chen, C., Green, R.E., Thomas, D.M., and Knuteson, J.A. (1995). Modeling 1,3-dichloropropene fumigant volatilization with vapor-phase advection in the soil profile. *Environ. Sci. Technol.* **29**: 1816–1821.

66. Wyatt, D.E., Richers, D.M., and Pirkle, R.J. (1995). Barometric pumping effects on soil gas studies for geological and environmental characterization. *Environ. Geol.* **25**: 243–250.
67. Eklund, B., Balfour, W.D., and Schmidt, C.E. (1985). Measurement of fugitive volatile organic emission rates. *Environ. Prog.* **4**: 199–202.
68. Batterman, S.A., McQuown, B.C., Murthy, P.N., and McFarland, A.R. (1992). Design and evaluation of a long-term soil gas flux sampler. *Environ. Sci. Technol.* **26**: 709–714.
69. Reinhart, D.R., Cooper, D.C., and Walker, B.L. (1992). Flux chamber design and operation for the measurement of municipal solid waste landfill gas emission rates. *J. Air Waste Manage. Assoc.* **42**: 1067–1070.
70. Eklund, B., Anderson, E.P., Walker, B.L., and Burrows, D.B. (1998). Characterization of landfill gas composition at the Fresh Kills municipal solid-waste landfill. *Environ. Sci. Technol.* **32**: 2233–2237.
71. Tillman, F. and Smith, J.A. (2004). Design and laboratory testing of a chamber device to measure total flux of volatile organic compounds from the unsaturated zone under natural conditions. *J. Contam. Hydrol.* **75**: 71–90.

APPLICATIONS OF SOIL VAPOR DATA TO GROUNDWATER INVESTIGATIONS

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This article describes the uses and interpretation of soil vapor data for a variety of common applications related primarily to groundwater. It begins with an overview of the applications of soil vapor surveys, a brief discussion of the various soil vapor methods, and then focuses on a number of specific issues relating to soil vapor surveys for groundwater investigations. The intent of this article is to guide professionals on when, why, and how soil vapor data can be useful for groundwater-related investigations and how to interpret the results.

BACKGROUND AND APPLICATIONS

Soil vapor in the pore spaces, also called soil gas, soil air, pore gas, and interstitial gas refers to the vapor that lies among the soil grains in the soil column lying between the ground surface and the water table (vadose zone). Soil vapor data are collected in a variety of ways, and the data can be used for various purposes. Soil vapor samples are most commonly analyzed for volatile organic compounds (VOCs). VOCs include simple hydrocarbons such as methane; lighter hydrocarbons such as gasoline; gasoline constituents such as benzene and methyl tert-butyl ether (MtBE); and chlorinated solvents such as trichloroethylene (TCE), trichloroethane (TCA), and tetrachlorethylene (PCE).

Soil vapor is surveyed for a variety of reasons. Historically, soil vapor surveys have been used primarily for site assessment to identify soil and groundwater contamination (1–4). More recent applications include evaluation of upward and downward vapor transport to monitor site remediation (natural and engineered) and to monitor landfills and migrating VOCs (5–7).

Soil vapor surveys are quick, relatively nondisruptive, and generally inexpensive. The surveys are frequently performed early in the site investigation, when investigation for numerous VOCs is performed. The data obtained are often used to focus subsequent soil and groundwater investigatory sampling programs.

Regulatory agencies across the country are increasingly concerned with human health risk due to the upward migration of contaminant vapors through the vadose zone into buildings. Vertical soil vapor profiles enable measuring actual soil vapor concentrations that give a more accurate calculation of the upward vapor migration than values calculated from soil or groundwater data. These data are used in risk based corrective action (RBCA) computer models (8).

Use of soil vapor data for monitoring site remediation takes many forms. Most commonly, concentrations of vapor contaminants are monitored to measure the progress of a vapor extraction system. Remediation of groundwater or soil by natural attenuation requires monitoring the concentrations of contaminants, by-products, and oxygen in the soil vapor to measure the progress of the degradation of the contaminant plume.

Soil vapor is frequently measured at the fringes of landfills to ensure that harmful compounds such as methane, chlorinated compounds (primarily vinyl chloride), and petroleum related carcinogens such as benzene are not migrating from landfills to neighboring developments.

SOIL VAPOR METHODS

Collection of Soil Vapor Samples

Three methods exist for collecting soil vapor data: (1) active, (2) passive, and (3) flux chambers. A brief overview of these methods follows. More comprehensive descriptions of soil vapor collection methods and protocols are given in documents written by Hartman (9,10), Hartman and Jacobs (5,11), EPA (1), ASTM (12), and Devitt et al. (4).

The *active* approach is quantitative and consists of the withdrawal of a volume of vapor from the subsurface, typically using a steel sampling rod driven into the ground from 0.9 to 6 meters below ground surface, and subsequent analysis of the withdrawn vapor. Originally, surveys were limited to shallow depths of 3 meters because the sampling

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rods were driven and extracted using hand techniques. Currently, active surveys can routinely achieve depths exceeding 30.5 meters due to the use of direct-push probe rigs, cone penetrometer (CPT) sampling rigs, and full-size drill rigs to collect soil vapor using newly developed sampling tools.

Sample containers for active vapor sampling include syringes, gas sampling Tedlar® bags, preevacuated stainless steel canisters (e.g., SUMMA canisters), and gastight vials (e.g., 40 mL preevacuated volatile organic analysis (VOAs) vials or headspace vials). Analysis can be performed on-site or off-site, usually within 48 hours of collection. The quantitative results are typically presented in concentration units (e.g., ppmv, μg/L vapor). The active method requires actively withdrawing soil vapor and is best suited to sites that have higher vadose zone permeabilities and higher contaminant concentrations (>0.1 μg/L vapor). The active method can be used for investigating groundwater contamination, and as discussed later in this chapter, the active method is also useful for groundwater issues relating to contaminant fate and transport because it gives concentration data.

The *passive* approach consists of emplacing a natural or synthetic absorbent into the subsurface (typically 0.15 to 0.9 meters) for an extended time, and subsequently removing and analysing the absorbent. The absorbent is typically placed in the upper end of an inverted container or sleeve that has openings for migrating vapors to enter and collect. Unlike the active method, which requires one visit to the site, the passive method requires one visit to the site to deploy the absorbents and a second trip to retrieve them.

The passive method is qualitative and does not allow for real-time data. Measured values are reported as total absorbed mass (e.g., μg) or relative units because the amount of vapor meeting the absorbent is unknown. The passive method offers more sensitivity than the active method; hence it offers advantages in sites of low vadose zone permeability and lower contaminant concentrations (>0.01 μg/L vapor). Contaminants must have an appreciable vapor pressure to be detected by this method, regardless of the deployment time or contaminant concentration in the soil or water. As a rule of thumb, one should not expect compounds whose vapor pressures are less than 10^{-6} atmospheres to be detectable by passive soil vapor methodology in a reasonable time frame (<50 days of exposure) for reasonable contaminant concentrations in the water.

Flux chambers consist of an enclosed chamber that is placed on the surface for a specific period of time. Vapor concentrations are measured in the chamber through time or after a period of time. This method is also quantitative and yields both concentration data in the chamber and flux data (mass/area-time). Flux chambers are the least common soil vapor method and are seldom used for groundwater assessment. Their most useful application is for sites where volatilization of contaminants from groundwater is of concern and direct fluxes are desired Hartman (9).

Analysis of Soil Vapor Samples

The type of analytical instrumentation employed depends upon the goals of the project and the type of soil vapor method used. For screening-level active soil vapor surveys, in which the primary goal is simply to find contamination qualitatively, simple handheld or portable instruments, such as organic vapor analyzer (OVAs), organic vapor meter (OVMs), gas-monitoring meters (e.g., IR detectors), and gas detector tubes, can be used. For applications where quantitative results are desired, the analytical methodology employed is typically gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS). These latter techniques differentiate a wide variety of compounds. These latter methods are also used to analyze passive soil vapor samples and flux chamber samples.

More comprehensive treatments of the available analytical options for soil vapor samples are given by Hartman & Jacobs (5) and the EPA (1).

APPLICATIONS OF SOIL VAPOR DATA TO GROUNDWATER ISSUES

This section discusses how to use and interpret soil vapor data for applications specifically related to groundwater.

Assessing and Defining Groundwater Contamination

Soil vapor surveys have frequently been used for initial site assessment to identify groundwater contamination, and the data are used to focus subsequent groundwater investigatory sampling programs (1,3,4). The soil vapor data are typically plotted as contours or as a raised surface. More sophisticated approaches, including three-dimensional visualizations of the soil column, cross sections, normalization, and statistical analysis, are sometimes used depending on the project goals.

The applicability of a soil vapor survey to detect potential groundwater contamination depends upon a number of factors, including the local geology, contaminant properties, and the concentration of the contaminant in the groundwater (11). The maximum concentration of a contaminant in the soil vapor due to volatilization from the groundwater can be estimated from Henry's law:

$$C_{sg} = HC_w \tag{1}$$

where C_{sg} is the soil gas concentration in equilibrium with the groundwater,
C_w is the groundwater concentration, and
H is the dimensionless Henry constant.

As an example, consider groundwater that has a benzene concentration of 10 μg/L. The dimensionless Henry constant for benzene is 0.22, giving an equilibrium soil vapor concentration of 2.2 μg/L vapor at the groundwater interface. Hence, a soil vapor survey conducted near groundwater could at best be expected to detect only a maximum value of 2.2 μg/L in the vapor if groundwater were the only source.

Equilibrium phase partitioning is rarely achieved in the subsurface, so measured soil vapor values

from groundwater volatilization will be significantly lower (generally one to two orders of magnitude) than predicted from Henry's constants. In addition, soil vapor concentrations decrease as distance increases from the groundwater due to other processes active in the vadose zone, such as biodegradation and sorption onto soils (13). For these reasons, the chances of detecting groundwater contamination from soil vapor data increases the closer the samples are collected to groundwater.

Due to its increased sensitivity for some compounds, the passive soil vapor method can offer advantages over the active method for this application. Similar to the active method, the ability of passive methods to detect groundwater contamination increases the closer the samples are collected to groundwater. However, regardless of sampling depth, the capability of passive methods to detect contaminants is still limited by the vapor pressure of the compound of concern (5).

Transport of Contaminant Vapors in the Subsurface

To understand the source of soil vapor and groundwater contamination, it is necessary to understand how contaminants move in the vapor phase. A condensed version of this topic is addressed in this section beginning with a discussion of the processes by which vapors move through the vadose zone. A more detailed presentation can be found in Hartman (6,7,14).

There are two types of physical processes by which contaminants are transported in the vapor phase. The first is advection, the bulk movement of the vapor itself. In advective transport, any contaminants in the vapor are carried along with the moving vapor. Advective transport processes can be important in soil vapor, for example, near the surface due to atmospheric pressure differences (15), near buildings that can create pressure gradients (16), and movement of vapor by density-induced flow (17).

The second type of transport process is gaseous diffusion, the motion of contaminants by molecular processes through a nonmoving vapor column, which is the primary mechanism for contaminant transport in the vapor phase through the vadose zone (18).

Contaminant transport by gaseous diffusion is described by Fick's first law as

$$\text{FLUX} = \frac{D_e\, C_{sg}}{X} \tag{2}$$

where Flux is the rate of movement of a compound per unit area,
D_e is the effective diffusion coefficient in the vadose zone,
C_{sg} is the contaminant concentration gradient in the soil vapor, and
X is depth in the vadose zone

Similar to momentum transfer (e.g., water running downhill) and heat transfer (movement from hot areas to cold areas), contaminant transfer by gaseous diffusion moves from areas of high concentration to areas of low concentration. The flux is always down the concentration gradient, regardless of the orientation of the concentration gradient with respect to the depth below the surface. Diffusional transport is a three-dimensional process, so contaminants move away from a source in all directions, similar to an expanding balloon.

Differentiating the Source of Soil Vapor/Groundwater Contamination

A common problem confronted by environmental geologists is determining the source of contamination at a site that has both soil vapor and groundwater contamination. Is the soil vapor responsible for the groundwater contamination, or is the groundwater responsible for the soil vapor concentration? Contaminant transfer by gaseous diffusion moves from areas of high concentration to areas of low concentration, so vertical profiles of the soil vapor through the vadose zone down to groundwater can provide this answer. Figure 1 shows the expected shape of soil vapor profiles in the vadose zone for three common conditions. Processes active in the vadose zone such as sorption, biodegradation, and advection may alter these ideal profiles, but the source of contamination must still be in the area of highest concentration, as dictated by Ficks law.

Vertical soil vapor is profiled by installing vapor monitoring wells at multiple depths through the vadose zone to the groundwater. For soil vapor, vapor wells are often constructed of small diameter 0.5 to 1.0 cm (1/8 in. to 1/4 in. OD) flexible tubing and "nested" in the same borehole (Fig. 2).

Repeated sampling of the vapor wells allows averaging any temporal effects. Thomson (19) describes two case histories of vertical profiling using nested vapor wells.

Contaminant Vapor Transport Rates

The distance that contaminant vapors can move by gaseous diffusion can be approximated from

$$\text{Distance} = (2 \times D_e \times t)^{1/2} \tag{3}$$

where D_e is the effective diffusivity and t is time.

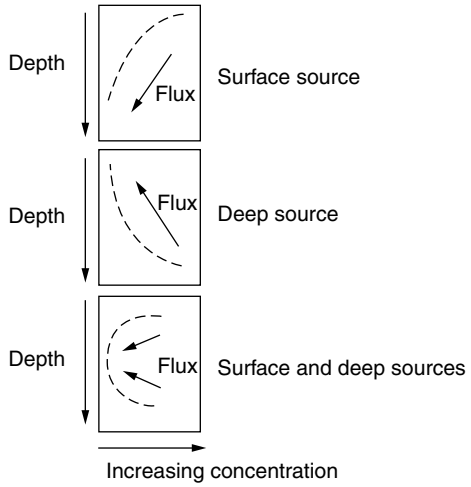


Figure 1. Common soil vapor profiles in the vadose zone for several one-dimensional situations (8).

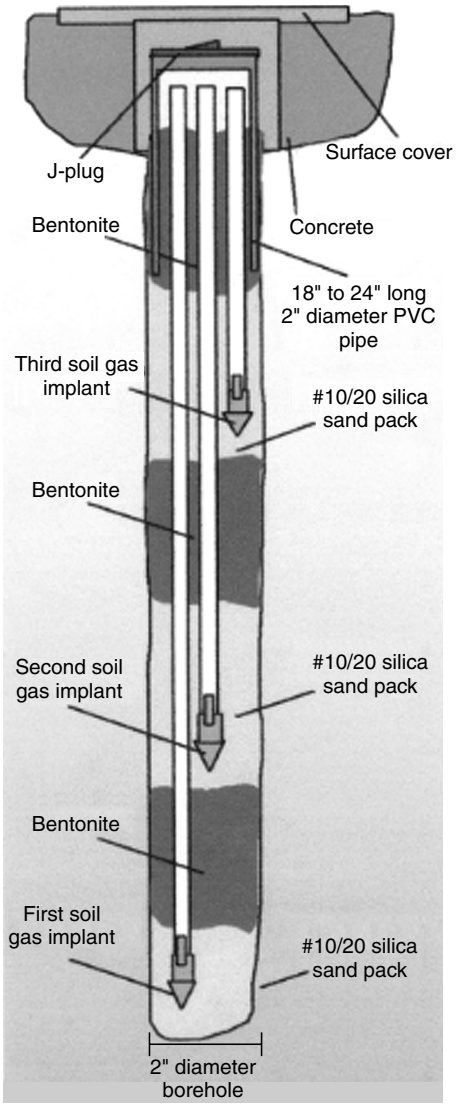


Figure 2. Schematic diagram of a multidepth, nested vapor monitoring well (19).

Through the Vadose Zone. For contaminant vapor transport through the vadose zone, the effective diffusion coefficient is the gaseous diffusion coefficient corrected for soil porosity. For many vapors, the gaseous diffusion coefficient is approximately 0.1 cm^2/s. The effect of soil porosity varies depending upon the type of soil, and several equations are available to calculate the effect of porosity on diffusivity. A general approximation is that the porosity reduces the gaseous diffusivity by a factor of 10. Thus, for vapors, D_e can be approximated as 0.01 cm^2/s.

The distance that contaminant vapors can move through the vadose zone in a year can be estimated as

$$\text{Distance} = (2 \times 0.01\ \text{cm}^2/\text{s} \times 31{,}536{,}000\ \text{s})^{1/2}$$
$$\sim 800\ \text{cm}$$

This calculation shows that contaminant vapors can move long distances through the vadoze zone in a short period of time. Within a few years, vapor contamination can move laterally underneath a neighboring room or building or downward to the groundwater surface.

Into or out of Groundwater. In contrast to movement through the vadose zone where contaminant vapors move through the soil vapor, the movement of contaminant vapors into or out of groundwater is controlled by the rate at which vapors partition into and move through the liquid. Because groundwater movement is so slow, the water interface remains relatively undisturbed (laminar flow), and vertical mixing of the water is minimal. The primary exchange process is again molecular diffusion, but in this case, the exchange rate is controlled by liquid diffusion, not gaseous diffusion. A general value for the liquid diffusion coefficient for compounds is approximately 0.00001 cm^2/s. Using the same factor of 10 reduction due to soil porosity, D_e for most liquids can be approximated as 0.000001 cm^2/s.

The distance that contaminants can move into and through groundwater in a year can be estimated as

$$\text{Distance} = (2 \times 0.000001\ \text{cm}^2/\text{s} \times 31{,}536{,}000\ \text{s})^{1/2}$$
$$\sim 8\ \text{cm}$$

These calculations show that although contaminant vapors can move through the vadose zone relatively quickly, they partition into and move through groundwater extremely slowly. The reverse situation is also true; the movement and partitioning of contaminants through groundwater and into soil vapor is also extremely slow.

Estimation of the Downward Transport of Contaminant Vapors into Groundwater

The calculations summarized in the preceding sections indicate that although contaminant vapors can move quickly down to groundwater, they do not partition into groundwater very quickly because phase partitioning across a liquid laminar interface is kinetically controlled. For this reason, phase partitioning rarely reaches equilibrium, and the use of Henry's constants to estimate groundwater concentrations from soil vapor data (or the reverse) often gives estimated values one to two orders of magnitude from measured values.

Using a modification of Fick's first law, the transfer rate of a contaminant from soil vapor into groundwater can be estimated, and in turn, reasonable estimates of the expected contaminant concentration in groundwater due to contamination in the overlying soil vapor can be estimated.

The flux is calculated as

$$\text{Flux} = K_L\ (C_{sg}/H - C_w) \qquad (4)$$

where K_L is the gas exchange coefficient (length/time),
C_{sg} is the soil gas concentration time (mass/volume),
H is the dimensionless Henry's law constant, and
C_w is the groundwater concentration (mass/volume).

The ratio C_{sg}/H represents the groundwater concentration in equilibrium with the overlying soil vapor at the interface between the soil vapor and groundwater.

The gas exchange coefficient has units of velocity and represents the distance that contaminants move through the groundwater per unit time. This coefficient is highly dependent on a compound's effective diffusivity and advective mixing of the groundwater interface. For groundwater velocities less than 30.5 meters per year and soil grain sizes less than 0.5 mm, diffusional transport dominates over dispersion, and K_L can be approximated as:

$$K_L = 1.1\ (D_e\ v/d)^{1/2} \quad (5)$$

where D_e is the effective diffusivity,
d is the horizontal distance (downgradient) over which the soil vapor plume and groundwater are in contact, and
v is the horizontal groundwater flow velocity.

For the groundwater conditions described above, the interface remains laminar (i.e., no turbulent mixing), and the gas transfer coefficient is approximately 8 cm/yr. Using this value for the gas exchange rate, estimates of the expected contaminant concentration in groundwater due to contamination in the overlying soil vapor for various soil vapor concentrations are summarized in Table 1. These calculations assume equilibrium partitioning at the soil vapor/groundwater interface, transfer into groundwater by molecular diffusion only, and uniform mixing of the contaminant into the groundwater over the well screen length.

Table 1 shows that for equilibrium concentrations (C_{sg}/H) up to 100 μg/L, the resulting ground water concentration after 5 years will be low (<10 μg/L) if liquid molecular diffusion is the only exchange process.

Table 1. Expected Contaminant Concentration in Groundwater for Various Soil Vapor Concentrations at the Groundwater Interface[a,b]

C_{sg}, μg/L	C_{sg}/H, μg/L	Flux, μg/cm^2-yr	Water conc at 1 yr, μg/L	Water conc at 5 yrs, μg/L
10	40	315	0.63	3.2
20	80	631	1.3	6.3
30	120	946	1.9	9.5
40	160	1261	2.5	13
50	200	1577	3.2	16
100	400	3154	6.3	32
500	2000	15,768	31	158
1000	4000	31,536	63	315

[a] Reference 5.
[b] Assumptions used to compute the tabulated values:
Henry's law constant: 0.25 (dimensionless)
Gas transfer coefficient: 8 cm/yr
Well screen interval: 5 m

Importance of Downward Vapor Transport for Several Common Contaminants

The potential importance of downward vapor migration for several of the more common compounds encountered by environmental consultants are given special consideration in this section.

Leaking Vapors from Chlorinated Solvents (Dry Cleaners and Vapor Degreasers). Many compounds, primarily chlorinated solvents, have relatively high vapor pressures and vapor densities three to six times greater than air. Because of these physiochemical properties, vapors may emanate from containers or pipes holding gaseous or liquid products. If air flow is restricted, such as in a closed room containing a washer unit, degreaser, or tank, leaking dense vapors can penetrate the floor and enter the upper vadose zone. Density-driven advection can continue to drive vapor downward through the vadose zone until the vapor is diluted to low enough concentrations (<1%) that density-driven advection is no longer an important factor in vapor transport and molecular diffusion takes over. Vapor clouds reaching tens of feet into the uppermost vadose zone have been documented in thousands of cases. Businesses and commercial operations that are most susceptible to this situation are those that deal with chlorinated solvents (dry cleaners, vapor degreasers, spray facilities, etc.).

The soil vapor concentration to yield an equilibrium water concentration of 100 μg/L is 35 μg/L vapor for TCA, 60 μg/L vapor for PCE, and 100 μg/L vapor for vinyl chloride. In areas of groundwater deeper than 9.1 meters, soil vapor concentrations for these compounds are generally less than these values at groundwater, unless in the presence of contaminated soil, suggesting that surface vapor leaks are not a significant contaminant pathway to groundwater in most cases. In areas of groundwater shallower than 6 meters, soil vapor concentrations exceeding these values are found, even in the presence of clean soil, suggesting that leaking dense vapors from the surface may be a significant contaminant pathway.

Leaking, Hydrocarbon Fuel Vapors. In contrast to chlorinated solvents, aboveground vapor releases are not common for petroleum hydrocarbons because they rarely are stored in confined spaces (due to their flammability). However, subsurface vapor leaks from petroleum hydrocarbons are possible from USTs and piping associated with them (vent pipes, pipe joints, and tank bungs. Gasoline vapor contains approximately 8000 μg/L vapor of benzene and lower, although still high concentrations (>1000 μg/L vapor) of toluene and xylene. Reformulated gasolines have very high concentrations of MtBE or ethanol, and their vapors contain approximately 130,000 μg/L vapor of MtBE and 11,500 μg/L vapor of ethanol. Due to these high concentrations, leaking vapors must be considered a potential source of groundwater contamination, as further described below.

Benzene and Light Aromatics (BTEX). For light aromatics, the soil vapor concentration to yield an equilibrium water concentration of 100 μg/L is approximately 25 μg/L

vapor. In areas of groundwater deeper than 9.1 meters, soil vapor concentrations of aromatics are generally less than 25 μg/L vapor at the groundwater, unless in the presence of contaminated soil from a leaking UST, suggesting that vapor leaks are not a contaminant pathway in most cases.

In areas of groundwater shallower than 3 meters, soil vapor concentrations exceeding 25 μg/L vapor have been found even in the presence of clean soil, suggesting that leaking gasoline vapors from the UST are a possible contaminant pathway. In areas where the groundwater is near or above the UST, vapor leaks could be very significant in groundwater contamination.

MtBE and Ethanol. Due to extremely low Henry constants, the soil vapor concentration to yield an equilibrium water concentration of 100 μg/L is only 2 μg/L vapor for MtBE and approximately 0.02 μg/L vapor for ethanol. Hence, leaking gasoline vapors from a UST are a likely contaminant pathway to groundwater for both compounds in shallow and deep groundwater. The likelihood is even more acute in locations where the water table is near or above the UST and/or in areas that have significant amounts of rainwater infiltration.

Summary. In areas of deeper groundwater (>10 m), slow groundwater flow rates less than 30.5 meters per year and low recharge, soil vapor concentrations for most contaminants at the groundwater surface are typically well below equilibrium values (C_{sg}/H) of 100 μg/L. Hence contamination of groundwater by downward vapor transport is not likely to be significant. For compounds with very low Henry constants (MtBE, ethanol), downward vapor transport could be important, even under these groundwater conditions.

In areas where groundwater is shallower than 10 meters or higher groundwater flow rates and high recharge, soil vapor concentrations for many contaminants at the groundwater surface may approach high enough values that contamination of the groundwater by downward vapor transport may be significant. This potential will be enhanced for compounds with low Henry constants and when vapor leaks occur directly into the groundwater.

Additional discussion of the downward migration of vapors can be found in Hartman (7,14).

The Upward Migration of Vapors from Groundwater Devolatilization

Attention has been raised in the past several years to the risk to human health by the upward migration of contaminant vapors into buildings and other enclosed spaces (20–22). In cases of contaminated groundwater, it is common to assess this risk pathway before site closure is obtained.

Simplified, the upward contaminant vapor flux into a building is computed by Fick's first law, requiring the soil vapor concentration at some depth underlying the structure. Soil vapor data may be measured directly, or alternatively, in the absence of actual soil vapor data, soil vapor concentrations can be calculated from groundwater data assuming equilibrium conditions using Henry's constants (23). As discussed in the preceding sections, soil vapor values calculated from groundwater using Henry's constants are likely to be overestimated by amounts as large as 10 to 100 times; hence the resulting risk will also be overestimated. The potential error in the calculated risk introduced by the incorrect vapor concentration can be orders of magnitude greater than errors introduced using default values for other parameters, such as porosity. Thus, if a site fails the upward risk calculation using calculated soil vapor values from groundwater data, direct measurement of actual soil vapor concentrations will yield more representative soil vapor values to be used in the calculation (13).

When groundwater is extremely shallow (1.5 meters) and representative soil vapor data are unobtainable, the use of surface flux chambers may yield the best estimate of the vapor flux (24).

A more detailed discussion of the upward vapor migration risk pathway, including a recommended protocol for determining the upward vapor flux, can be found in Hartman (8).

BIBLIOGRAPHY

1. EPA. (1997). *Expedited Site Assessment Tools For Underground Storage Tank Sites*. U.S. Government Printing Office, Washington, DC.
2. Marrin, D.L. and Kerfoot, H.B. (1988). Soil gas surveying techniques. *Environ. Sci. Technol.* **22** (7): 740–745.
3. Ullom, W.L. (1995). Soil gas sampling. In: *Handbook of Vadose Zone Characterization and Monitoring*. L.G. Wilson, L.G. Everett, and S.J. Cullen (Eds.). Lewis, Boca Raton, FL, pp. 555–567.
4. Devitt, D.A., Evans, R.B., Jury, W.A., Starks, T.H., Eklund, B., and Gholson, A. (1987). *Soil gas sensing for detection and mapping of volatiles organics*, EPA/600/8-87/036. (NTIS PB87-228516).
5. Hartman, B. and Jacobs, J. (2000). Applications and interpretation of soil vapor data to volatile organic compound contamination. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr and J. Lehr (Eds.). McGraw-Hill, New York.
6. Hartman, B. (1999). Applications and interpretation of soil vapor data. In: *Chlorinated Solvent Contamination: Legal and Technical Issues*. Morrison et al. (Eds.). Argent Communications Group, Foresthill, CA.
7. Hartman, B. (1998). Applications and interpretation of soil vapor data. In: *Petroleum Hydrocarbon Contamination: Legal and Technical Issues*. Morrison et al. (Eds.). Argent Communications Group, Foresthill, CA.
8. Hartman, B. (1997). The upward migration of vapors. *LUSTLine Bull.* **27**, NEIWPCC, Wilmington, MA, December 1997.
9. Hartman, B. (2003). How to collect reliable soil gas data for risk based applications. Part 2: Flux chamber method. *LustLine* # **44**, NEIWPIC, August 2003.
10. Hartman, B. (2002). How to collect reliable soil gas data for risk based applications. Part 1: Active soil gas method. *LustLine* # **42**, NEIWPIC, October 2002.
11. Hartman, B. and Jacobs, J. (2000). Soil vapor principles. In: *Standard Handbook of Environmental Science, Health, and Technology*. J. Lehr and J. Lehr (Eds.). McGraw-Hill, New York.

12. ASTM. (1993). *Standard guide for soil gas monitoring in the vadose zone*, D5314-93. *Annual Book of ASTM Standards*. Philadelphia, PA.
13. McNeel, P.J. and Dibley, V. (1997). Case study comparisons of vapor inhalation risk estimates: ASTM RBCA model predictions vs site specific soil vapor data. *Proc. 1997 Superfund XVIII Conf.*, Washington, DC, December 1997, pp. 509–516.
14. Hartman, B. (1998). The downward migration of vapors. *LUSTLine Bull.* **28**, NEIWPCC, December 1998.
15. Massman, J. and Farrier, D.F. (1992). Effects of atmospheric pressures on gas transport in the vadose zone. *Water Resourc. Res.* **28** (3): 777–791.
16. Little, J.C., Daisey, J.M., and Nazaroff, W.W. (1992). Transport of subsurface contaminants into buildings. *Environ. Sci. Technol.* **26** (11): 2058–2066.
17. Cherry, J. and Smyth, D. (1996). Non-aqueous phase liquids in the subsurface environment: Assessment & remediation. *Am. Soc. Civ. Eng., 1996 Annu. Convention & Exposition*, Washington, DC, November 10–14, 1996.
18. Thorstenson, D. and Pollock, D. (1989). Gas transport in unsaturated porous media: The adequacy of Fick's law. *Rev. Geophys.* **27**: 61–78.
19. Thomson, K.A. (1995). Soil gas sampling. In: *Handbook of Vadose Zone Characterization and Monitoring*. L.G. Wilson, L.G. Everett, and S.J. Cullen (Eds.). Lewis, Boca Raton, FL, pp. 569–588.
20. Jury, W.A., Russo, D., Streile, G., and El Abd, H. (1990). Evaluation of volatilization by organic chemicals residing below the surface. *Water Resourc. Res.* **26**: 13–20.
21. Johnson, P.C. and Ettinger, R.A. (1991). Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. *Environ. Sci. Technol.* **25**: 1445–1452.
22. Jeng, C.-Y., Kremesec, V.J., and Primack, H.S. (1996). Models of hydrocarbon vapor diffusion through soil and transport into buildings. In: *Proc. 1996 Pet. Hydrocarbons & Org. Chem. Ground Water: Prevention, Detection, and Remediation*, Houston, TX, November 1996.
23. ASTM. (1995). Standard guide for risk-based corrective action (RBCA) applied at petroleum release sites, E-1739-95. *Annual Book of ASTM Standards*. Philadelphia, PA.
24. Smith, J.A., Tisdale, A.K., and Cho, H.J. (1996). Quantification of natural vapor fluxes of trichoroethen in the unsaturated zone at Picatinny Arsenal, New Jersey. *Environ. Sci. Technol.* **30**: 2243–2250.

GROUNDWATER VELOCITIES

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Groundwater flows through interconnected pore spaces in subsurface soil in response to differences in fluid pressure and elevation. Groundwater flow rates are extremely slow, compared to surface water, and they are also highly variable. For example, in clayey soils, groundwater moves as slowly as a fraction of a millimeter per day; however, in sandy soils, it moves faster, even up to more than a meter per day. Hydrology is concerned with both the speed and the direction of groundwater movement. Groundwater velocity is very important in dealing with contaminant migration and arrival time, mass flux, site characterization, reactive barrier design, and calibration of transport processes.

Hydraulic head drives flow through porous media. Two main components contributing to the hydraulic head at a given point in a groundwater flow system are pressure head and elevation head, as shown in Fig. 1. The pressure head is due to the porewater pressure at that point, which can be measured by a piezometer. The elevation head is due to gravitational energy. The higher the elevation of a fluid from sea level or some selected datum, the more gravitation potential energy it has. The third component, kinetic energy, can be ignored, as groundwater flow velocities are usually very small in magnitude. Thus, the hydraulic head (h) is the sum of the pressure head (Ψ) and the elevation head (z), expressed usually in the units of length (meters).

Henry Darcy, a French engineer who studied the movement of water through sand in 1856, found that the rate of water flow through a pipe filled with sand is proportional to the difference in the height of the water between the two ends of the tube, and inversely proportional to the length of the tube (Fig. 2). The constant of proportionality, K, is called hydraulic conductivity. This law, universally known as Darcy's law, is given as

$$Q = -KA[(h_A - h_B)/L]$$

or

$$Q = -KA(dh/dL) \tag{1}$$

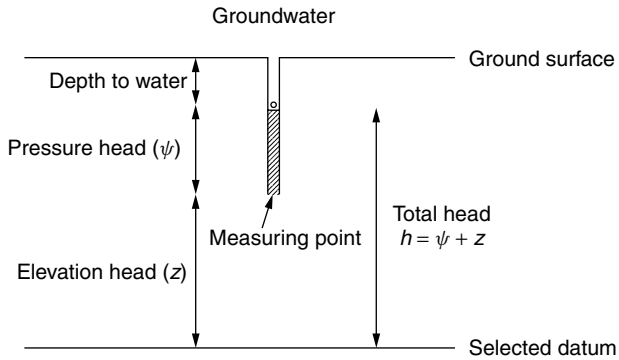


Figure 1. Elevation head, pressure head, and total head (adapted from Reference 1).

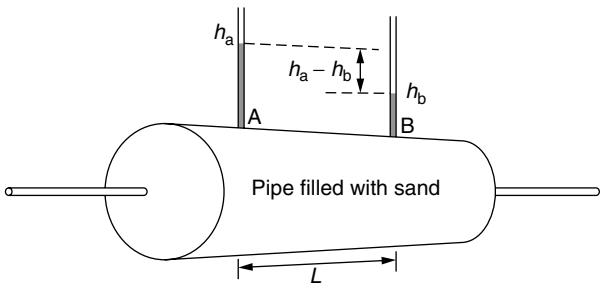


Figure 2. Darcy's law.

or

$$q = Q/A = -K\,(dh/dL) \tag{2}$$

where Q is the quantity of flow per unit of time (m^3/day); K = hydraulic conductivity (m/day); A = cross-sectional area (m^2); h_A and h_B are the hydraulic head at points A and B, respectively; and dh/dL = hydraulic gradient. The term Q/A in Eq. 2 is also known as the specific discharge (q), which is the flow per unit area [LT^{-1}]. The specific discharge is sometimes referred to as Darcy flux, Darcy velocity, or bulk velocity.

The negative sign in Eq. 2 indicates that the fluid moves in the direction of decreasing hydraulic head. Darcy's law assumes that the flow is laminar, that is, the water follows distinct flow lines rather than mixing with other flow lines, which is the case for most groundwater flow in porous media. Most groundwater movements occur in small interstices, so that there is considerable resistance to flow imposed by the aquifer material, making the flow laminar. When the flow velocity increases, especially in media having large pores, the occurrence of turbulent eddies dissipates kinetic energy, rendering the hydraulic gradient less effective in inducing flow. In very large interstices, such as those in many limestone and volcanic areas, groundwater flow is almost identical to the turbulent flow of surface water. Darcy's law is not valid for turbulent flow, for unusually high velocity that may be found in fractures or in granular aquifers.

Equation 2 yields only an apparent velocity value, the macroscopic velocity, through the cross-sectional area of a solid matrix and interstices, which, however, is not the true velocity of water moving through the pores. Clearly, flow velocities through interstices alone will be much higher than the macroscopic value. The interstices themselves vary in shape, width, and direction, so the actual velocity in the soil or rock is highly variable. Furthermore, the flow path of a water particle around and between the grains in an aquifer is tortuous, so water particles must travel longer than the apparent distance given by the measured length of the porous medium in the direction of flow, as shown schematically in Fig. 3.

To calculate the true linear velocity, one must take into account the fact that water travels only through the pores of the sediment. The fraction of the area covered by open space is equal to the effective porosity (n_e). Thus, the effective velocity (v), also known as the porewater velocity, is obtained by dividing the macroscopic velocity by the effective porosity:

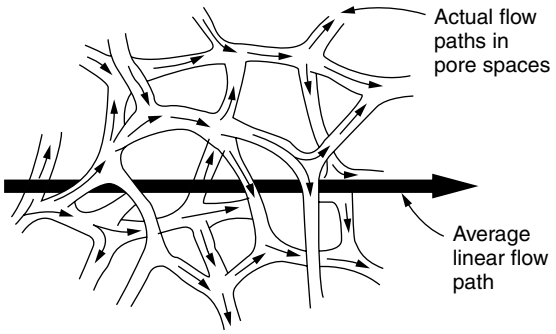


Figure 3. Concept of average linear velocity (2).

$$v = -(K/n_e)dh/dL \tag{3}$$

or

$$v = Q/n_e/A$$

or

$$v = q/n_e$$

From Eq. 3, it can be seen that, for sand with an effective porosity of 33%, the actual velocity is three times the Darcy velocity. Therefore, to define the actual velocity, one must consider the microstructure of the material. Usually, actual velocities tend to decrease with depth as porosities and hydraulic conductivities also decrease.

BIBLIOGRAPHY

1. Ward, R.C. and Robinson, M. (2000). *Principles of Hydrology*, 4th Edn. McGraw-Hill, London.
2. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.

VISCOUS FLOW

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INTRODUCTION

This text describes the elementary concepts of viscous fluid flow. The principal laws that govern the motion of fluids are also discussed. From our common experience, we know that fluids deform under the action of external forces. The deforming forces and rate of deformation are related to each other through a proportionality constant known as the coefficient of viscosity. The value of this constant depends upon the chemical identity, material properties, and thermodynamic state of a given fluid. To develop a theory that shows how viscosity affects fluid dynamics, one must understand the relationships between stress and the rate of strain. The outlines given in this article provide basic concepts of viscous flow. For more detailed analysis, the reader should consult specialized texts on this topic. Some of these texts are listed in the references at the end of this article.

VISCOSITY AND NEWTON'S LAW OF VISCOSITY

The physical property by which the resistance to fluid flow can be characterized is known as viscosity. A more

fundamental approach to viscosity shows that it is the property of a fluid that relates applied stress to a resulting strain rate. By experience, we come across many different types of fluids. For example, consider water and lubricating oil such as that used in automobiles. Water can flow more freely compared to lubricating oil under isothermal conditions. Hence, we say that the viscosity of water is less than that of oil.

When we deform a solid, so that it is strained, we know that the solid will exert a restoring force that opposes the strain; for small strains, the restoring force is proportional to the strain, the familiar Hooke's law. Real fluids also oppose strains; however, in a fluid it is not the amount of strain that is important but the rate at which the strain is produced.

Consider simple fluid flow between the two plates shown in Fig. 1. If the force per unit area of the top plate is F, we find that

$$\frac{F}{A} = \mu \frac{v}{d} \tag{1}$$

where d is the separation between the plates, which defines the viscosity μ (sometimes called the absolute or dynamic viscosity). Equation 1 can be written in a more generalized form given by Eq. 2. The shear stress exerted in the x direction on a fluid surface of constant y by the fluid in the region of lesser y is designated as τ_{yx}, and the x component of the fluid velocity vector is designated as v_x:

$$\tau_{yx} = -\mu \frac{dv_x}{dy} = \mu \dot{\gamma} \tag{2}$$

This equation is commonly known as *Newton's law of viscosity*. It states that the shear force per unit area is proportional to the negative of the local velocity gradient. The left-hand side of Eq. 2 represents the shear stress, and the right-hand side represents the rate of strain $\dot{\gamma} \cdot \tau_{yx}$ from Eq. 2 can also be interpreted as the viscous flux of the x momentum in the y direction. It can be seen that the viscous momentum flux is in the direction of the negative velocity gradient, that is, the momentum tends to go in the direction of decreasing velocity. A velocity gradient can thus be considered a driving force for momentum transport.

Fluids in which shear stress is directly proportional to the rate of deformation are termed *Newtonian fluids*. The viscosity of such fluids is independent of the rate of shear and rate of strain and always remains constant under given conditions. Examples of Newtonian fluids are air, water, and gasoline. In SI units, the units of viscosity are kg/m · s or Pa · s. In the cgs system, the unit of viscosity is g/cm · s, also called the poise (after Poiseuille) and equals 0.1 Pa · s. In fluid mechanics, the ratio of absolute viscosity to density is also termed kinematic viscosity which is often denoted by η. Generally, the viscosity of liquids decreases as temperature increases. Gases, on the other hand, have viscosities which generally increase with increasing temperature. More detailed explanations are based on the kinetic theory of gases and can be found in (1).

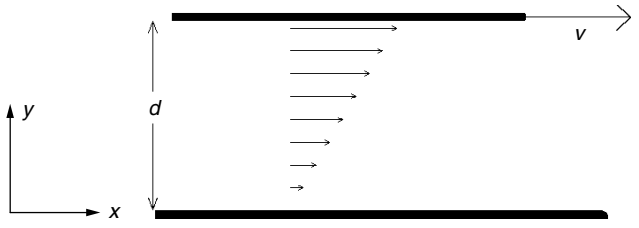


Figure 1. Viscous drag between two plates, which the bottom plate is held fixed.

NON-NEWTONIAN FLUIDS

There are fluids that do not obey the simple relationship between shear stress and shear strain rate given by Eq. 2 for a Newtonian fluid. These fluids are known as *non-Newtonian* fluids. Examples are paints, solutions of various polymers, food products such as applesauce and ketchup, emulsions and suspensions of various solids, and coal slurries. The subject of non-Newtonian flow is actually a subdivision of the science of *rheology*, which is also known as the "science of deformation and flow."

We categorize non-Newtonian fluids and discuss them under three general classifications:

1. The first is the time independent non-Newtonian fluid in which the shear rate is a unique but nonlinear function of shear stress.
2. In the second category are the time dependent non-Newtonian fluids that have more complicated shear stress and shear strain relationships. In these fluids, the shearing rate is not a single valued function of the shear stress. The shear rate depends on shearing time or on the previous shear stress rate history of that fluid.
3. In the third category are viscoelastic fluids. Unlike a truly viscous fluid in which all its energy of deformation is dissipated, some of the energy of deformation of a viscoelastic fluid may be recoverable as in the deformation of an elastic fluid.

Time-Independent Fluids

For time-independent non-Newtonian fluids,

$$\dot{\gamma} = f(\tau) \tag{3}$$

A Newtonian fluid is a special case of this category where the function $f(\tau)$ is linear.

Time-independent non-Newtonian fluids can be commonly represented by three distinct rheograms shown in Fig. 2:

1. Bingham plastics
2. pseudoplastics
3. dilatant fluids

Bingham Plastics. Bingham plastics exhibit yield stress at zero shear rate, followed by a straight-line relationship between shear stress and shear rate. The characteristics

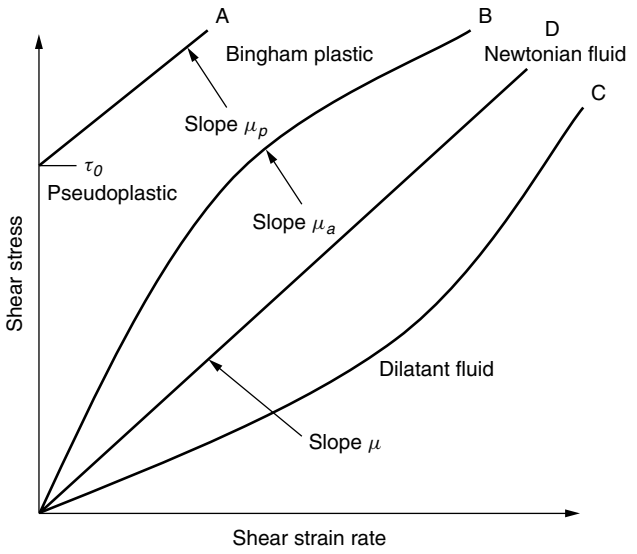


Figure 2. Shear stress–strain rate relationships for non-Newtonian fluids.

of such fluids are defined by two constants. The first is the yield stress denoted by τ_0; this is the stress that must be exceeded for the flow to begin. The second is the plastic viscosity μ_p which is the slope of the straight-line portion on curve A, Fig. 2. The model for Bingham plastics can be represented by Eq. 4:

$$\tau_{yx} = \mu_p \dot{\gamma} + \tau_0 \qquad if\ \tau_{yx} > \tau_0 \tag{4}$$

This model closely approximates the behavior of many real fluids such as slurries, plastics, emulsions such as paints, and suspensions of finely divided solids in a liquid. However, different constitutive models representing this type of fluids have been proposed by Herschel and Bulkley (2), Oldyroyd (3), and Casson (4).

Pseudoplastic fluids. Pseudoplastics (curve B, Fig. 2) do not have any yield stress. A pseudoplastic fluid is characterized by a progressively decreasing slope of shear stress versus strain rate. The slope has been defined as apparent viscosity,

$$\mu_a = \tau_{yx}/\dot{\gamma} \tag{5}$$

At very high shear rates, the apparent viscosity becomes constant, and the shear stress versus shear strain becomes linear. A number of empirical relations have been used to describe the behavior of pseudoplastic fluids. The simplest of these is the power law model proposed by Ostwald in 1923 [refer to (5)] and expressed in the form of Equation 6.

$$\tau_{yx} = k\dot{\gamma}$$

where $n < 1$ and k and n are constants for a particular fluid. k is known as the consistency coefficient for a given fluid, and n is the power law index. n also represents the deviation of a particular fluid from a Newtonian fluid. For a Newtonian fluid, $n = 1$, and $k = \mu$, the viscosity of the fluid. Combining Eqs. 5 and 6,

$$\mu_a = k\dot{\gamma}^{(n-1)} \tag{7}$$

The value of n is greater than unity for pseudoplastic fluids.

Dilatant Fluids. Dilatant fluids (curve C, Fig. 2) are similar to pseudoplastics in having no yield stress. They differ from pseudoplastics in a fashion such that the apparent viscosity increases as shear rate increases. The power law model given by Eq. 7 is also applicable to dilatant fluids, and so are Eqs. 6 and 7. The only difference here is that the power law index n is greater than unity. Pseudoplastic and dilatant fluids are also known as shear thinning and shear thickening fluids.

Time-Dependent fluids. Some fluids are more complex than those just described, and the apparent viscosity depends not only on the shear rate but also on the time for which the shear has been applied. Such fluids can be classified in two categories;

1. thixotropic fluids
2. rheopectic fluids

The shear stress decreases with time for a thixotropic fluid, whereas the shear stress increases with time for a rheopectic fluid. Rheopexy and thixotropy are complex phenomena resulting from transient changes of the molecular structure of time-dependent fluids under an applied shear stress. The proposed models for such fluids are hence based on many simplifying assumptions (6).

Thixotropic Fluids. The apparent viscosity of thixotropic fluids depends on the length of time of shearing as well as on the shear rate. As the fluid is sheared from the state of rest, it breaks down (on a molecular scale), but then the structural reformation increases with time. An equilibrium state is achieved when the breakdown rate is equal to the build up rate. If allowed to rest, the fluid builds up slowly and eventually regains its original consistency. As the shear is decreased, the apparent viscosity is less than that for increasing shear. For more detailed discussions, refer to (7).

Rheopectic Fluids. Molecular structure in rheopectic fluids, is formed by shear, and the behavior is opposite to that of thixotropy. A simple example of the formation of shear structure is the beating and thickening of egg whites. Many substances lose their rheopectic properties at extremely high shear rates and behave as thixotropic fluids.

Viscoelastic Fluids. A viscoelastic fluid exhibits both viscous and elastic properties. The simplest type of such a material is one which is Newtonian and obeys Hooke's law for the elastic part. The shear rate for such fluids can hence be written as

$$\dot{\gamma} = \tau_{yx}/\mu_0 + \dot{\tau}_{yx}/\lambda \tag{8}$$

where λ is the rigidity modulus. Under steady-state flow, $\dot{\gamma} = \tau_{yx}/\mu_0$ and the fluid behaves like a simple Newtonian

fluid. However, if the shear is changed, an elastic effect is added. Maxwell first proposed Eq. 8 in the form

$$\tau_{yx} + \dot{\tau}_{yx}\,(\mu_0/\lambda) = \mu_0\dot{\gamma} \tag{9}$$

Liquids that obey Eq. 9 are known as Maxwell liquids. The constant $(\mu_0/\lambda)^{-1}$ is known as the relaxation time, which is the time constant for the exponential decay of stress at constant strain. If the motion is stopped, the stress relaxes at $e^{-t\lambda/\mu_0}$. Rather complex models of viscoelastic materials have been developed in which higher time derivatives of τ_{yx} and $\dot{\gamma}$ appear. A very readable text for these models is (8).

MICROSCOPIC BALANCES OF MASS, MOMENTUM, AND ENERGY

We define the control volume as a region in space within which our fluid flow system is present. Laws of conservation (or change) of mass, momentum, and energy desribe the behavior of fluid flow within this system. To yield the detailed descriptions of variables of interest, the control volume must be of infinitesimal dimensions that can shrink to zero, yielding a point volume. This approach reduces the quantities to point variables. The application of conservation principles to this infinitesimal system produces microscopic or differential conservation equations.

Shell Momentum Balances

Shell momentum balances are written to represent a fluid flow problem mathematically. The momentum balance for any fluid flow system can be written as

$$\begin{aligned}&(\text{Rate of momentum in}) - (\text{rate of momentum out})\\ &\quad + (\text{sum of forces acting on the system})\\ &\quad = (\text{rate of momentum accumulation})\end{aligned} \tag{10}$$

Momentum can enter the system by momentum transfer according to Newtonian (or non-Newtonian) expressions for momentum flux. Momentum can also enter from overall fluid motion, bulk transfer. The forces acting on a system in fluid flow problems are pressure forces (acting on surfaces) and gravity forces (acting on the entire volume as a whole). The general procedure for solving any viscous flow problem is

1. Write a momentum balance in form of Equation 10 for a shell of finite thickness, a microscopic shell momentum balance.
2. Let this thickness approach zero, and use the mathematical definition of the first derivative to obtain the corresponding differential equation describing the momentum flux distribution.
3. Insert the appropriate Newtonian or non-Newtonian expression for momentum flux to obtain a differential equation for the velocity distribution.
4. Integrate these differential equations which yields the momentum flux and velocity distributions for the system under consideration.

Refer to (1) to get more acquainted with shell momentum balance concepts, where this approach has been applied to simple flow problems.

EULERIAN AND LAGRANGIAN COORDINATE SYSTEMS

Conservation equations and the constitutive equation are expressed in terms of relative kinematics, velocities, gradients of velocities, strains, and rates of strain, so it is very important to quantify these variables.

Flow kinematics, the relative motion of fluid particles, can be described by using either a *Lagrangian* or a *Eulerian* description. In the Lagrangian system, the motion of an individual particle is tracked where the coordinates locate the position of a particle and are functions of time. In the Eulerian system, dependent variables such as the velocity vector and pressure are considered functions of fixed spatial coordinates and of time.

The Lagrangian framework is considered a more natural choice to represent the actual kinematics and stresses experienced by fluid particles. However, to solve complex flow problems, this approach is limited (e.g., due to the necessity of tracking particles along unknown streamlines). This system is particularly convenient in flows of viscoelastic fluids with memory that require particle tracking and calculation of deformation and stresses along streamlines. The Eulerian formulation is, in general, more convenient to use because it deals only with local or present kinematics. In most cases, all variables of interest, such as strain, rate of strain, stress, and streamlines, can be obtained from the velocity field. An additional advantage of the Eulerian system is that it involves only time as a variable in unsteady-state flow, whereas the Lagrangian system uses traveling time as a variable, even in steady-state flow. All equations described in subsequent sections have been represented in the Eulerian coordinate system.

EQUATIONS OF CHANGE

The shell balance approach was used to acquaint the beginner with the application of the principle of conservation of momentum to viscous flow problems. It is, however, not always necessary to formulate a momentum balance. It is quicker and easier to start with the equations of continuity and motion in general form and then to simplify them to fit the problem in hand. These two equations describe all problems of the viscous flow of a pure isothermal fluid.

EQUATION OF CONTINUITY

The equation of continuity is developed by applying the law of conservation of mass to a small 3-D volume element within a flowing fluid, as shown in Fig. 3.

$$\begin{aligned}&(\text{Rate of mass accumulation})\\ &\quad = (\text{rate of mass in}) - (\text{Rate of mass out})\end{aligned} \tag{11}$$

We consider each of the six faces of this volume element and evaluate the mass entering and exiting the system:

$$\text{Rate of mass in} = \Delta y\Delta z\rho v_x\Big|_x + \Delta x\Delta z\rho v_y\Big|_y + \Delta x\Delta y\rho v_z\Big|_z \tag{12}$$

$$\text{Rate of mass out} = \Delta y\Delta z\rho v_x\Big|_{x+\Delta x} + \Delta x\Delta z\rho v_y\Big|_{y+\Delta y} + \Delta x\Delta y\rho v_z\Big|_{z+\Delta z} \tag{13}$$

$$\text{Rate of mass accumulation} = \Delta x\Delta y\Delta z\frac{\partial \rho}{\partial t} \tag{14}$$

After inserting, Eqs. 12–14 in Eq. 11, dividing the entire equation by $\Delta x\Delta y\Delta z$, and taking the limit of dimensions approaching zero, we get the equation of continuity.

For generality, we have expressed the equation of continuity in vector form:

$$\frac{\partial \rho}{\partial t} = -(\nabla \cdot \rho v) \tag{15}$$

Here $(\nabla \cdot \rho v)$ is called the "divergence" of $\rho\mathbf{v}$. Vector $\rho\mathbf{v}$ is the mass flux and is the net rate of mass efflux per unit volume. Equation 15 states that the rate of increase of density within a small volume element fixed in space is equal to the net rate of mass influx to the element divided by its volume. Note that the derivation can be performed for a volume element of any shape.

A very special form of the equation of continuity is Eq. 16, which is applicable to fluids of constant density, *incompressible fluids*.

$$(\nabla \cdot \mathbf{v}) = 0 \tag{16}$$

EQUATION OF MOTION

Using the shell momentum balance approach for the 3-D volume element shown in Fig. 5, an equation of motion is developed. It should be emphasized that momentum is a vector quantity, and hence the equation of motion has components in each of the three coordinate directions x, y, and z, respectively. For simplicity, we consider only the x component here; y and z components can then be handled analogously. Momentum flows in and out of the control volume by two mechanisms; convection, which is a result of the bulk fluid flow and molecular transfer (i.e., viscous transfer), that is, by virtue of velocity gradients.

The important forces acting on the cubic element in Fig. 4 are the fluid pressure p and the gravitational force g_x. Hence, to write Eq. 10 in mathematical form,

$$\begin{aligned}\text{Rate of momentum in} = {} & \text{Rate of momentum in by (convection + viscous transfer)} \\ = {} & \Delta y\Delta z\rho v_x v_x\Big|_x + \Delta x\Delta z\rho v_y v_x\Big|_y \\ & + \Delta x\Delta y\rho v_z v_x\Big|_z + \Delta y\Delta z\tau_{xx}\Big|_x \\ & + \Delta x\Delta z\tau_{yx}\Big|_y + \Delta x\Delta y\tau_{zx}\Big|_z\end{aligned} \tag{17}$$

$$\begin{aligned}\text{Rate of momentum out} = {} & \text{Rate of momentum out by (convection + viscous transfer)} \\ = {} & \Delta y\Delta z\rho v_x v_x\Big|_{x+\Delta x} + \Delta x\Delta z\rho v_y v_x\Big|_{y+\Delta y} \\ & + \Delta x\Delta y\rho v_z v_x\Big|_{z+\Delta z} + \Delta y\Delta z\tau_{xx}\Big|_{x+\Delta x} \\ & + \Delta x\Delta z\tau_{yx}\Big|_{y+\Delta y} + \Delta x\Delta y\tau_{zx}\Big|_{z+\Delta z}\end{aligned} \tag{18}$$

$$\begin{aligned}\text{Sum of forces acting} = {} & \text{body forces} + \text{pressure} \\ = {} & \Delta y\Delta z\left(p\Big|_x - p\Big|_{x+\Delta x}\right) \\ & + \rho g_x\Delta x\Delta y\Delta z\end{aligned} \tag{19}$$

$$\text{Rate of accumulation of } x \text{ component of momentum} = \Delta x\Delta y\Delta z\frac{\partial \rho v_x}{\partial t} \tag{20}$$

These stresses developing in viscous transfer can be divided into normal and shear stresses. For example, τ_{xx} is the normal stress, whereas τ_{yx} is the shear stress resulting from viscous forces. At each point in a continuous medium, whether it is solid or fluid, we need six components; each represents a component of force per unit area to define

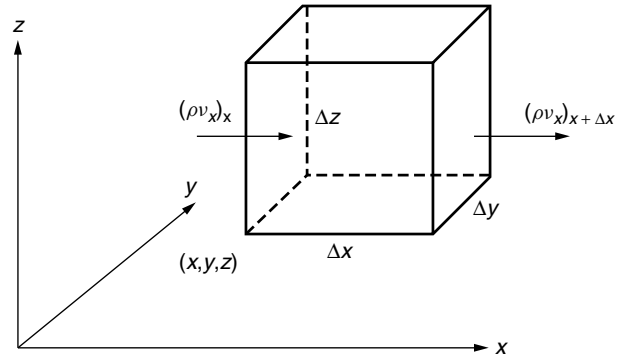


Figure 3. Region of volume in $\Delta x\Delta y\Delta z$ through which fluid is flowing.

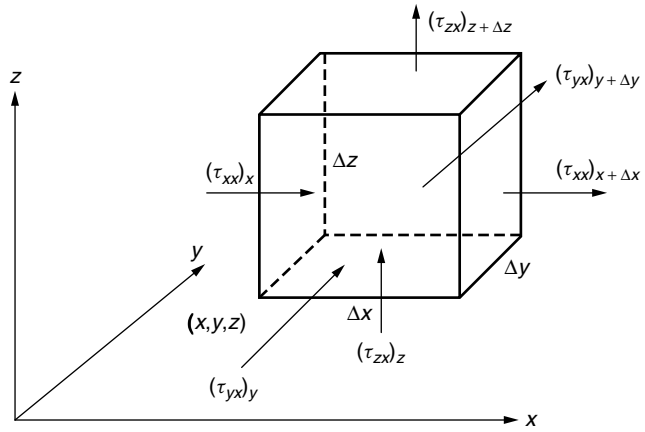


Figure 4. Direction of transfer of x component of momentum through the surfaces.

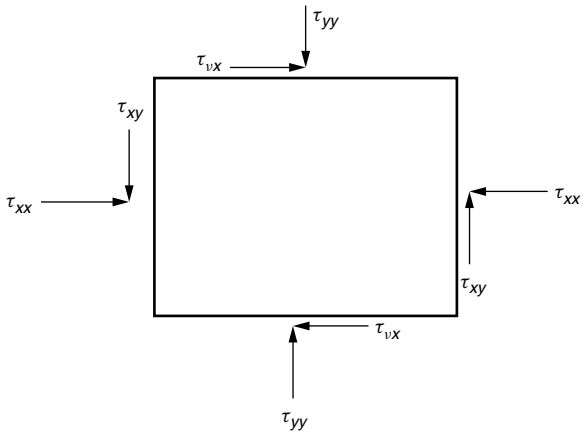


Figure 5. Local stresses acting on a cubic element in an $x-y$ plane.

the local stress completely. The local stresses acting in the $x-y$ plane are shown in Fig. 5.

Using Eqs. 17–20, dividing the entire equation by $\Delta x \Delta y \Delta z$, and taking the limit of the dimensions approaching zero, we get the x component of the equation of motion. Analogously, we can find the components for the y and z components. Adding the three components of equation of motion, the equation of motion can be expressed in vector notation as

$$\begin{array}{lll} \dfrac{\partial}{\partial t}\rho\mathbf{v} = & [\nabla \cdot \rho\mathbf{vv}] & -[\nabla p] \\ \text{Rate of increase of momentum per unit volume} & \text{Rate of momentum gain by convection per unit volume} & \text{Pressure on element per unit volume} \\ & -[\nabla \cdot \boldsymbol{\tau}] & +\rho\mathbf{g} \\ & \text{Rate of momentum gain by viscous transfer per unit volume} & \text{Gravitational force on element per unit volume} \end{array} \tag{21}$$

$\boldsymbol{\tau}$ is known as the "stress tensor", $[\nabla \cdot \rho vv]$ represents the rate of loss of momentum per unit volume by fluid flow, and $(\nabla \cdot \rho v)$ represents the rate of loss of mass per unit volume. To use Eq. 21 to determine the velocity distribution, we must insert expressions for various stresses in terms of velocity gradients and fluid properties. For Newtonian fluids, these expressions can be written as

$$\tau_{xx} = -2\mu\frac{\partial v_x}{\partial x} + \frac{2}{3}\mu(\nabla \cdot \mathbf{v}) \tag{22}$$

$$\tau_{yy} = -2\mu\frac{\partial v_y}{\partial y} + \frac{2}{3}\mu(\nabla \cdot \mathbf{v}) \tag{23}$$

$$\tau_{zz} = -2\mu\frac{\partial v_z}{\partial z} + \frac{2}{3}\mu(\nabla \cdot \mathbf{v}) \tag{24}$$

$$\tau_{xy} = \tau_{yx} = -\mu\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) \tag{25}$$

$$\tau_{yz} = \tau_{zy} = -\mu\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \tag{26}$$

$$\tau_{zx} = \tau_{xz} = -\mu\left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z}\right) \tag{27}$$

Equations 22–27 have been presented with proof in (9) and can be applied to various complex situations. Equations 22–24 are normal stresses and should contain an additional term. For example, Eq. 22 should be written as

$$\tau_{xx} = -2\mu\frac{\partial v_x}{\partial x} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla \cdot v) \tag{28}$$

Similarly, Eqs. 23 and 24 are also written as

$$\tau_{xx} = -2\mu\frac{\partial v_x}{\partial x} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla \cdot v) \tag{29}$$

$$\tau_{xx} = -2\mu\frac{\partial v_x}{\partial x} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla \cdot v) \tag{30}$$

κ is known as "bulk viscosity." The bulk viscosity is zero for low-density monoatomic gases and not too important for dense gases and liquids which are almost incompressible. Experimental measurements to estimate the value of "bulk viscosity" have been discussed by Karim and Rosenhead (10). Formulas to estimate the value of bulk density can be found in (11). When the fluid flows in the x direction between two parallel plates perpendicular to the y direction and v_x is only a function of y, then this set of six equations reduces to Eq. 2 described previously. Equations 22–27 inserted in Eq. 21 yield the equations of motion for a Newtonian fluid with varying density and viscosity.

1. For constant ρ and μ, the equation of motion can be written as

$$\rho\left(\frac{\partial v}{\partial t} + v \cdot \nabla v\right) = -\nabla p + \mu\nabla^2 v + \rho g \tag{28}$$

Equation 28 is the well-known **Navier–Stokes** equations, first developed by Navier in France in 1822.

2. When viscous effects are ignored, Eq. 28 reduces to

$$\rho\left(\frac{\partial v}{\partial t} + v \cdot \nabla v\right) = -\nabla p + \rho g \tag{29}$$

Equation 29 model laminar flow when viscous effects are negligible. These flows are termed Euler, potential, or inviscid flows. Equation 29 is the well-known **Euler** equation.

3. When the motion of a fluid is "very slow," the flow is said to be creeping or Stokes flow. Viscous forces dominate creeping flows and hence, the nonlinear inertia term in Eq. 28 is neglected. Then,

$$\rho\frac{\partial v}{\partial t} = -\nabla p + \mu\nabla^2 v + \rho g \tag{30}$$

Equation 30 is the well-known **Stokes** equations.

The equations of motion together with the equation of continuity, the equation of state $p = p(\rho)$, viscosity models illustrated in previous sections, and the intial and

the boundary conditions, complete the problem specification for any viscous flow problem. These equations, when solved mathematically, determine completely the density, pressure, and velocity components in a flowing isothermal fluid.

Boundary Conditions

Boundary conditions are constraints imposed on conservation equations to describe how flow behavior conforms to the surroundings. Boundary conditions come from nature and are mathematical descriptions of the physics at the boundary. These may describe conditions along the boundary dealing with motion, external stresses, rate of mass and momentum flux, boundary values of field variables as well as the relations among them. When the solution involves the time evolution of flow fields, initial conditions are also needed. The number of boundary conditions required to solve a particular problem is determined by the nature of the governing partial differential equation. In general, elliptical equations require boundary conditions on each portion of the boundary; hyperbolic equations require boundary conditions at upstream but not at downstream boundaries; parabolic equations require initial conditions and boundary conditions everywhere except downstream. The Navier–Stokes equations are hyperbolic at high Reynolds numbers and elliptical at low Reynolds numbers. The Euler equation is the upper limit of hyperbolicity, whereas Stokes equations are the lower limit of ellipticity. Different types of boundary conditions in mathematical form have been described by Papanastasiou (12) and are applicable to a wide range of viscous flow problems.

In general, there are three types of boundary conditions:

1. First kind or *Dirichlet* boundary conditions: The value of the dependent variable along the boundary is imposed as the condition. Typical Dirichlet boundary conditions are no-slip boundary conditions for velocity and the specification of inlet/outlet velocities.
2. Second kind or *Neumann* boundary conditions: The normal derivative of the dependent variable is specified along the boundary. Examples are symmetry conditions and free surface and interface stress conditions.
3. Third kind or *Robin's* boundary condition: The dependent variable and its normal derivative are related. Slip wall conditions are typical Robin conditions.

BIBLIOGRAPHY

1. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (1994). *Transport Phenomena*. John Wiley & Sons, New York.
2. Herschel, W.H., and Bulkley, R. (1926). Flow of Non-Newtonian fluids. In: *Encyclopaedia of Fluid Mechanics*. Gulf Publishers, Houston, TX, Vol. 9, Chap. 4.
3. Oldyroyd, J.G. (1947). A rational formulation of the equations of plastic flow for a Bingham solid. *Proc. Camb. Philos. Soc.* **43**: 100–105.
4. Casson, N. (1959). *Rheology of Disperse Systems*. Pergamon Press, London.
5. Bird, R.B., Armstrong, R.C., and Hassager, O. (1977). *Dynamics of Polymeric Liquids: Fluid Mechanics*. John Wiley & Sons, New York.
6. Slibar, A. and Paslay, P.R. (1959). Retarded flow of Bingham materials. *Trans. ASME* **26**: 107–113.
7. Tanner, R.I. (1985). *Engineering Rheology*. Clarendon Press, Oxford, UK.
8. Wilikinson, W.L. (1960). *Non-Newtonian Fluids*. Pergamon Press, New York.
9. Lamb, H. (1945). *Hydrodynamics*. Dover, New York.
10. Karim, S.M. and Rosenhead, L. (1952). *Rev. Mod. Phys.* **24**: 108–116.
11. Papanastasiou, T.C., Georgiou, G.C., and Alexandrou, A.N. (2000). *Viscous Fluid Flow*. CRC Press, New York.
12. Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B. (1954). *The Molecular Theory of Gases and Liquids*. John Wiley & Sons, New York.

Nomenclature

A	Area
F	Force
$\mathbf{g}$	Gravity force vector
n	Power law index
p	Pressure
$\mathbf{v}$	Velocity vector
t	Time variable
Greek Symbols	
$\dot{\gamma}$	Rate of strain
κ	Bulk viscosity
μ	Viscosity of a fluid
τ	Stress
$\dot{\tau}$	Rate of shear
λ	Elasticity modulus
ρ	Density of a fluid
Subscripts	
a	Stands for apparent
p	Stands for plastic
o	Stands for yield stress
x	Stands for x component
y	Stands for y component
z	Stands for z component

VULNERABILITY MAPPING OF GROUNDWATER RESOURCES

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WHAT IS GROUNDWATER VULNERABILITY?

Groundwater vulnerability is a measure of the likelihood that pollution or contamination at the land surface reaches a production aquifer. It is a measure of the "degree of insulation" that natural and man-made factors provide to keep pollution away from groundwater. The term was first used in Europe in the 1960s. In defining groundwater vulnerability, a number of issues must be examined and

clarified; all refer to these two questions: vulnerability *of what?* and vulnerability *to what*? Exact definitions of groundwater vulnerability have therefore varied (1).

In principle, all groundwater is vulnerable to human activity; no groundwater is completely isolated from the aboveground environment. The degree of vulnerability depends on environmental conditions, on how we define groundwater and the part of groundwater in which we are interested in (hence the question, "vulnerability *of what*?"), and on the timescale of interest. In addition, it depends on whether or not a vulnerability measure is intended to account also for the presence and type of pollutants (hence, "vulnerability *to what*?").

Vulnerability of What?

Groundwater is produced from a wide variety of hydrogeologic environments. When defining vulnerability, therefore, we need to define the portion of groundwater to be assessed. Because the shallowest groundwater zone is typically the most vulnerable, vulnerability assessments are mostly concerned with the vulnerability of the uppermost aquifer (in a multiaquifer system) or with the water table (in an unconfined aquifer system). Deep groundwater is considered less vulnerable than shallow groundwater because of the longer travel times necessary for a pollutant to reach these deeper aquifers.

Some methods of assessing vulnerability therefore account, directly or indirectly, for the travel time between the water table and a well by considering aquifer permeability or travel-time zones (e.g., 2). Timescales are important in defining vulnerability. The practical question is, should we consider groundwater vulnerable to today's activities only if the recharge time is a few years or also if recharge timescales are tens, hundreds, thousands, or tens of thousands of years? The potential travel time between contaminant source and groundwater or groundwater wells is an important consideration for protection, monitoring, and assessment. Timescales are also important when mapping vulnerability to specific pollutants that become less harmful over time and with travel distance due to radioactive decay, degradation, inactivation (in the case of pathogens), filtration, or strong sorption to soils and aquifer materials.

Vulnerability to What?

An assessment of groundwater vulnerability may or may not include consideration of the presence of pollutants. Vulnerability that is independent of whether or not contaminants (pollutants) are present and focuses primarily on a description of natural environmental conditions is often (though not always) referred to as "susceptibility," "natural vulnerability," "aquifer sensitivity," or "intrinsic vulnerability." Pollution-type-dependent vulnerability, or vulnerability to specific land uses, is sometimes referred to as "specific vulnerability" or "integrated vulnerability" (1).

WHY ASSESS GROUNDWATER VULNERABILITY?

The purpose of vulnerability assessments is to provide a decision-making tool based on the best available data and good scientific judgment. It is generally not intended to be a scientifically rigorous analysis of groundwater resources. The National Research Council (3) identified four general objectives typically achieved by groundwater vulnerability assessments: (1) to facilitate policy analysis and development at the local and regional level, (2) to provide program management, (3) to inform land use decisions, and (4) to provide general education and awareness of a region's hydrogeologic resources.

The usefulness of vulnerability maps is limited (some would say, arguable). The scientific literature lists pros and cons to vulnerability assessments (1). The facts that speak for implementing assessments are that land use decisions have to be made, land management practices need to be sensitive to the risk for groundwater contamination, and not all anthropogenic activities can be carried out isolated from groundwater. Timescales and distinctions based on travel time are important, at least with respect to some pollutants. Timescales are also important in placing groundwater monitoring wells and in scheduling and providing for planning and action–response time if pollution does occur. So a need exists to provide at least some general guidance to land use planners, decision makers, and water users. Carefully prepared vulnerability assessments allow them to make decisions that are economically sensible and at the same time hydrogeologically reasonable.

On the other hand, some may argue against the use of vulnerability maps for land use planning because groundwater flow conditions and the transport properties of the subsurface are too complex to be appropriately captured by any vulnerability tool. A second group of arguments against vulnerability zoning arises from the fact that all groundwater is vulnerable to land pollution. The only geographically differing factor is the timescale for the pollution to reach groundwater.

WHAT FACTORS DETERMINE VULNERABILITY?

We distinguish between intrinsic factors (natural conditions) and extrinsic factors (anthropogenic activities). Among intrinsic factors, the thickness and hydraulic properties of the geologic formations above the aquifer—the unsaturated zone and confining layers above the aquifer—are key factors in determining the vulnerability of an aquifer system. They are the principal natural controls that determine the recharge rate and recharge time to the aquifer. The unsaturated zone also provides key groundwater protection by

- intercepting, sorbing, and eliminating pathogenic viruses and bacteria;
- sorbing and degrading many synthetic organic chemicals; and
- attenuating heavy metals and other inorganic chemicals through sorption and complexation with mineral surfaces within the unsaturated zone and through uptake into plants and crops (e.g., fertilizer).

The potential of the soil and the unsaturated zone to sorb, degrade, or eliminate substances depends on the type of

pollutant and therefore is considered only in vulnerability studies that are specific to certain land uses.

The amount of recharge at the land surface is another important factor that determines vulnerability. The higher the recharge, the higher the vulnerability of the aquifer. If climatic conditions are such that little or no recharge occurs at the land surface, downward movement of moisture through the unsaturated zone is very limited, regardless of the hydraulic properties of the unsaturated zone.

In vulnerability assessments that encompass more than just aquifer susceptibility (see above), the presence of contamination sources or possible contaminating activities is considered an important factor. The amount, spatial distribution, and chemical properties of the contaminants (possibly) released into the subsurface are highly specific to individual sources and regions.

CHARACTERIZATION OF GROUNDWATER VULNERABILITY

Numerous schemes have been developed for assessing and mapping vulnerability. These methods can be grouped into three major categories:

- index-and-overlay methods
- process-based computer simulations
- statistical analyses

Index-and-Overlay Methods

Index-and-overlay methods are based on assembling information on the most relevant factors affecting aquifer vulnerability (soil type, geologic formation type, recharge, etc.), which then is interpreted by scoring, integrating, or classifying the information to produce an index, rank, or class of "vulnerability." The scoring, ranking, and integration methods are based on expert opinion rather than processes and are inherently subjective to some degree. In the United States, the most prominent vulnerability assessment method in this category is "DRASTIC" (2). Others include the vulnerability analysis specified by California's Drinking Water Source Assessment Program (4) and the British "GOD" method (1). A brief overview of DRASTIC and GOD is given below.

The advantage of index-and-overlay methods is that they provide relatively simple algorithms or decision trees to integrate a large amount of spatial information into maps of simple vulnerability classes or indexes. The methods are designed to rely on data that are readily available from local, state, or federal agencies, such as information on soils, water level depth, precipitation, and geology. These methods are particularly suitable for use with computerized geographic information systems (GIS), which is a digital form of mapmaking, because they usually involve overlaying and aggregating multiple maps showing soil properties, depth to water table, recharge, and so on.

DRASTIC Vulnerability Mapping (2). DRASTIC is the most popular vulnerability mapping tool in the United States. Put together by a group of experts and the EPA in the mid-1980s, it has been applied to a number of groundwater basins, regions, even states.

The name stands for *d*epth to groundwater, *r*echarge rate, *a*quifer media, *s*oil media, *t*opography, *i*mpact of vadose zone media, and hydraulic *c*onductivity of the aquifer. In DRASTIC, scores of 0 to 10 are assigned to each parameter, 0 means low risk of groundwater contamination; 10 means high risk of contamination. The scores are multiplied by a parameter-specific weight. The weighted scores of all seven parameters are then added for the final DRASTIC score. Two sets of weights can be used: one for general (intrinsic) vulnerability analysis, one for specific vulnerability to pesticides.

GOD (1). GOD is a vulnerability assessment method developed in Great Britain, where most groundwater resources are in hardrock aquifers, primarily sandstone and limestone aquifers. Unconsolidated overburden or soil layers cover the fractured hardrock in many places. Like DRASTIC, GOD is an index-and-overlay method designed to map groundwater vulnerability across large regions based on a few important parameters; GOD stands for *g*roundwater occurrence, *o*verall lithology of the unsaturated zone or overlying aquitard, and *d*epth to the groundwater table. Scores are assigned to each of the three categories and then multiplied to yield a final score. In developing GOD, the method's authors have given particular consideration to the likelihood of fractures or fracture systems to develop in the soils, overburden, or overlying geologic units of the aquifer.

Process-Based Computer Simulations

Process-based computer simulations afford a great amount of realistic complexity and detail to be built into the vulnerability assessment. Computer models can account for complex physical and chemical processes on a very detailed scale. Unlike the two-dimensional maps and map layers used with other methods, computer modeling allows for complete three-dimensional resolution. Geologic and hydrogeologic variations with depth can therefore be reproduced to evaluate their effect on vulnerability. Process-based computer models focus on re-creating the flow and transport patterns within the unsaturated zone or in an actual aquifer and can be used to compute travel times or concentrations of a contaminant in the unsaturated zone or in the aquifer. Computer models do not compute vulnerability directly. Rather, vulnerability is defined as a function of what the computer models simulate. For example, high vulnerability may be defined as any region in the aquifer for which the computer model shows a travel time of less than 5 years.

The most advanced computer models also allow the analyst to compute the uncertainty that is inevitably associated with the computer model predictions due to shortcomings in the database fed into the computer and due to our limited knowledge of the "underground world". These methods use statistical methods to quantify uncertainty. However, even simple computer models can include a sensitivity analysis, that is, an investigation

of the sensitivity of the model predictions to the input provided.

Computer models are not commonly used for vulnerability assessment due to their considerable data requirements and the expertise required to implement models. In other words, computer simulation models are rarely an economical alternative for vulnerability mapping. However, computer modeling is an excellent and economical tool for vulnerability mapping if

- a more localized analysis of specific vulnerability to particular land uses (particular contaminants) is required and sufficient data are available or can be collected to prepare the computer model, and
- a number of "what-if" scenarios involving complex processes need to be evaluated for making important land use planning decisions.

Four computer model codes are particularly popular for computing the fate and transport of contaminants as those contaminants travel downward through the unsaturated zone to the water table: VLEACH (EPA), PRZM (EPA), LEACH (Cornell University), and HYDRUS (U.S. Department of Agriculture/Agricultural Research Service Salinity Laboratory, Riverside, California) (for up-to-date information on these codes, see the web pages of these agencies). All four codes (listed here roughly in order of complexity and user expertise required; VLEACH is least complex and HYDRUS the most complex) compute the downward movement of water (flow) and contaminants (transport). These codes are designed specifically to determine the amounts of sorption and degradation that occur in soils and in the unsaturated zone and are typically used to compute the residual, nondegraded mass of a contaminant that arrives, over time, at the water table. For vulnerability assessments, subregions or smaller sections of land with similar unsaturated zone properties are selected and grouped. One simulation is performed for each group or section, and the results are mapped in various ways; a map of the travel time to the water table (perhaps specific to a contaminant), a map of the percent removal of a contaminant within the vadose zone, and so on.

The most common computer code used for groundwater modeling (in all three dimensions) is MODFLOW (U.S. Geological Survey). This model and other 3-D computer models can be used for highly specific site studies of groundwater contamination that are far beyond the purpose of a typical vulnerability assessment. The data requirements for running these models are tremendous and require careful data preparation and data processing, particularly in a fully three-dimensional simulation. Sometimes, groundwater models are used to compute explicitly the complex source area of the water reaching a well. In that case, the same computer model can also be used to compute specific vulnerability for particular contaminants of concern within the source area of the well. If a well-calibrated and well-documented groundwater model exists, it may be preferrable to use the groundwater model to address specific vulnerability issues rather than using a basic index or a scoring-based vulnerability assessment.

Statistical Methods

Statistical methods are used to quantify the risk of groundwater pollution by determining the statistical dependence or relationship between observed contamination, observed environmental conditions that may or may not characterize vulnerability (e.g., unsaturated zone properties, recharge), and observed land uses that are potential sources of contamination (e.g., fertilizer applications, septic tank occurrence). Once a model of this dependence or relationship has been developed from the statistical analysis, it can be used to predict—in a similar area elsewhere—the chance or risk of contamination. Such an application requires, of course, knowledge of significant environmental conditions for that area. When statistical methods are used, the risk of contamination is essentially a quantitative measure of "vulnerability." The higher the contamination risk, the higher the vulnerability.

In principle, statistical methods are not much different from index-and-overlay methods. Both establish a relationship between inherent natural conditions and groundwater vulnerability (which the statisticians refer to as groundwater contamination risk). In overlay methods, the relationship is established by a team of experts. In statistical methods, the relationship is established by statistical analysis. The advantage of the statistical method is that the statistical significance can be explicitly calculated, which provides a measure of uncertainty or certainty of the model. The disadvantage is that statistical methods are difficult to develop and, once established, can be applied only to regions that have environmental conditions similar to those of the region for which the statistical model was developed.

Few statistical methods have been developed for vulnerability assessment, primarily because they rely on large data sets from regions already contaminated. The key to the development of a statistical method is a large, high quality data set of a specific contaminant or several specific contaminants commonly found in a region. That data set is then correlated in one fashion or another to specific properties of the subsurface (depth to water, soil permeability, slope, hydraulic conductivity, etc.) to create a statistical predictive model that can be used to make a quantitative statement about the contamination risk, such as, "if this kind of unsaturated zone, aquifer, and land use properties exist in a location, then the risk for groundwater contamination is X%, with a confidence interval of plus or minus Y%." Some examples follow.

CALVUL. In California, a statistical method has been developed by the California Department of Pesticide Regulations (DPR) to determine the specific vulnerability of groundwater to pesticide residues. The method is nicknamed CALVUL (California Vulnerability approach; (5)). DPR uses the vulnerability analysis to determine, for each section of agricultural land in California, whether groundwater in that section of land is vulnerable or not. If it is vulnerable, the land section (square mile) becomes part of a groundwater protection area with restricted pesticide use. The DPR method distinguishes two types of vulnerability: (1) vulnerability to pesticide leaching in coarse soils

with a shallow water table and (2) vulnerability to pesticide runoff over hardpan soils (and subsequent leaching in dry wells). Pesticide management practices depend on whether pesticide leaching or pesticide runoff is of concern.

A pesticide database for the San Joaquin Valley was used to determine the statistical relationship between pesticide residue in groundwater and a large number of soil (unsaturated zone) properties, including water holding capacity, texture, organic matter content, permeability, shrink-swell potential, slope, and infiltration. By determining which soil and geographic properties are good predictors of pesticide residue in groundwater, the statistical model can be used to identify sections of land that have similarly "vulnerable" soil and geographic conditions but no past or current pesticide residue detections (5). Presumably, the most vulnerable areas are identified and can be targeted for implementation of mitigation management practices.

Texas Case Study. In Texas, a statistical analysis similar to DPR's San Joaquin study, albeit based on a different set of statistical tools, was developed by Evans and Maidment (6). Instead of pesticide residues in groundwater, this method uses an analysis of nitrate in groundwater as the basis for delineating vulnerable groundwater areas. As in CALVUL, the assumption made by the developers of the method was that where high contamination exists, the aquifer is more vulnerable than elsewhere. Nitrate was used as the target variable because a large amount of data was available throughout Texas and because nitrate is neither sorbed nor significantly degraded in groundwater (except under anaerobic conditions). The analysis was done by using data from the entire state. From a 30-year statewide database, the probability (risk) that a well would have nitrate levels in excess of some threshold value (1, 2, 5, or 10 mg/L NO_3-N) was computed separately for each analysis unit. The exceedance probability is used as a quantifiable measure of vulnerability; the higher the chances that nitrate is found in wells within an analysis unit (area), the higher the vulnerability. The study illustrates that overall results of the statistical analysis follow the general patterns laid out by the index-and-overlay methods, albeit at considerably higher expense.

National Groundwater Nitrate Vulnerability Assessment. The U.S. Geological Survey recently published a national assessment of the probability of nitrate contamination in recently recharged groundwater (7). The assessment relied on a specialized statistical regression analysis among major factors affecting the specific vulnerability of groundwater to nitrate and the measured occurrence of elevated nitrate levels in wells. The data set used to develop the regression model included wells from 20 major groundwater basins across the United States; each contained 20–30 test wells. Nitrogen fertilizer loading and percent cropland were significant extrinsic (nitrogen use related) factors. The presence of well-drained soils, depth to a seasonally high water table, and the presence of unconsolidated sand and gravel aquifers were the key intrinsic factors that determine groundwater nitrate vulnerability.

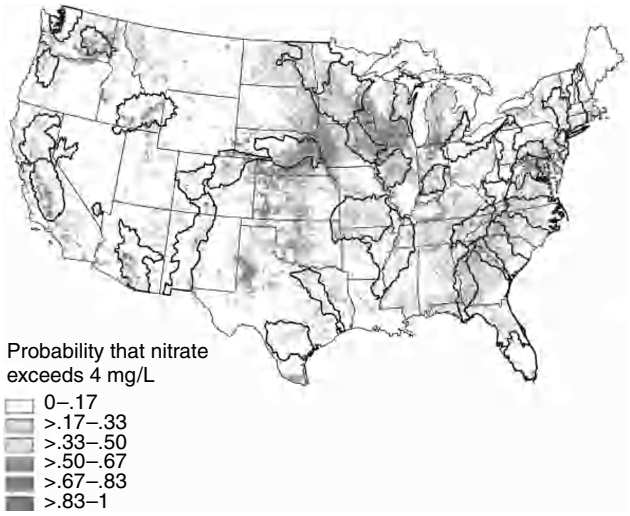


Figure 1. Groundwater vulnerability map for the United States, where vulnerability is here defined as the probability that nitrate concentration in groundwater exceeds 4 mg/l. (reprint from (7), also published at http://water.usgs.gov/nawqa/nutrients/pubs/est_v36_no10/fig3.html).

The regression model was validated (tested) on a large set of well records not used in developing the regression model and then applied to predict the probability of elevated nitrate (a measure of nitrate vulnerability) in groundwater throughout the United States at a resolution of 1 km^2 (Fig. 1, from Reference 7). The study demonstrates the advantage of the statistical method over index-and-overlay methods. The statistical assessment model uses objective, quantifiable measures to assess vulnerability. Its predictive capability has been quantified as well (through the validation test).

WHAT ARE THE LIMITATIONS OF VULNERABILITY ASSESSMENTS?

Because of the implied imprecise nature of vulnerability assessments and the inevitable subjectiveness of the underlying interpretive scheme, the National Research Council (3) issued "three rules of groundwater vulnerability." These rules, or limitations, should be spelled out explicitly with every vulnerability assessment:

- All groundwater is vulnerable to some degree.
- Uncertainty is inherent in all vulnerability assessments.
- There is a risk that the obvious may be obscured and the subtle may become indistinguishable.

The last refers to the danger, especially when using complex vulnerability assessment tools, that in light of the final vulnerability index or ranking, one may lose sight of the data used for the analysis and of the assumptions underlying vulnerability assessment schemes. The results of vulnerability assessments may mask real differences between specific sites or aquifer conditions.

AFTER THE ASSESSMENT: VERIFICATION AND POSTAUDIT

Verification refers to some independent procedure that can verify the results of the vulnerability analysis. *Postaudit* is essentially the same as verification but typically occurs years later, when additional data have been sampled that can be compared with the predictions made by the vulnerability analysis.

Verification and postaudits of vulnerability assessments can be done in many different ways. The most common approach, particularly for verifying assessments done with index-and-overlay methods, is to compare the vulnerability map with the actual occurrence of some common pollutant in groundwater. Typical pollutants used are nitrate and pesticides. However, such verification works well only where the appropriate pollution source is actually present and has been present for some time.

BIBLIOGRAPHY

1. Robins, N.S. (Ed.). (1998). *Groundwater Pollution, Aquifer Recharge and Vulnerability*. Geological Society Special Publication No. 130, Geological Society, London.
2. Aller, L., Bennett, T., Lehr, J.H., and Petty, R.J. (1985). DRASTIC—A standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings. U.S. EPA, Robert S. Kerr Environmental Research laboratory, Office of Research and Development, EPA/600/2-85-018.
3. National Research Council. (1993). *Ground Water Vulnerability Assessment, Contamination Potential under Conditions of Uncertainty*. National Academy Press, Washington, DC.
4. California Department of Health Services. (2000). Drinking Water Source Assessment and Protection Program. Available: http://www.dhs.ca.gov/ps/ddwem/dwsap/DWSAP_document.pdf.
5. Troiano, J., Spurlock, F., and Marade, J. (1999). Update of the California Vulnerability Soil Analysis for Movement of Pesticides to Ground Water. Department of Pesticide Regulation, Sacramento, CA 95814-3510, Document EH 00-05. Available: http://www.cdpr.ca.gov/docs/empm/pubs/ehapreps/eh0005.pdf.
6. Evans, T.A. and Maidment, D.R. (1995). A Spatial and Statistical Assessment of the Vulnerability of Texas Groundwater to Nitrate Contamination. Technical Report CRWR 260, Center for Research in Water Resources, Bureau of Engineering Research, The University of Texas at Austin, Austin, TX.
7. Nolan, B.T., Hitt, K.J., and Ruddy, B.C. (2002). Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. *Environ. Sci. Technol.* **36**(10): 2138–2145.

READING LIST

Blodgett, R. (1993). Drinking Water Vulnerability Assessments in Texas. *Proc.*, 1993 *Ann. Conf.*, American Water Works Association, Denver, CO.

Holtschlag, D.J. and Luukkonen, C.L. (1998). Assessment of Ground-Water Vulnerability to Atrazine Leaching in Kent County, Michigan: Review, Comparison of Results of Other Studies, and Verification, Water-Resources Investigations Report 98-4006. U.S. Geological Survey, Lansing, MI.

Rupert, M.G. (2001). Calibration of the DRASTIC ground water vulnerability mapping method. *Ground Water* **39**(4):625–630.

Snyder, D.T., Wilkinson, J.M., and Orzol, L.L. (1998). Use of a Ground-Water Flow Model with Particle Tracking to Evaluate Ground-Water Vulnerability, Clark County, Washington, Water-Supply Paper 2488. U.S. Geological Survey, Denver, CO.

Vrba, J. and Zoporozec, A. (Eds.). (1994). *Guidebook on Mapping Groundwater Vulnerability*. International Association of Hydrogeologists: International Contributions to Hydrogeology Vol. 16, Verlag Heinz Heise, Hannover, Germany.

WATER/ROCKS INTERACTION

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Water–rock interaction is a process whereby solid earth materials and aqueous phases in the Earth system exchange matter and, ultimately, energy through chemical and biochemical reactions. The extent of reactions is determined by how far the system is away from equilibrium, and the rate of reactions is controlled largely by the kinetics of mineral-water interfacial processes. In a broad sense, these reactions can be classified into two categories based on the reactants involved: (1) those between H_2O and the mineralogical components of rocks and (2) those between solutes dissolved in natural waters and the minerals. Water–rock interactions participate in many geological processes such as ore deposit formation, weathering, and pedogenesis. The outcome of these interactions plays an important role in regulating geochemical cycling of elements, the atmospheric CO_2 level, and the chemistry and nutrient availability of surface/near-surface waters at both local and global scales.

Water–rock interactions are heterogeneous reactions because of the involvement of multiple phases (that is, solid and liquid phases in most cases). Despite the complexity associated with the heterogeneity and variations in mineral assemblages, water chemistry, and environmental conditions, reactions between aqueous phase and rocks at the fundamental level can be regarded as consisting of only two types of mechanistic movement (1), chemical species attachment to and detachment from mineral surfaces. Individual or combined development of the two basic actions over time yields three primary types of water–rock interactions: adsorption (including ion exchange), dissolution, and precipitation. Following is a detailed discussion of the three types of reactions.

ADSORPTION

Chemical sorption results directly from the occurrence of undercoordinated sites and associated charges on mineral surfaces. Development of surface charge in aqueous environments can be understood as a consequence of surface complexation, by which water molecules form chemical bonds with the undercoordinated surface atoms (2). These surface-bound water molecules are then subject to a proton transfer process that shifts hydrogen

ions onto neighboring surface anions. This dissociative sorption of water molecules results in one or more types of surface species, depending on the chemical composition of the minerals in question. For (hydr)oxide materials, hydroxylated surface cation centers $>X(OH)^0$, where $>$ symbolizes lattice bonds and X represents the cationic component, seem to be the only concern. For salt-type minerals X_mA_n, an additional, second-type nonhydroxylated surface anion site $>AH^0$ has to be taken into consideration.

When present in solution environments, the surface hydroxyl groups can undergo protonation or deprotonation to form charged surface species. The relative abundance of protonated and deprotonated species thus governs the surface electric properties. Consider an oxide mineral XO. The sign and quantity of surface charges incurred in pure water will be controlled by the following reactions

$$\equiv XOH_2^+ \Leftrightarrow \equiv X(OH)^0 + H^+ \qquad K_{a1}^{app} \tag{1a}$$

and

$$\equiv X(OH)^0 \Leftrightarrow \equiv XO^- + H^+ \qquad K_{a2}^{app} \tag{1b}$$

where K_{a1}^{app} and K_{a2}^{app} are the apparent equilibrium constants of reactions 1a and 1b. The participation of hydrogen ions in the above reactions indicates that the relative concentrations of the protonated and deprotonated surface species, and hence the amount of surface charges, are controlled by the pH of the aqueous environment. The pH at which there are equal amounts of $>XOH_2^+$ and $>XO^-$ (i.e., an uncharged surface) is defined as the pH of zero net proton charge, below which the surface is positively charged for $>XOH_2^+$ is more abundant than $>XO^-$ and above which the surface is negatively charged because of the excess of $>XO^-$.

In the presence of other sorbing ions, say $M^{(n+1)+}$ and $L^{(n+1)-}$, in solutions, competitive complexation becomes operative as M can exchange for H and L for OH at the $>X(OH)^0$ sites to result in the formation of surface complexes such as $>XOM^{n+}$ and $>XL^{n-}$. Surface complexation under this condition becomes adsorption where both chemical bonding and electrostatic interaction take place between solute particles and surface atoms (3). Empirical approaches to adsorption employ simple equations to describe the adsorption isotherm (relationship between the solution concentration or activity and the surface concentration of an adsorbate), without concerning the specific interfacial interactions between adsorbate and adsorbent. For example, the Langmuir isotherm, one of the most common empirical models, simply treats adsorption as a free surface site $>S$ occupied by an adsorbate A to form a sorbed site $>SA$:

$$>S + A \Leftrightarrow >SA \tag{1c}$$

The adsorption constant K_{ad} given by the mass law is

$$K_{ad} = \frac{[>SA]}{[>S][A]} \tag{1d}$$

Because the total amount of surface sites is $[>S]_{tot} = [>S] + [>SA]$, Eq. 1d can be rewritten as

$$[>SA] = [>S]_{tot}\frac{K_{ad}[A]}{K_{ad}[A] + 1} \tag{1e}$$

High concentrations of $[A]$ lead to $[>SA] \cong [>S]_{tot}$, whereas low values of $[A]$ reduces Eq. 1e to a linear form of $[>SA] \cong K_d[A]$. Another common empirical adsorption model, the Freundlich isotherm, uses a logarithmic relationship between $[>SA]$ and $[A]$ so that

$$[>SA] = k_f[A]^n \tag{1f}$$

where both k_f and n are constants. The Freundlich model can be thought of as the Langmuir isotherm integrated over many types of surface sites (4).

In the surface complexation model, adsorption is treated as a chemical reaction

$$>X(OH)^0 + M^{(n+1)+} \Leftrightarrow >XOM^{n+} + H^+ \tag{1g}$$

The equilibrium constant K^{app}

$$K^{app} = \frac{[>XOM^{n+}][H^+]}{[>XOH^0][M^{(n+1)+}]} = K^{int}K^{coul} \tag{1h}$$

now has contributions from chemical (intrinsic) as well as electrostatic (coulombic) interactions between the reactants. Quantitatively, $K^{coul} = \exp(F\Delta Z\Psi)$, where ΔZ is the change of charges in surface species because of adsorption. The surface potential Ψ is a function of surface charge σ, and the charge-potential relationship can be derived from electrochemistry theories. A common one

$$\sigma = (8RT\varepsilon\varepsilon_0 I)^{1/2}\sinh(z\Psi F/2RT) \tag{1i}$$

is given by the Gouy–Chapmen theory (diffuse double-layer model). Here ε is the relative dielectric constant of water, ε_0 is the permittivity of vacuum, I is the ionic strength of the bulk solution, and z is the valence of the symmetrical background electrolyte. The quantity of surface charge can be computed from the concentration of charged surface species. For Eq. 1g,

$$\sigma = F[\equiv XOM^{(n-1)+}]/AS \tag{1j}$$

where A and S are the specific area (m^2/g) and solid concentration (g/l) of the adsorbent material, respectively. Overall, assuming the total amount of surface sites in Eq. 1g is approximated by $[>XO]_{tot} = [>X(OH)^0] + [>XOM^{n+}]$, one can rearrange Eq. 1h into

$$[>XOM^{n+}] = [>XO]_{tot}\left[\frac{\exp(nF\Psi)K^{int}[M^{(n+1)+}]}{\exp(nF\Psi)K^{int}[M^{(n+1)+}] + [H^+]}\right] \tag{1k}$$

It becomes apparent that, after inspecting Eqs. 1e, 1f, and 1h, the surface complexation approach is advantageous over the empirical isotherms in that the formal provides additional insight into the dependence of adsorption upon pH and ionic strength (through Eq. 1i). Moreover, the

use of K^{int} in surface complexation models makes it possible to compare results from different experiments because, unlike empirical parameters such as K_{ad} (Eq. 1d) and K_f (Eq. 1f), the intrinsic surface complex formation constant is not experimental condition dependent.

It is noteworthy to point out that although surface complexation reactions can occur on any mineral crystals, effective adsorption requires small grain sizes. Because of the inverse relationship between particle size and specific surface area (defined as the ratio of surface area to volume of a particles), small grains ($<1\ \mu m$) tend to have a significant percentage of surface-bound atoms. Consequently, small particles have large numbers of active surface sites available to undergo complexation reactions. Micron-scale suspended particles and sub-micron-scale colloids of minerals are a common occurrence in surface waters and groundwaters (Ref. 5). It is estimated that 80% of the materials transported by rivers and discharged into the oceans is in the form of suspended particles. Although the exogenic cycle of the major cations and anions is controlled by solution process, in most cases the geochemistry of trace elements in natural waters is governed by adsorption on separate mineral grains (6).

DISSOLUTION

Minerals dissolve because the chemical potential of solute in solid and liquid phases has not reached equality, which indicates that the driving force of any dissolution reaction may be estimated by the free energy difference, ΔG, between reactants and products. As the reaction approaches equilibrium conditions where ΔG becomes zero, dissolution should cease to proceed.

Consider the dissolution of a solid compound ML,

$$ML \Leftrightarrow M^{n+} + L^{n-} \tag{2a}$$

The free energy change in this system is described by

$$\Delta G = \Delta G^{o} + RT \ln(a_M a_L) \tag{2b}$$

where ΔG^{o} is the standard free energy change, R is the gas constant, and T is the temperature; a_M and a_L are the activity of aqueous species M^{n+} and L^{n-}, respectively. At equilibrium conditions, $\Delta G = 0$ and Eq. 2b can be rewritten as

$$a_M a_L = \exp(-\Delta G^{o}/RT) \tag{2c}$$

Because ΔG^{o} can be computed as the difference between the standard free energy of formation for the dissolved species and the solid phase, Eq. 2c yields a numerical value defined as the standard equilibrium constant or solubility constant, K_{sp}, of the compound ML.

When the solid–fluid interface is concerned, surface energies and grain sizes have to be taken into account to define the equilibrium conditions. Consider a mineral crystal of any geometry with any number of faces that are not related by any symmetry operations. At constant temperature and pressure, the free energy change in a system containing the crystal in contact with an undersaturated solution can be described by

$$dG = -\sum_i \nu_i \mu_i dn + \sum_j \gamma_j dA_j \tag{3a}$$

where μ_i is the chemical potential of the ith species in the liquid phase; ν_i is the stoichiometric coefficient of the ith species in the solid phase; n is the number of moles of solute that are involved in the dissolution reaction; and γ_j and A_j are the surface free energy and the surface area of the jth type of faces, respectively. Using the definition of chemical potential,

$$\mu_i = \mu_i^{o} + RT \ln \alpha_i \tag{3b}$$

one can rewrite Eq. 3a as

$$\frac{dG}{dn} = -\sum_i \nu_i \mu_i^{o} - RT \ln \prod_i \alpha_i^{\nu_i} + \sum_j \gamma_j (dA_j/dn) \tag{3c}$$

where μ_i^{o} and α_i are the standard chemical potential and the activity of the ith species, respectively. At equilibrium conditions, $dG/dn = 0$, $\sum_i \nu_i \mu_i^{o} = -RT \ln K_{sp}$, it then follows that the crystal solubility $K_b = \prod_i \alpha_i^{\nu_i}$ can be expressed as

$$\ln K_b = \ln K_{sp} + \frac{1}{RT} \sum_j \gamma_j (dA_j/dn) \tag{3d}$$

Equation 3d states that the solubility of a crystal is always greater than the standard solubility product of the solute. Rewrite Eq. 3d using the volume v and density ρ of the crystal and the molecular weight W of the solute, one gets

$$\ln K_b = \ln K_{sp} + \frac{W/\rho}{RT} \sum_j \gamma_j (dA_j/dv) \tag{3e}$$

For isotropic crystals with any characteristic dimension l (i.e., length, width, or height), $\Sigma \gamma_j (dA_j/dv)$ can be approximated by $(2\gamma)/(3l)$ and Eq. 3e can be simplified to

$$\ln K_b = \ln K_{sp} + \frac{2W/\rho}{3RT} (\gamma/l) \tag{3f}$$

Equation 3f is the statement of the classic Gibbs–Thomson relationship, which predicts that the difference between crystal solubility and K_{sp} is size-dependent, and the solubility of any crystals can only be approximated by the standard solubility product of the solute when the crystal is infinitely large. In a practical sense, the "infinite" size is usually no larger than a few micrometers. For anisotropic minerals, each crystal face has to be considered individually because the surface energy is face-specific and Eq. 3e cannot be easily simplified. Nonetheless, the conclusions drawn from Eq. 3f are just as well applicable.

Dissolution not only takes place in the form of dissociation reactions (Eq. 2a), but it can also result from reduction–oxidation reactions where the number

of valence electrons changes on one or more reactant elements. Redox reactions particularly affect water–rock interactions involving minerals that contain multivalence state elements such as S and Fe. However, because of the relatively few minerals concerned, the contribution of redox chemistry to the exogenic cycle of elements is considered auxiliary (7). Most natural redox reactions are mediated by microbial communities or induced by solar radiation. In the formal scenario, oxidized mineral species are often used as electron acceptors for metabolism, whereas in the latter situation, electrons in the reactants' molecular orbital are excited photochemically to pair up with more electrons or to be released to lower the energy state of the system.

Traditionally, geochemists treat redox reactions as reactants' gaining or losing oxygens. The more modern approaches, on the other hand, choose to use electron as a basic component. In this convention, reductants are electron donors that release e^- and oxidants electron acceptors that receive e^-. The activity of electron can be expressed as a potential (Eh, in volts) or as an activity unit ($\mathrm{p}e = -\log a_{e^-}$). Quantitatively, Eh and pe can be converted to each other through

$$\mathrm{p}e = \frac{F}{2.303RT}Eh \tag{4a}$$

where F is the Faraday constant. In addition, Gibbs free energy and the activity of electrons are related by

$$\Delta G = -nFEh \tag{4b}$$

where n is the number of electrons in the reaction. If a redox dissolution reaction can be written as

$$\mathrm{Ox\ (solid)} + ne^- \Leftrightarrow \mathrm{Rd\ (aqueous)} \tag{4c}$$

the standard free energy expression (Eq. 2b) becomes

$$Eh = E^\circ - \frac{RT}{nF}\ln a_{\mathrm{Rd}} \tag{4d}$$

or

$$\mathrm{p}e = \mathrm{p}e^\circ - \frac{1}{n}\log a_{\mathrm{Rd}} = \frac{1}{n}\log K^\circ - \frac{1}{n}\log a_{\mathrm{Rd}} \tag{4e}$$

where E° and pe° are the activity of electrons under standard conditions. Notice that the equilibrium constant of redox reaction K° can still be calculated from the difference between the standard free energy of formation for the dissolved species and the solid phase (i.e., Eq. 2c).

In general, the rate R of dissolution reactions can be related to ΔG by (8)

$$R = k(1 - e^{\Delta G/RT}) \tag{5a}$$

where k is the rate constant. When the reaction is sufficiently close to equilibrium (i.e., $|\Delta G| \ll RT$), Eq. 5a reduces to

$$R = -(k/RT)\Delta G \tag{5b}$$

This expression depicts a linear relationship between the driving force and the kinetics of dissolution reactions at near-equilibrium conditions. When applying Eq. 5b to water–rock interactions, however, caution has to be used because the dissolution of many minerals in aqueous environments is initiated by the formation of etch pits on crystal surfaces. Etch pit nucleation usually requires one to overcome an energy barrier that decreases with descending saturation state (9,10). At very close to equilibrium conditions, the saturation state may be too high to bring down the barrier to the extent that allows pit formation, which indicates that dissolution kinetics may change discretely, rather than in a linear fashion, with decreasing saturation state (11,12).

A unique characteristic of mineral dissolution is that some (alimino)silicate minerals may dissolve in an incongruent or nonstoichiometric manner. This type of reaction is best exemplified by the dissolution process of Na- and K-feldspars in acidic environments. It is generally agreed that the dissolution starts with an initial fast ion exchange of hydrogen ions for alkali and alkaline earth metals, followed by a slow process that disrupt the Si-O-Al-O framework. The disruption seems to proceed by preferential release of aluminum (i.e., nonstoichiometric surface leaching) so SiO_2 accumulates *in situ*. Observations by numerous workers indeed reveal the presence of a Si-rich surface coating on feldspar crystal faces when the minerals are exposed to solutions with pH <3–5 (Ref. 13). What researchers are not in complete agreement on is to what extent the Si-rich layer is originated from surface alteration. Although results from investigations up to the end of the last century imply that most coating (up to several thousand angstroms in depth) forms through nonstoichiometric leaching of the underlying minerals (Ref. 13), recent studies using more modern experimental techniques suggest otherwise. Synchrotron radiation and high-resolution transmission electron microscopy show that the incongruent dissolution may be operative only for, at most, the first few unit cells at the mineral-water interface, and the thick surface alteration thus forms largely by interfacial dissolution–reprecipitation (14,15).

PRECIPITATION

Much of the discussion on reaction driving forces in dissolution section is directly transferable to precipitation reactions. However, precipitation is not a pure mirror image of dissolution in that the former is a combination of two separate but sequentially occurring processes, nucleation and growth. Nucleation refers to the atomic process in which solute components congregate to form a thermodynamically stable cluster, whereas the following accretion of the cluster is termed growth. Both nucleation and growth require the occurrence of supersaturation, but each of the two processes has its unique physiochemical controls.

Homogeneous nucleation occurs when a thermodynamically stable 3-D cluster is born directly from solution. On the other hand, solute particles can assemble onto an existing surface, and hence through heterogeneous nucleation,

to form a stable 2-D cluster. No matter how nucleation takes place, the classic nucleation theory requires the sizes of the clusters to satisfy the following energetics for the atomic assemblage to become stable nuclei: A surface energy increase associated with the emergence of the solid phase precisely offsets the chemical potential decrease in the solution because of losing solute. Mathematically, free energy change upon formation of a spherical cluster of radius r can be expressed as

$$\Delta G = 4\pi r^2 \overline{\gamma} - (4/3\pi r^3/\overline{\mathrm{v}})\Delta\mu \tag{6a}$$

where $\overline{\gamma}$ is the average surface free energy and $\overline{\mathrm{v}}$ is the specific molecular volume of the solid. The minimal size of a stable cluster

$$r_{\mathrm{c}} = 2\overline{\mathrm{v}}\overline{\gamma}/\Delta\mu \tag{6b}$$

can be found by solving the equation $d(\Delta G)/dr = 0$. Any cluster with $r < r_{\mathrm{c}}$ is unstable and will be dissolved, whereas the ones with $r > r_{\mathrm{c}}$ will move on to the growth stage. Inserting Eq. 6b into 6a, one has an expression that estimates the energy barrier, ΔG^*, for nucleation:

$$\Delta G^* = \frac{16\pi\overline{\gamma}^3\overline{\mathrm{v}}^2}{3\Delta\mu} \tag{6c}$$

The nucleation rate R_{n}, according to the conventional rate theory, is then available through

$$R_{\mathrm{n}} = \overline{A}\exp(\frac{-\Delta G^*}{k_B T}) \tag{6d}$$

where k_B is the Boltzmann constant and $\overline{A}$ is a constant related to the efficiency of particle collision (16). All implications from Eqs. 6a–6d apply to heterogeneous nucleation, except that, quantitatively, ΔG^* is usually smaller when nucleation occurs on a substrate surface. This result leads to a general conclusion that heterogeneous nucleation often occurs at a lower supersaturation than does homogeneous nucleation.

Precipitation enters the growth stage with the onset of enlargement of the minimal sized clusters. Nuclei increase their size through attachment of individual solute particles onto the cluster surfaces. During growth, crystallographic control becomes strongly operative. That is, faces that are more closely packed will prevail, whereas the ones with smaller packing density will be phased out. The more closely packed faces usually are the flat face (F-face) on the ideal Kossel crystals (17); the growth of flat surfaces is commonly recognized as following a layer-by-layer mechanism where solute particles attach to kink sites along steps (i.e., the edges of individual layers) generated either by crystal imperfection or surface nucleation. The net rate of step advance, v_s, is determined by the difference between solute fluxes attaching to and detaching from the step kinks. This relationship can be described mathematically by (18,19)

$$v_s = (d^2/\lambda_{\mathrm{o}})\upsilon\{\exp[(\mu_{\mathrm{S}} - \overline{\mathrm{E}})/k_B T] - \exp[(\mu_{\mathrm{L}} - \overline{\mathrm{E}})/k_B T]\} \tag{6e}$$

Here, d is the size of the attaching species in the lattice, λ_{o} is the interlink distance, and υ is the fundamental frequency (20) that can be approximated by $k_B T/h_p$ where h_p is the Planck constants; μ_{L} and μ_{S} are the chemical potentials of solute in liquid (solution) and solid (crystal), respectively, and $\overline{\mathrm{E}}$ is the free energy of an intermediate activated complex.

Equation 6e can be further rearranged into

$$v_s = (d^2/\lambda_{\mathrm{o}})\upsilon\exp[(\mu_{\mathrm{L}} - \overline{\mathrm{E}})/k_B T]\{\exp[(\mu_{\mathrm{S}} - \mu_{\mathrm{L}})/k_B T] - 1\} \tag{6f}$$

Considering that the term $\exp(\mu_{\mathrm{L}} - \overline{\mathrm{E}})$ has an entropy factor, $\exp(\Delta\overline{\mathrm{S}}/k_B)$, and an energy factor, $\exp(-\Delta E/k_B T)$, and that $(\mu_{\mathrm{S}} - \mu_{\mathrm{L}})$ is essentially the driving force for growth and is quantitatively related to supersaturation, σ, by

$$\Delta\mu = k_B T\ln(a/a_e) = k_B T\sigma \tag{6g}$$

one can rewrite Eq. 6f as

$$v_s = \{(d^2/\lambda_{\mathrm{o}})\upsilon\exp(-\Delta\overline{\mathrm{S}}/k_B)\exp(-\Delta E/k_B T)\}/ k_B T]\}\{(a - a_e)/a_e\} \tag{6h}$$

Notice that step velocity has a linear dependence on the difference between solute activity and its equilibrium value $(a - a_e)$. By convention, the quantity between the first two curly parentheses in Eq. 6h is termed the kinetic coefficient, β, of step growth. This parameter, as shown here, is characterized by the activation energy barriers, ΔE, and the corresponding entropic changes for the formation of activated intermediate complexes.

Complementary to the classic approach of atom-by-atom growth, recent findings suggest that crystals can also grow by oriented aggregation of nano-sized clusters (21,22). In this growth mode, adjacent nanocrystallites coagulate after spontaneous self-organization that situates the two parties to a common crystallographic orientation. The new, larger particles gain thermodynamic stability by forming chemical bonding between the original clusters to eliminate the interface between them. It is entirely possible that different growth mechanisms operate at different conditions. When nucleation rates are low and nuclei are far apart in the media, growth may only be accomplished by atom-by-atom attachment on growing surfaces. When sufficient nuclei are present, they can coalesce, through orientated coagulation, to form larger crystals, as long as the system is shifting toward a lower energy state.

It is important to be informed that the kinetics of interfacial reactions such as dissolution and growth can be controlled either by the pace of the actual chemical reactions or the speed at which the reactants and products are delivered to and removed from the reaction sites, or both. To date, it is generally agreed that surface reactions, rather than transport, play a predominant role in controlling the rate of mineral-water interactions. This point of view is supported by the nearly ubiquitous occurrence of etching features on both laboratory dissolved and naturally weathered grains of many minerals. The significance of this understanding is directly reflected by the intensive interests in mineral surface geochemistry that has been growing for more than two decades.

BIBLIOGRAPHY

1. Hochella, M.F., Jr. and White, A.F. (1990). *Rew. Mineral.* **23**: 1–16.
2. Schindler, P.W. and Stumm, W.W. (1987). The surface chemistry of oxides, hydroxides, and oxide minerals. In: *Aquatic Surface Chemistry*. W. Stumm (Ed.). John Wiley & Sons, New York, pp. 83–110.
3. Stumm, W. and Morgan, J.J. (1981). *Aquatic Chemistry*. 2nd Edn. John Wiley & Sons, New York, pp. 600–601.
4. Stumm, W. (1992). *Chemistry of the Solid-Water Interface*. John Wiley & Sons, New York, p. 95.
5. Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice-Hall, Englewood, Cliffs, NJ, p. 344.
6. Morel, F.M.M. and Hering, J.G. (1993). *Principles and Applications of Aquatic Chemistry*. John Wiley & Sons, New York, p. 509.
7. Morel, F.M.M. and Hering, J.G. (1993). *Principles and Applications of Aquatic Chemistry*. John Wiley & Sons, New York, p. 421.
8. Lasaga, A.C. (1998). *Kinetic Theory in the Earth Sciences*. Princeton Univ. Press, Princeton, NJ, p. 188.
9. Frank, F.C. (1951). *Acta Cryst.* **4**: 497–501.
10. Cabrera, N. and Levine, M.M. (1956). *Phil. Mag.* **1**: 450–458.
11. Nagy, K.L. and Lasaga, A.C. (1992). *Geochim. Cosmochim. Acta* **56**: 3093–3111.
12. Lasaga, A.C. and Luttge, A. (2001). *Science* **291**: 2400–2404.
13. Blum, A.E. and Stillings, L. (1995). *Rev. Mineral.* **31**: 291–351.
14. Teng, H.H., Chen, L., Fenter, P.P., and Sturchio, N.C. (2001). *Geochimica et Cosmochimica Acta.* **65**: 3459–3474.
15. Hellmann, R. et al. (2003). *Phys. Chem. Minerals* **30**: 192–197.
16. Stumm, W. (1992). *Chemistry of the Solid-Water Interface*. John Wiley & Sons, New York, p. 216.
17. Kossel, W. (1927). *Nach. Ges. Wiss.*, Gottingen, p. 135.
18. Chernov, A.A. (1961). *Soviet Phys.* **4**: 116–148.
19. Chernov, A.A. and Komatsu, H. (1995). Topics in crystal growth kinetics. In: *Science and Technology of Crystal Growth*. J.P. van Eerden and O.S.L. Bruinsma (Eds.). Kluwer Academic, Amsterdam, pp. 67–80.
20. Lasaga, A.C. (1998). *Kinetic Theory in the Earth Sciences*. Princeton Univ. Press, Princeton, NJ, p. 178.
21. Penn, R.L. and Banfield, J.F. (1998). *Science* **281**: 967–971.
22. Penn, R.L. and Banfield, J.F. (1999). *Geochimica et Cosmochimica Acta.* **63**: 1549–1557.

GROUND WATER: WELLS

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There's a good chance that the average Joe who had to dig a well in ancient Egypt probably did the work with his hands, a shovel, and a bucket. He would have kept digging until he reached the water table and water filled



the bottom of the hole. Some wells are still dug by hand today, but more modern methods are available. It's still a dirty job, though!

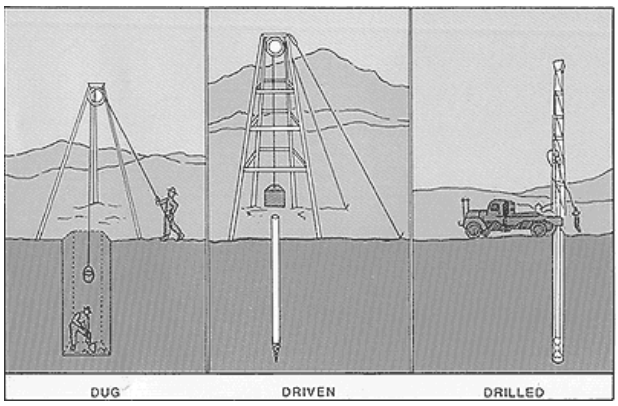
Wells are extremely important to all societies. In many places wells provide a reliable and ample supply of water for home uses, irrigation, and industries. Where surface water is scarce, such as in deserts, people couldn't survive and thrive without ground water.

TYPES OF WELLS

Digging a well by hand is becoming outdated today (would YOU want to do it?). Modern wells are more often drilled by a truck-mounted drill rig. Still, there are many ways to put in a well—here are some of the common methods.

Dug Wells

Hacking at the ground with a pick and shovel is one way to dig a well. If the ground is soft and the water table is shallow, then dug wells can work. They are often lined with stones to prevent them from collapsing. They cannot be dug much deeper than the water table—just as you



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cannot dig a hole very deep when you are at the beach... it keeps filling up with water!

Driven Wells

Driven wells are still common today. They are built by driving a small-diameter pipe into soft earth, such as sand or gravel. A screen is usually attached to the bottom of the pipe to filter out sand and other particles. Problems? They can only tap shallow water, and because the source of the water is so close to the surface, contamination from surface pollutants can occur.

Drilled Wells

Most modern wells are drilled, which requires a fairly complicated and expensive drill rig. Drill rigs are often mounted on big trucks. They use rotary drill bits that chew away at the rock, percussion bits that smash the rock, or, if the ground is soft, large auger bits. Drilled wells can be drilled more than 1,000 feet deep. Often a pump is placed at the bottom to push water up to the surface.

WATER LEVELS IN WELLS

Ground-water users would find life easier if the water level in the aquifer that supplied their well always stayed the same. Seasonal variations in rainfall and the occasional drought affect the "height" of the underground water level. If a well is pumped at a faster rate than the aquifer around it is recharged by precipitation or other underground flow, then water levels around the well can be lowered. The water level in a well can also be lowered if other wells near it are withdrawing too much water. When water levels drop below the levels of the pump intakes, then wells will begin to pump air—they will "go dry."

WELL SCREENS

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A well screen is a fairly generic term that denotes the component of a well that provides (1) an opening for water to enter the well casing from the aquifer; and (2) stabilizes material in the "near-well zone" (i.e., materials immediately adjacent to the well) and prevents it from entering the well.

Proper design of well screens therefore is paramount in successful water wells. Most modern wells are constructed using a filter pack placed between the well screen and the aquifer. In a proper well screen/filter pack design (i.e., gravel envelope well), the fundamental principle is: *The purpose of the filter pack is to stabilize the aquifer; the purpose of the well screen is to stabilize the filter pack*.

A properly designed well screen therefore allows sand-free water to flow into the well with minimum drawdown. Features of a properly designed well screen include:

1. Adequate open area (typically greater than 3–5%) to maximize well efficiency[1]
2. Strong pipe-based well screen (e.g., horizontal louver shutter screen) to provide maximum collapse strength.
3. Constant diameter throughout the entire length of the well screen.
4. Single material type (e.g., all copper-bearing or all stainless steel) to avoid galvanic corrosion from two different metals coming in contact with one another.

Well screens may be constructed with a variety of different materials and designs. The screen material can be different steels, such as carbon, copper-bearing, high strength low-alloy, and stainless, or PVC materials. The type of material used is dependent on the purpose of the well, strength requirements, groundwater quality (corrosion potential), the expected well life, and cost factor. There are many different types of well screens; however, the most commonly used are discussed below.

HORIZONTAL LOUVER SCREENS

Horizontal louver screens are a pipe-based well screen manufactured by punch-formed downward facing horizontal louver-shaped openings (Fig. 1). This type of screen is particularly suited for use in large diameter, deep, gravel envelope wells. The horizontal louver screen can be manufactured in a variety of patterns, with various percentages of open areas. Percentage open areas range from approximately 3.4% to 7.4% for Ful Flo to Super Flo patterns (2). The smooth, unobstructed interior of the horizontal louver screen allows for efficient use of highly effective development techniques such as swabbing and also facilitates employment of efficient maintenance and repair methods. Disadvantages of horizontal louver screen include

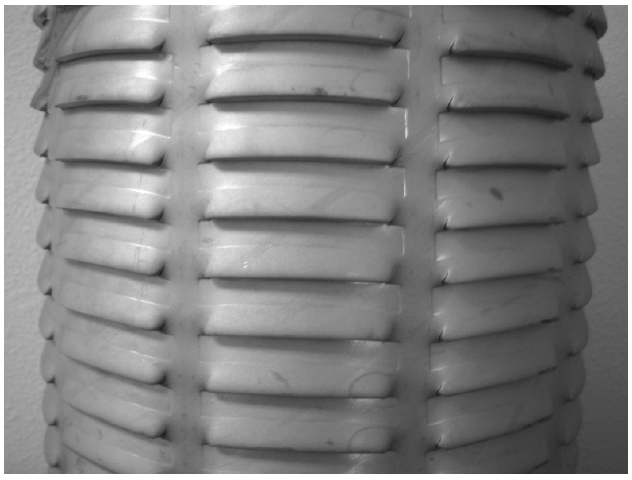


Figure 1. Horizontal louver screen.

[1][It has been demonstrated (1,2) that if the percentage open area is above 3–5%, well efficiencies do not significantly increase. It has also been demonstrated that entrance velocity is not a critical design factor and only needs to be below 0.5 m/s (1.5 ft/s).]

unavailability of slot size smaller than 1 mm (0.040 in.), and difficulty in perforating though thick walled pipe [i.e., greater than 9.5 mm (0.375 in.)]. However, the superior strength capabilities and long-life characteristics have made horizontal louver screens an industry standard in deep high capacity water supply wells.

CONTINUOUS WIRE WRAP SCREEN

Wire wrap screen is manufactured by wrapping a shaped wire (steel or plastic) around an internal array of longitudinal rods (Fig. 2). The wire and rod are joined by resistance welding, which produces a cage-shaped cylindrical configuration. Continuous slot screens are very effective in naturally developed wells in uniform fine-grained sands in relatively shallow, thin aquifers since they are able to be manufactured with very small slot sizes and yet still maintain the necessary open area to minimize frictional head loss. Continuous wire wrap screens typically have open areas greater than 25%. Additionally, the design allows small particles to pass completely through the screen without becoming wedged in and causing clogging of the screen. Disadvantages of the continuous slot screen are associated with its relatively low strength, which necessitates special handling during installation and development, and also restricts the extent of future well maintenance and repair efforts. As the interior is obstructed by rods, the use of highly effective well development techniques such as swabbing is precluded. Should the screen be damaged, repair by swedging is impractical.

BRIDGE SLOT SCREENS

Bridge slot screens are manufactured on a press from flat sheets or plates. The slot opening is usually vertical and provides two orifices, longitudinally aligned to the axis. The perforated steel sheets or plates are then rolled into cylinders and the seam is welded (Fig. 3). A bridge slot screen is usually installed in gravel envelope wells. Its chief advantages are reasonably high area of opening (approximately 4.8%) and minimum frictional head losses at relatively low cost. One important disadvantage is its low collapse strength due to the large number of vertically oriented slots. The manufacturing process is restricted with respect to wall thickness, which is limited to a maximum of 6.35 mm (0.250 in.).

MACHINE-SLOTTED (MILLED) SCREENS

Horizontal and vertical machine-slotted screens are manufactured from casing in which openings are milled with axially oriented precision cutters (Fig. 4). Vertical slotted screens are also manufactured by prepunching flat sheets of steel prior to fabrication into cylinders. Machine-slotted screens have disadvantages that include clogging due to the parallel surfaces within the opening. As slot

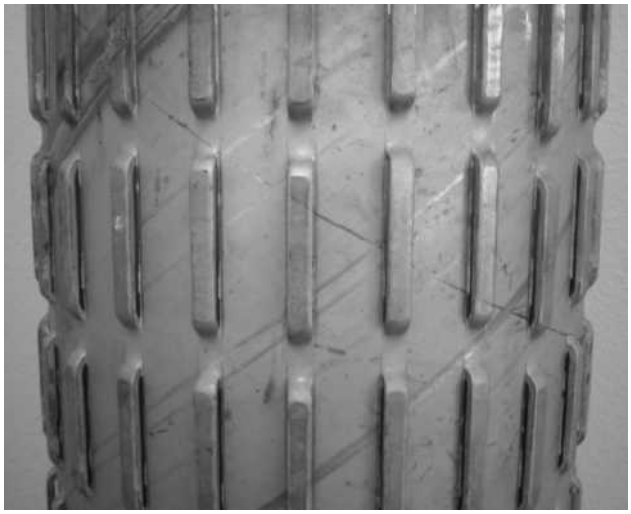


Figure 3. Bridge slot screen.



Figure 2. Continuous wire wrap screen.



Figure 4. Horizontal machine-slotted screen.

clogging is directly related to wall thickness, thicker material encourages greater plugging. Some vertical machine-slotted casings are machined with an undercut to reduce this tendency. A second drawback is the low area of openings (less than 1%), although this can be overcome at higher cost by increasing the number of slots. Collapse strength of vertically machine-slotted casings, however, is substantially reduced when the number of openings is increased. The main positive characteristics of machine-slotted screens are low cost, uniform openings, and availability in a fairly wide range of apertures and patterns.

WELL CASING PERFORATED IN PLACE

Well casing perforated in place has historically been used with cable tool wells drilled in unconsolidated alluvium. Once the casing has been driven or jacked to its total depth, a mills knife (vertical slots) or hydraulic louver-type perforator (horizontal slots) is used down the hole to perforate the casing at specific intervals. The hydraulic louver-type perforator is superior to the mills knife in producing slots due to better physical casing characteristics and more control over the aperture size; in addition, the louver-shaped openings provide greater stabilization of particles in relative fine-grained sand formations. The hydraulic louver-type perforator is limited to a slot size of 3.2–4.0 mm (0.125–0.156 in.). Typically, a well casing perforated in place would have a percentage open area of less than 1%.

The design of the screen slot or aperture size for gravel envelope wells requires the filter pack to be designed first. The screen slot size must result in 90% retention of filter pack material outside the screen.

BIBLIOGRAPHY

1. Williams, D.E. (1985). Modern techniques in well design. *J. AWWA* **77**: 9.
2. Moss, R. (1990). *Handbook of Ground Water Development*. John Wiley & Sons, Hoboken, NJ.

WELL TEST

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A well test is a test conducted in a completed and developed well from which data can be collected to calculate certain hydraulic parameters of the well and surrounding aquifer. Hydraulic parameters may then be used, for example, to design the maximum safe pumping rate of the well, determine well field spacing, calculate aquifer storage, or determine the rate of movement of contaminants in the groundwater. Well tests include pumping tests, recovery tests, and slug tests. Essential measurements and data collected during well tests include time, depth to water, and discharge rate. Obtaining accurate data from a pumping test involves a carefully planned test program, including consideration of continuous operation and execution of the necessary steps.

Step-drawdown tests are generally the first type of test performed on a newly completed production well following final well development. A step-drawdown test involves pumping the well at several discharge rates and measuring the change in depth to pumping level in the well as time progresses (Fig. 1). At least three "discharge steps" are required for the test with subsequent discharge rates increasing over the previous steps. Data obtained from step-drawdown tests are used to determine well production and drawdown characteristics, from which the permanent production pump can be designed. The discharge step rates are determined based on results from the final development pumping. For example, if during final development, the maximum discharge rate reached 2500 gpm with good groundwater level stabilization, then the three rates for the step-drawdown test might be 750, 1500, and 2200 gpm. The discharge rates for a step-drawdown test should be reasonably spread out over the maximum range available for the well (as determined during development).

Following the step-drawdown test, a constant-rate pumping test is usually performed. The purpose of the constant-rate test is to verify the design discharge rate estimated from the step-drawdown test and also to measure longer-term (usually greater than 24 h) drawdown effects on the pumping well and any nearby wells. Data obtained from both the pumping well and nearby wells can be used to calculate aquifer parameters, which can then be used to design spacing between wells, calculate groundwater storage volumes, or determine the rate of movement of groundwater. The discharge rate during the constant-rate test should be kept constant for the entire duration of the test and should be at the design discharge rate for the well (Fig. 2). The design discharge rate may be based on both development pumping and results from the step-drawdown test. The step-drawdown test is seldom performed for a duration sufficient to design the permanent pump and should always be verified with a longer-term constant-rate test. However, the final design pumping rate is still subject to "sound engineering

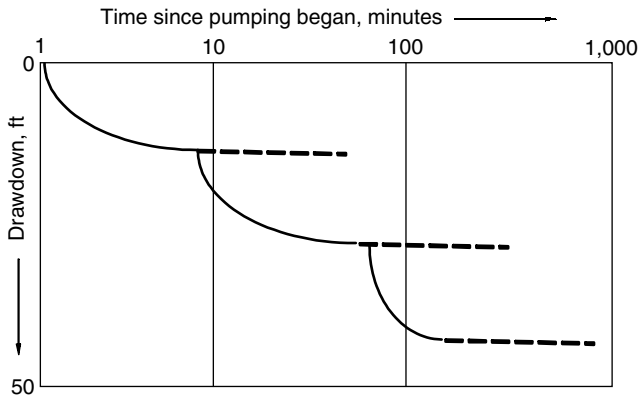


Figure 1. Step-drawdown test data.

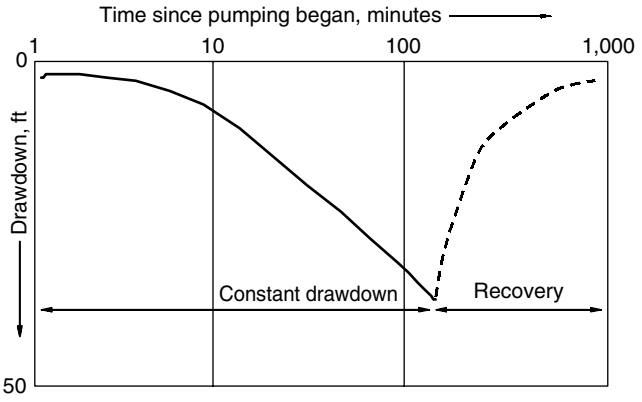


Figure 2. Constant-rate test with recovery data.

judgment" and should consider both demand requirements and pumping test results.

Recovery tests are carried out after pumping tests. The test involves measuring the rate at which the groundwater level recovers to its initial level after pumping has stopped. In general, water level data from recovery tests are more reliable due to the lack of water level fluctuations caused by discharge variations.

A slug test is a popular and inexpensive method of estimating the hydraulic properties of aquifers in small diameter wells when the hydraulic conductivity of the aquifer materials is too low to conduct a pumping test. Slug testing involves either rapidly adding or removing a "slug of water" from a well and measuring the rate at which the water level recovers (either falling-head or rising-head). Disadvantages with this method are that it can only be used to determine the aquifer's hydraulic conductivity in the immediate vicinity of the well, and results can be influenced by filter pack material adjacent to the well screen.

The type of test to be performed depends on the test purpose, available resources, and site-specific limitations. For example, in an area containing only a single well, it is not possible to calculate aquifer storage parameters from a pumping test without an observation well (i.e., nonpumping well). Similarly, observation wells not screened in the same aquifer as the pumping well cannot provide reliable interference data.

Once groundwater level data from the well tests have been collected, compiled, and graphically plotted, the data are evaluated using various methods to determine hydraulic parameters of the aquifer and well. In many cases, the calculation of parameters requires only solving simple equations or a set of equations. For each method there are basic underlying assumptions from which the method equation was derived. These assumptions need to be carefully considered with respect to the test data and specific aquifer conditions when a method is used. In addition to the basic assumptions, each of the analysis methods has other assumptions specific to the method. Many of the analytical solutions are based on the basic differential equation of groundwater flow, which can be derived from fundamental laws of physics.

SAFE YIELD OF AN AQUIFER

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Safe yield is a controversial term and concept that may be defined for common usage as the amount of water an aquifer system can yield over a long period without producing unacceptable effects. Unacceptable effects may include an excessive decline in groundwater level, sometimes described as groundwater mining; reduction or elimination of riparian vegetation; reduction or elimination of water in streams, lakes, springs, and wetlands; aquifer compaction and land subsidence; reduction in groundwater underflow to downgradient aquifer systems; a change in groundwater temperature; an undesirable change in the chemical quality of groundwater; and salt water intrusion into aquifer systems adjacent to oceans or saline lakes.

The definition of safe yield has evolved for nearly a century; initially, it was defined by Lee (1) as "...the limit and quantity of water which can be withdrawn regularly and permanently without dangerous depletion of the storage reserve." The definition was modified and expanded by Meinzer (2), Conkling (3), and Todd (4). Due to ambiguity and lack of agreement on the definition, many authors have suggested abandoning the term (5–7) for an alternate term such as "sustainable yield."

Incorrect concepts, regulations, or laws may indicate that safe yield is equal to recharge. This incorrect concept has been described by Bredehoeft et al. (8) as the "water-budget myth" because the concept oversimplifies the necessary information needed to understand the effects of groundwater development on an aquifer system.

It is a great deal more difficult to define safe yield of an aquifer based on analyzing the unacceptable effects of overpumping than to assume simply that safe yield is equal to recharge. When water is pumped from an aquifer, even in amounts equal to recharge, natural groundwater discharge continues. The initial result of pumping is the decline of groundwater levels near the pumping well, and with time, across larger areas of the aquifer. This water level decline increases the hydraulic gradient and assists in drawing groundwater from marginal parts of the aquifer system into the central part of the aquifer system, but eventually water levels drop sufficiently that natural groundwater discharge becomes smaller. As a result, even by pumping groundwater at rates equal to recharge, a decline in groundwater discharge may occur. This decline in discharge could possibly be defined as unacceptable, and the aquifer may not be in a state of safe yield.

When considering the pragmatic aspects of safe yield, it is important to address the principal elements of the water budget expressed by the law of conservation of mass and the water budget equation:

$$\text{Inflow} = \text{outflow} \pm \text{change in storage}$$

Pumping from an aquifer system over time changes the amount of water in storage and subsequently changes

values of inflow and outflow, thus changing values in the water budget equation. Theis (9) stated that groundwater withdrawals are balanced, over time, by a loss of water somewhere. Groundwater withdrawals by pumping result in one or more of the following: (1) a decrease in the amount of groundwater in storage; (2) capture of previously rejected recharge, if available; (3) an increase in water entering the aquifer system through increased underflow, if available; (4) decreased outflows by way of underflow to downgradient aquifers; or (5) decreased outflow by reduction of discharge to streamflow or to evapotranspiration. The hydraulics of an aquifer system evolve toward, and eventually may approach, a new dynamic equilibrium under increased pumping. An exception may occur in hydraulically isolated, arid environments where little recharge is available. Under these conditions, if pumping exceeds the meager natural recharge, no subsequent equilibrium will be reached and groundwater mining is expected.

Groundwater withdrawal or development of water resources of an aquifer system occurs in stages. These stages include the predevelopment stage, partially developed stage, and fully developed stage. Under natural or predevelopment conditions, an aquifer system is in dynamic equilibrium among change in aquifer storage, groundwater underflow, and interaction between groundwater and surface water. As additional development occurs, water budget values change as a result of an extended period of groundwater pumping. A partially developed aquifer system will see moderate declines in groundwater level and decreases in groundwater in storage; an increase in recharge may occur, and a decrease in natural discharge is expected. Full development of an aquifer system results in a large magnitude of groundwater level decline, additional depletion of groundwater in storage, maximization of recharge, elimination of discharge to surface waters, and underflow to downgradient aquifers may cease.

Safe yield cannot be defined solely on the basis of hydrologic conditions. Hydrologists may describe and quantify the effect of groundwater withdrawals on an aquifer system, but safe yield is properly a determination by a team of natural resource managers, and the results must be acceptable to concerned citizens. It is often difficult to reach consensus on the true safe yield of an aquifer system. Although difficult, the term and concept are the basis of many water management programs and groundwater laws and therefore must be given careful attention.

Wood (10) states, "...scientists and engineers must avoid the trap of blurring the boundary between scientific investigations and management decisions. Neither I nor any other scientist or engineer can say whether any given volume of water or delivery rate meets the needs of anyone beyond the minimum personal requirement of two or three liters per day necessary for long-term survival. 'Meeting the needs' requires many value judgments, and their assessment lies outside the realm of science or engineering. In many ways, sustainability appears to be analogous to the management concept of aquifer 'safe yield' that has been extensively used and misused in the last 85 years."

BIBLIOGRAPHY

1. Lee, C.H. (1915). The determination of safe yield of underground reservoirs of the closed basin type. *Trans. Am. Soc. Civ. Eng.* **78**: 148–251.
2. Meinzer, O.E. (1923). *Outline of Ground-Water Hydrology with Definitions*. U.S. Geological Survey Water-Supply Paper 494.
3. Conkling, H. (1946). Utilization of ground-water storage in stream system development. *Trans. Am. Soc. Civ. Eng.* **3**: 275–305.
4. Todd, D.K. (1959). *Ground Water Hydrology*. John Wiley & Sons, New York.
5. Thomas, H.E. (1951). *The Conservation of Ground Water*. McGraw-Hill, New York.
6. Kazmann, R.G. (1956). Safe yield in ground-water development, reality or illusion? *J. Irrig. Drainage Div. Am. Soc. Civ. Eng.* **82**(IR3): 12.
7. DeWiest, R.J.M. (1965). *Geohydrology*. John Wiley & Sons, New York.
8. Bredehoeft, J.D., Papadopulos, S.S., and Cooper, H.H., Jr. (1982). Groundwater: The water-budget myth. In: *Scientific Basis of Water-Resource Management*. National Academy Press, Washington, DC, pp. 51–57.
9. Theis, C.V. (1940). The source of water derived from wells—essential factors controlling the response of an aquifer to development. *Civ. Eng.* **10**: 277–280.
10. Wood, W. (2001). Water sustainability—science or management. *Ground Water* **39**(5): 641.

SPECIFIC YIELD STORAGE EQUATION

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The specific yield, S_y, is the ratio of the volume of water that can be drained by gravity from a mass of porous rock (unconsolidated or consolidated) and the volume of that mass:

$$S_y = \frac{V_W}{V_T},$$

where V_W is the volume of drainable water and V_T is the total volume of porous rock or sediments (Fig. 1). Specific yield, S_y, is typically expressed as a percentage.

Specific yield is part of the total porosity of a porous rock or sediment. The total porosity (total pore space) of a rock or sediment formation is much larger than the specific yield. Total porosity includes the fraction of pore space that is interconnected (called "effective porosity") and porosity due to isolated pores. The effective porosity itself includes specific retention and specific yield. Specific retention is that volume fraction of water that is held back by adhesion and capillary forces, when an aquifer is drained. Specific yield is the amount of water that is actually available for groundwater pumping, when sediments or rocks are drained due to lowering of the water table.

Specific yield depends on the distribution of pores, their shape, and grain size (Table 1). The larger the surface area of the rocks or sediment particles per unit volume

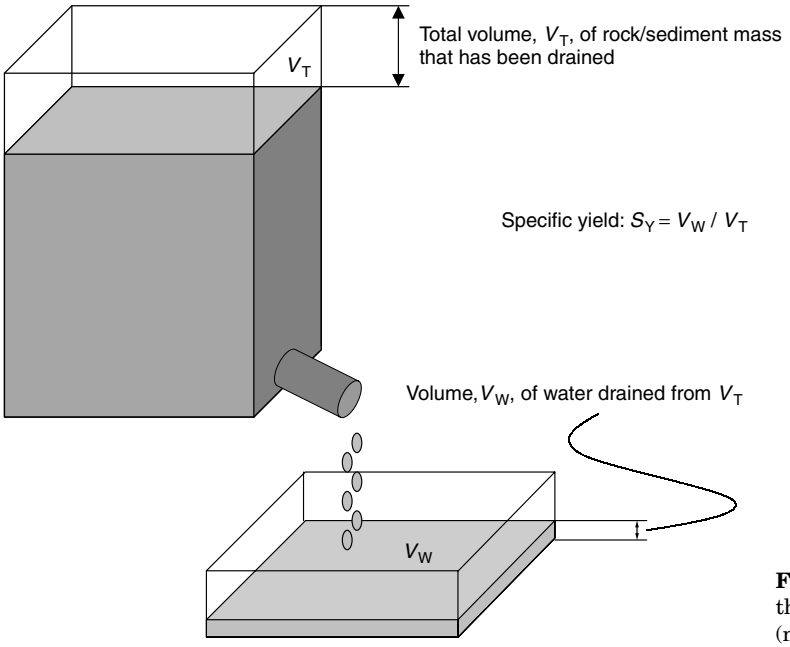


Figure 1. Illustration of the concept of specific yield. Note that the drained volume V_T contains sediment particles (not shown here). The volume V_W is much less then V_T.

("specific surface area"), the more water adheres to these surfaces. This decreases the specific yield in favor of specific retention. Fine-grained sediments have the largest specific surface area, the highest specific retention, and the lowest specific yield. Coarse-grained sediments have a very small specific surface area; hence, the specific retention is small, and the specific yield is large. Specific yield typically decreases with depth due to compaction of sediments.

Clay, silt, and fine sand have relatively high effective porosities, but their specific yields vary widely. The specific yield of clay is often 2% or less, due to its extremely small grain size. In contrast, the specific yield of fine sand can be over 20%. The highest specific yield is obtained in coarse sands and gravels (20–30%), where little water is held back by retention (large pores have only small capillary forces). This makes sand and gravel aquifers good storage reservoirs for groundwater. Peat stands out for its large effective porosity: 90% of its total volume consists of pores, half of which is drainable (specific yield: $\sim$ 45%). These properties (high specific retention and high specific yield) make it a good amendment for garden and potting soil.

Table 1. Specific Yield of Various Sediments and Rocks

Sediment or Porous Rock	Specific Yield, in %,[a]
Gravel, coarse	10–25
Gravel, medium	15–25
Gravel, fine	20–35
Sand, gravelly	20–35
Sand, coarse	20–35
Sand, medium	15–30
Sand, fine	10–30
Silt	1–30
Clay, sandy	3–20
Clay	1–20
Sandstone	10–40
Limestone	1–25
Dune sand	30–40
Loess	15–35
Peat	30–50
Siltstone	1–35
Till	5–20
Tuff	2–35

[a] Compiled by Reference 1.

The specific yield is used to determine how much water can be produced from an unconfined aquifer per a unit (foot, meter) decline in the water table (Fig. 1). An example may illustrate this. A shallow, unconfined sand and gravel aquifer in a small montane basin has an extent of 10 km^2, an average thickness of 10 m, and a specific yield of 20%. Let us assume that there is a drought and the aquifer does not receive any recharge. How much water has been produced from the aquifer, if the water table across the entire aquifer drops by 1 m? The answer: The total volume of aquifer drained is 10 $km^2 \times 1$ m. Then the volume of water obtained is 20% of that volume, or 10 $km^2 \times 0.2$ m.

The same example can be turned around. Let us assume there is no pumping from the aquifer during a 6-month rainy period. During this time, recharge from a river and from precipitation amounts to a total volume of 10 $km^2 \times 0.1$ m or an average of 100 liters/m^2. How much will this raise the water level? With specific yield at 20%, the 100 liters/m^2 recharge will fill an aquifer volume of 100 liters/0.2 = 500 liters/m^2 (0.5 m^3/m^2) in each empty cubic meter of aquifer. Hence, the water level rises by 0.5 m.

Specific yield is measured by a variety of laboratory and field methods, or by estimation from computer models (for recent reviews and applications, see references). The most common field technique is evaluation of well-pumping test data (2,3).

BIBLIOGRAPHY

1. Walton, W.C. (1991). *Principles of Groundwater Engineering*. CRC Press, Boca Raton, FL.

2. Neuman, S.P. (1987). On methods of determining specific yield. *Ground Water* **25**(6): 679–684.
3. Moench, A.F. (1994). Specific yield as determined by type-curve analysis of aquifer-test data. *Ground Water* **32**(6): 949–957.

READING LIST

Frohlich, R.K. and Kelly, W.E. (1988). Estimates of specific yield with the geoelectric resistivity method in glacial aquifers. *J. Hydrol.* **97**(1–4): 33–44.

Grimestad, G. (2002). A reassessment of ground water flow conditions and specific yield at Borden and Cape Cod. *Ground Water* **40**(1): 14–24.

Howle, J.F., Phillips, S.P., Denlinger, R.P., and Metzger, L.F. (1997). *Determination of Specific Yield and Water-Table Changes Using Temporal Microgravity Surveys Collected During the Second Injection Storage and Recovery Test at Lancaster*, Antelope Valley, California, November 1996 through April 1997. U.S. Geological Survey, Water-Resources Investigations Report 03–4019.

Johnson, A.I. (1976). *Specific Yield; Compilation of Specific Yields for Various Materials*. U.S. Geological Survey Water-Supply Paper 1662-D.

Nwankwor, G.I., Cherry, J.A., and Gillham, R.W. (1984). A comparative study of specific yield determinations for a shallow sand aquifer. *Ground Water* **22**(6): 764–772.

Pool, D.R. and Eychaner, J.H., (1995). Measurements of aquifer storage change and specific yield using gravity surveys. *Ground Water* **33**(3): 425–432.

Robson, S.G. (1993). *Techniques for Estimating Specific Yield and Specific Retention from Grain-size Data and Geophysical logs from Clastic Bedrock Aquifers*. U. S. Geological Survey Water-Resources Investigations Report, WRI 93–4198.

Tritscher, P. and Read, W.W. (2000). Specific yield for a two-dimensional flow. *Water Resour. Res.* **36**(6): 1393–1402.

MICROBIAL PROCESSES AFFECTING MONITORED NATURAL ATTENUATION OF CONTAMINANTS IN THE SUBSURFACE

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INTRODUCTION

The EPA Regional Ground Water Forum is a group of EPA professionals representing Regional Superfund and Resource Conservation and Recovery Act (RCRA) Offices, committed to the identification and resolution of ground-water issues impacting the remediation of Superfund and RCRA sites. Innovative technologies for subsurface remediation are being evaluated more often for specific sites, as the limitations to conventional technologies are recognized. The purpose of this Issue Paper is to provide those involved in assessing remediation technologies with some basic information regarding monitored natural attenuation (MNA) processes, specifically in determining overall contribution of microbial processes.

On April 21, 1999, the Office of Solid Waste and Emergency Response (OSWER) issued Directive 9200.4-17P, titled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites." It specifies the current EPA policy regarding the use of MNA for the remediation of contaminated soil and ground water at OSWER sites. The Directive's aim is to promote consistency in the manner in which MNA remedies are proposed, evaluated, and approved. Accordingly, "EPA does not consider MNA to be a presumptive or default remedy—it is merely one option that should be considered with other applicable remedies." Thus, during the process of selecting a site remedy, MNA may be evaluated and compared with other remedial technologies and chosen upon attainment of each relevant remedy selection criteria, including the full protection of human health and the environment, and achieving the intended site remedial objectives within a time frame that is comparable to the other remedial techniques. The Directive expects that "source control and long-term performance monitoring will be fundamental components of any MNA remedy" (U.S. EPA, 1999).

It should be emphasized that this document is not intended to be used in establishing protocol involved in natural attenuation investigations or policies leading to the interpretation of the results of those investigations. To that end, the reader is referred to the EPA Protocol for chlorinated solvents (U.S. EPA, 1998a), and ASTM for petroleum hydrocarbons (ASTM, 1998). EPA is also preparing a guidance for long term monitoring (LTM) for MNA.

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BACKGROUND

Interest in the natural attenuation of ground-water contaminants has increased in recent years as the result of dealing with complexities of subsurface systems and the inherent problems and costs associated with more conventional remedial technologies, such as pump-and-treat systems. There is a growing perception in the environmental community that, under favorable conditions, the selection of natural attenuation as a remedy will result in significant savings in cost over more intrusive remedial alternatives which are exacerbated by the complex geochemical, biochemical, and hydrogeological uncertainties which are dominant

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at most sites. While this perception may or may not be true, depending upon site specific characteristics, like all relatively new technologies, actual cost and performance data will be required as the remediation alternative matures. Natural attenuation, which is also referred to as natural assimilation, intrinsic remediation, intrinsic bioremediation, natural recovery, or passive remediation, is the use of natural processes to remove contaminants from soil or ground water. While the mechanisms of chemical transformation, dispersion, dilution, sorption and volatilization have been identified, aerobic and anaerobic degradation comprise the major processes for the reduction of contaminant mass in the subsurface. Some considerations needed for the evaluation of these processes are depicted in Table 1.

There is little question that naturally occurring biodegradation processes are taking place at many sites where sediments have been contaminated (Davis et al., 1994; Lee, 1988). To those who have examined subsurface sediment, the reduced mineralogy (darkening) and unpleasant odors (anaerobic metabolic products) are indicators of microbial degradation processes. While there are limitations to natural attenuation due to factors such as complex hydrogeology, microbial toxicity of contaminants, and other physical, biological, chemical and environmental factors, many of the organic compounds introduced into the subsurface can be transformed by indigenous microorganisms. The primary challenge in evaluating natural attenuation is not in demonstrating that biodegradation is occurring. This can be a relatively easy task accomplished by determining that the production of metabolites and the loss or electron acceptors are concomitant with the distribution of contaminants. As with any other remedial technology, the appropriate evaluation of natural attenuation as a remedial alternative is to make the determination that the transformation processes are taking place at a rate that is protective of human health and the environment. The evaluation should include a reasonable expectation that these processes will continue at an acceptable rate for an acceptable period of time.

Chlorinated aliphatics are among the most widespread contaminants in ground water (Fig. 1) and soil due to their use for degreasing, dry cleaning, and as solvents (Westrick et al., 1984). At the same time, the impact of petroleum hydrocarbons among the various environmental media is ubiquitous (Tiedje and Stephens, 1988; Sharples, 1992; Kennedy and Hutchins, 1992). Because of their prominence as environmental contaminants, these two groups of chemicals will be used as case examples in this issue paper.

MONITORED NATURAL ATTENUATION MODEL

Contaminants in the subsurface partition into four phases including sorption to the soil and aquifer solids, a free phase which displaces water from the pore spaces, dissolved in the water, and vapor (Fig. 2). The degree to which contaminants partition into these phases is determined by their physical/chemical properties or notably the sorption coefficient, Henry's Law Constant (gas partition coefficient), octanol-water coefficient, and solubility (water partition coefficient). The mass in each phase will therefore depend on the preference of the contaminants of concern for each phase.

Plume movement is dependent on the same partition coefficients, in addition to the hydrology of the site itself. In most instances, chemicals will prefer to partition to organic

Table 1. Some Information Needed for Prediction of Organic Contaminant Movement and Transformation in Ground Water. (Reprinted from *Biotic and Abiotic Transformation of Halogenated Aliphatic Compounds*, T.M. Vogel, Ph.D. Thesis, Stanford University, Stanford, CA, p. 42, 1988, with permission of T.M. Vogel)

BIOLOGICAL	**Ground-Water Characteristics**	**Aquifer Characteristics**	**Contaminant Characteristics**
	ionic strength	grain size	potential products
	pH	active bacteria number	toxicity
	temperature	Monod rate-constants	concentration
	nutrients		
	substrate		
	O_2, NO_{3^-}, $SO_{4^=}$ macro (P, S, N)		
	trace		
	organism		
CHEMICAL	**Ground-Water Characteristics**	**Aquifer Characteristics**	**Contaminant Characteristics**
	ionic strength	potential catalysts metals, clays	potential products
	pH		concentration
	temperature		
	NO_{3^-}, $SO_{4^=}$, O_2		
	toxicants		
HYDRAULIC	**Contaminant Source**	**Wells**	**Hydrogeologic Environment**
	location	location	extent of aquifer and aquitard
	amount	amount	
	rate of release	depth	characteristics of aquifer
		pump rates	hydraulic gradient
			ground-water flow rate
SORPTION	**Distribution Coefficient**	**Characteristics of the Aquifer Solid**	**Contaminant Characteristics**
	characteristic of concentration	organic carbon content	octanol/water partition coefficient
		clay content	solubility

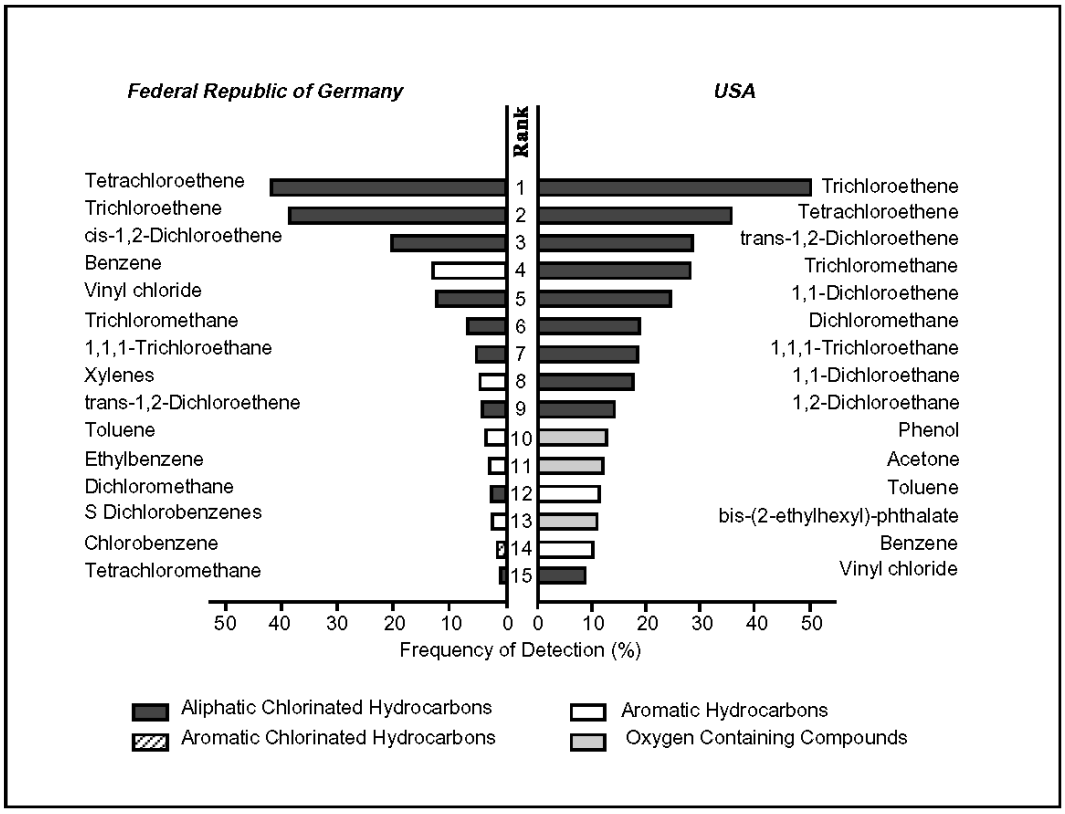


Figure 1. The 15 most frequently detected organic compounds in groundwater at waste disposal sites in Germany and the U.S. (Reprinted from *The Landfill*, Baccini, P., Ed., p. 399, 1989. Arneth, J.-D., Milde, G., Kerndorff, H., and Schleyer, R. with permission of Springer-Verlag. New York, Inc., New York, NY.).

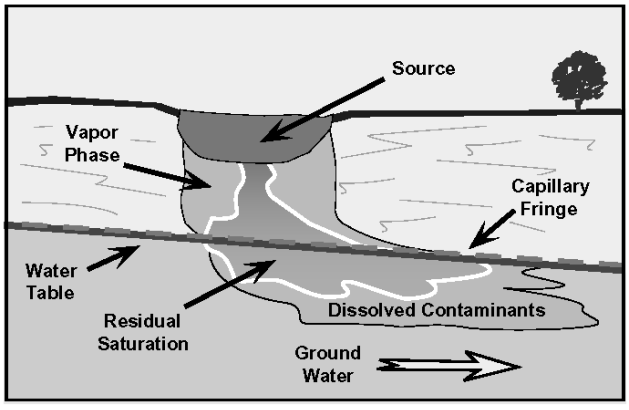


Figure 2. Distribution of contaminants in the subsurface. (Modified from *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*, p. 2, 1993, by Norris et al., EPA/600/R-93/124.).

matter within sediments, to oily or free-phase material that may completely fill pore spaces, or be dissolved in water at solubility levels. The mass of the contaminants in the aqueous phase is usually lower than that in the other phases.

As water moves through pore spaces, chemicals are desorbed from sediments or dissolved from free-phase liquids. Once in solution, these chemicals move with the aqueous phase. Their movement downgradient is impeded by further sorption to sediments and biodegradation. The basis of natural attenuation is that the partition of chemicals into the aqueous phase reaches equilibrium with the processes of biological transformation at an acceptable time and distance from the source. To understand these biological processes, some knowledge of microbiology is required.

MICROBIAL PHYSIOLOGY

Bacteria, although unicellular, share characteristics with most living things. Information is encoded in DNA (deoxyribonucleic acid) and transferred through RNA (ribonucleic acid) to ribosomes to make proteins or enzymes which are used to operate systems within the organism. In regard to this discussion, enzymes are responsible for the degradation of organic carbon, which is used by the bacterial cell to produce both the building blocks of life and energy. The degradation of any organic molecule, including contaminants, requires the production and efficient utilization of enzymes. In most instances, degradation is merely a complex oxidation/reduction reaction. The electrons or reducing equivalents (hydrogen or electron-transferring molecules) produced must be transferred to a terminal electron acceptor (TEA). During the transfer process, energy is produced which is utilized by the cell.

In regard to TEAs, bacteria are generally grouped into three categories:

1. *Aerobic bacteria*—Bacteria which can only utilize molecular oxygen as a TEA. Without molecular oxygen, these bacteria are not capable of degradation.
2. *Facultative aerobes/anaerobes*—Bacteria which can utilize molecular oxygen or when oxygen concentrations are low or nonexistent, may switch to nitrate, manganese oxides or iron oxides as electron acceptors.
3. *Anaerobes*—Bacteria which cannot utilize oxygen as an electron acceptor and for which oxygen is toxic. Though members may utilize nitrate or other electron acceptors, it can be said that they generally utilize sulfate or carbon dioxide as electron acceptors.

In this discussion, three modes of contaminant degradation are addressed including aerobic, cometabolic, and anaerobic. The first is the case in which the contaminants, for example, petroleum hydrocarbons, are utilized by bacteria as a sole source of carbon. Petroleum hydrocarbons are degraded through a series of enzymatic reactions to produce needed cellular constituents. Electrons or reducing equivalents must be regenerated. If a contaminant serves as a sole source of carbon and energy, conditions must be within acceptable pH, Eh, and temperature limits and the appropriate TEA must be present. In this case, the rate of degradation will be determined by the rate of dissolution of toxic end products away from the microbial population and the rate at which the TEA is replenished. Some of the lesser chlorinated solvents, such as dichloroethene (DCE), may also serve as sole sources of carbon; however, tetrachloroethene (PCE) and trichloroethene (TCE) are not thought to serve as sole sources of carbon.

In the case of TCE (and lesser chlorinated solvents), degradation may occur through cometabolic processes. Under aerobic conditions, the enzymes necessary for the degradation, however, must be induced. Inducible enzymes are those that are not produced unless an inducer compound is present within the bacterial cell. Pertinent to this discussion are the inducers for methane monooxygenase and various mono- and dioxygenase enzymes produced by aromatic degrading bacteria.

In the presence of oxygen and methane, methanotrophic bacteria are known to produce the enzyme methane monooxygenase (Hanson and Hanson, 1996; Patel et al., 1982). The substrate for this enzyme is methane, but it has been shown to have a broad substrate specificity including chlorinated solvents (Mayer et al., 1988). Methanotrophs downgradient from a chlorinated solvent event may feed on methane produced within the anaerobic portion of the plume and cometabolically degrade some chlorinated solvents.

Numerous authors have shown that oxygenase enzymes produced by bacteria capable of degrading aromatic hydrocarbons are capable of degrading chlorinated solvents. Aromatic compounds, such as toluene and phenol, have been shown to induce the responsible enzymes. In contaminated aquifers which contain both aromatic hydrocarbons and chlorinated solvents, degradation of both may occur.

It should be noted that reports on the degradation of PCE under aerobic conditions do not exist in the peer-reviewed literature. The structure and oxidative state of PCE may preclude its aerobic degradation (Chen et al., 1996). The anaerobic process for degradation of chlorinated solvents is known as reductive dechlorination (Bouwer et al., 1981; Bouwer, 1994). Chlorinated solvents are not utilized as a carbon source, rather as an acceptor for electrons produced during the metabolism of other oxidizable carbon (electron donor). Thus, this process cannot be termed cometabolism. Electrons or reducing equivalents formed during metabolism are accepted by the chlorinated solvent. As an example, PCE will accept electrons or reducing equivalents formed during metabolism. This results in the reduction of PCE, the concomitant release of a chloride ion and the formation of TCE. While almost any degradable carbon appears capable of driving reductive dechlorination, in most instances, a low percentage of the electrons or reducing equivalents are utilized in the reductive process. This is a function of other metabolic requirements for reducing equivalents (substrate specific) and the presence or absence of more suitable TEAs.

The behavior of the chlorinated solvent plumes can be classified into three types based on their primary substrate source (U.S. EPA, 1998a).

- *Type 1 Behavior*—Primary substrate is adequate amount of anthropogenic organic carbon, solvent plume degrades
- *Type 2 Behavior*—Primary substrate is adequate amount of native organic carbon, solvent plume degrades
- *Type 3 Behavior*—Low native organic carbon concentrations or low anthropogenic organic carbon concentrations, PCE, TCE, and DCE do not degrade

For complete detoxification, the parent chlorinated solvent must be dechlorinated in a stepwise fashion to the environmentally benign ethene. This is illustrated in Fig. 3. While PCE and TCE are readily reduced as a result of their oxidative states, the more reduced daughter products (DCE and VC) are less prone to reductive processes. These intermediates tend to accumulate in anaerobic aquifers where contaminants are allowed to naturally attenuate (Lesage et al., 1990). While this may indeed be a function of the oxidative state of the lesser-chlorinated compounds, it may also be a function of the concentration of degradable organic matter within the contaminated system.

The efficacy of an anaerobic microbial population for natural degradation of chlorinated solvents is determined by the same environmental factors as for the other systems (i.e., pH, Eh, temperature, osmotic potential), the presence of a carbon source which can be readily degraded (electron donor), and a TEA other than chlorinated solvents (Vogel et al., 1987). In addition to organic carbon and a TEA, bacteria require macro- and micronutrients, most notably nitrogen and phosphorous, for the production of DNA, RNA

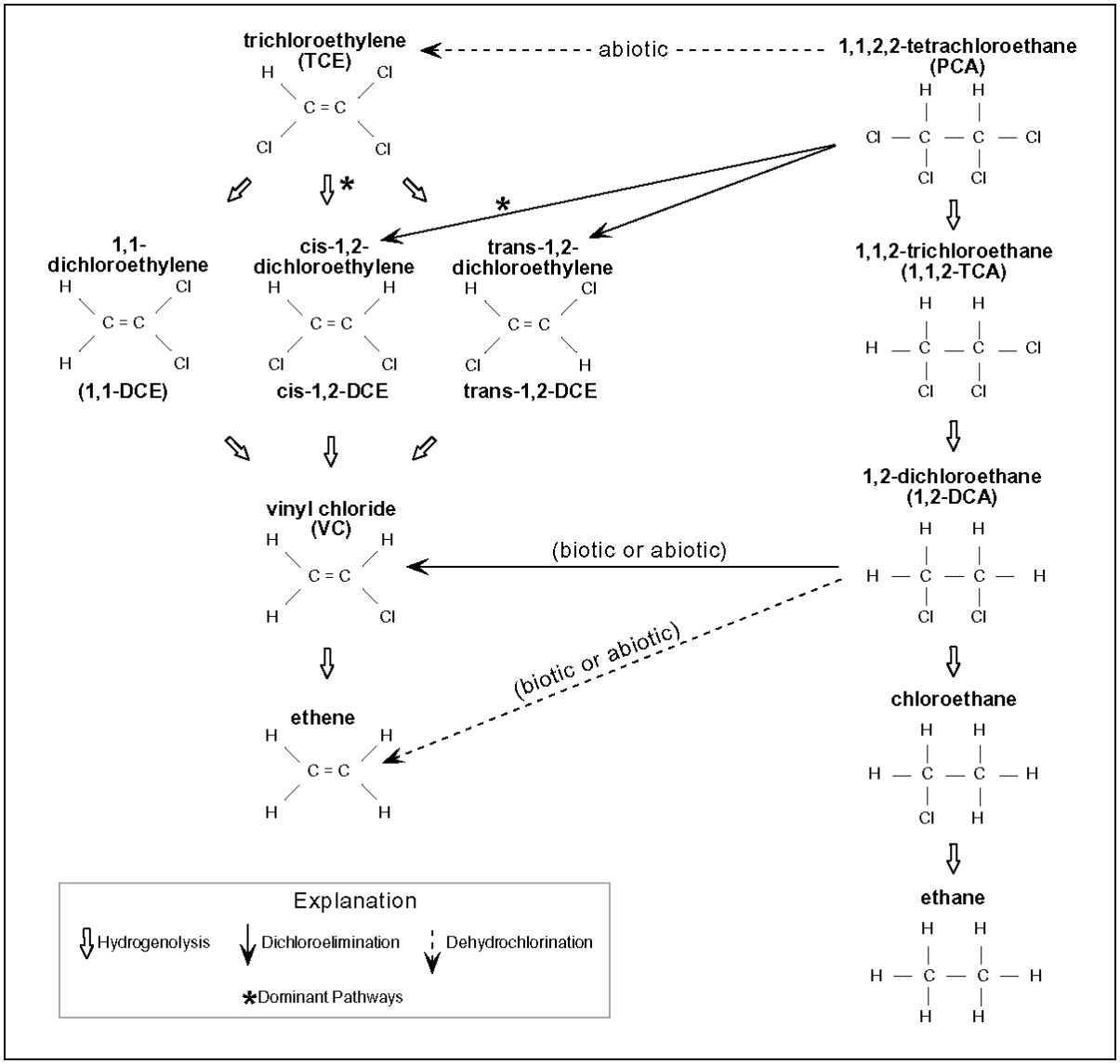


Figure 3. Anaerobic degradation pathways for trichloroethylene and 1,1,2,2-tetrachloroethane. (Modified from Chen et al., 1996; McCarty, 1996; Nyer and Duffin, 1997; and Vogel et al., 1987.).

and other needed cellular constituents. In most instances within an aquifer, sufficient macro- and micronutrients will be available for microbial processes. On the other hand, the availability of organic carbon can often be the limiting factor in the continuance of these processes. For example, during the reductive dechlorination of chlorinated solvents, the ratio of the mass of the electron donor to that of the contaminant ranges between 100/1 and 1000/1 (Bouwer, 1994).

MECHANISMS OF BIODEGRADATION

In theory, in any environment in which microbial activity occurs, there is a progression from aerobic to anaerobic (methanogenic) conditions. There is a definite sequence of electron acceptors used in this progression through distinctly different redox states (Fig. 4).

The rate, type of active microbial population, and level of activity under each of these environments are controlled by several factors. These include the concentration of the electron acceptors, substrates which can be utilized by the bacteria, and specific microbial populations leading to the progression of an aquifer from aerobic to methanogenic conditions (Salanitro, 1993). This results in a loss of organic carbon and various electron acceptors from the system as well as a progression in the types and physiological activity of the indigenous bacteria.

If microbial activity is high, the aquifer environment would be expected to progress rapidly through these conditions. The following scenario outlines a general sequence of events in which aerobic metabolism of preferential carbon sources would occur first. The carbon source may be contaminants of interest or other more readily degradable carbon which has entered

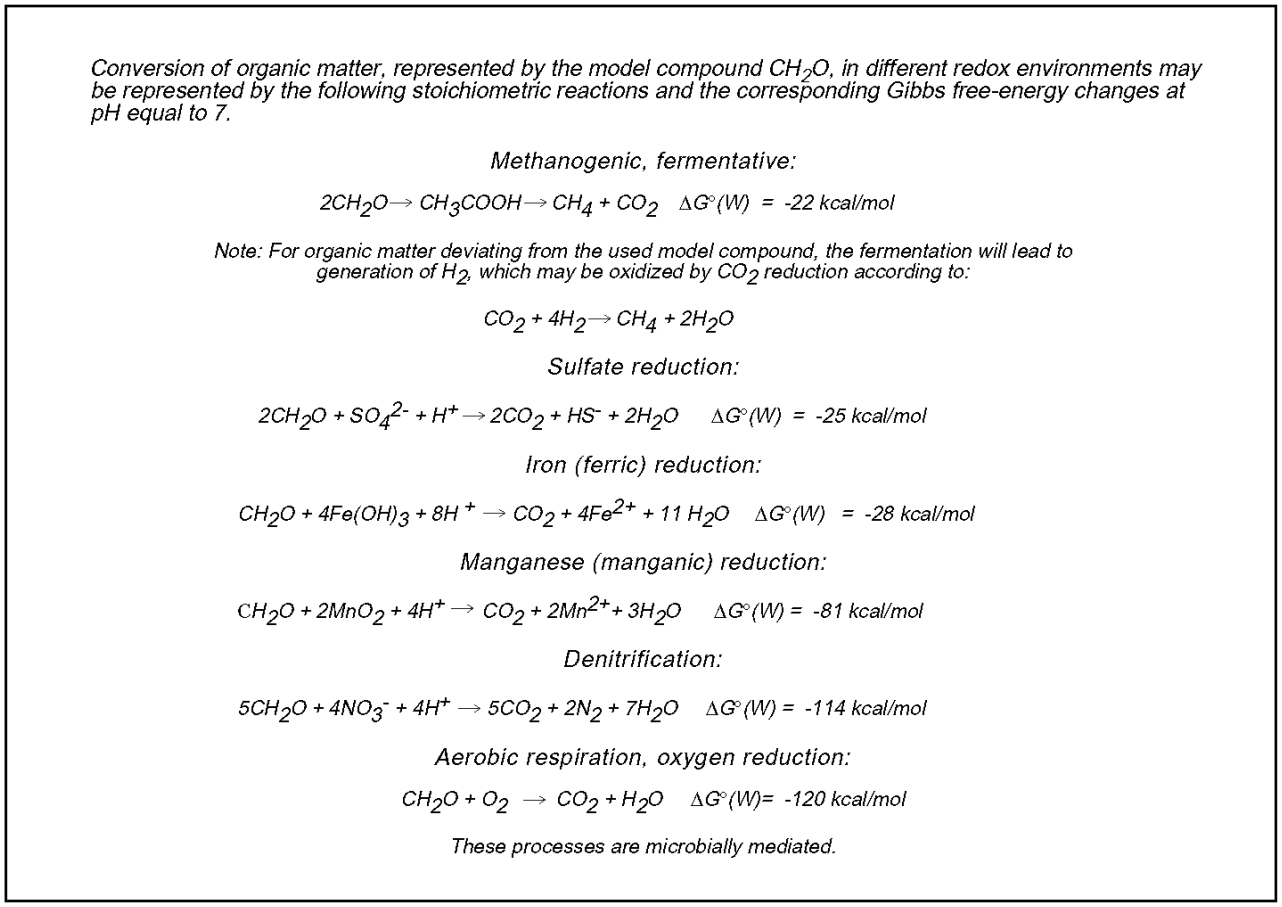


Figure 4. Examples of redox reactions involved in degradation of organic matter (expressed as the model compound CH_2O) in different redox environments. (Reprinted from *Attenuation of Landfill Leachate Pollutants in Aquifers*, box 1, p. 138, 1994, by Christensen, T.H., P. Kieldsen. H-J. Albrechtsen, G. Heron, P.H. Nielsen, P.L. Bjerg, and P.E. Holm, with permission of CRC Press, Inc., Boca Raton, FL.).

the system previously or simultaneously with the contamination event.

Oxygen-Reducing to Nitrate-Reducing Conditions

Once available oxygen is consumed, active aerobic populations begin to shift to nitrate respiration. Denitrification will continue until available nitrate is depleted, or usable carbon sources become limiting.

Nitrate-Reducing to Manganese-Reducing Conditions

Once nitrate is depleted, populations which reduce manganese may become active. Bacterial metabolism of substrates utilized by manganese-reducing populations will continue until the concentration of manganese oxide becomes limiting.

Manganese-Reducing to Iron-Reducing Conditions

When manganese oxide becomes limiting, iron reduction becomes the predominant reaction mechanism. Available evidence suggests that iron reduction does not occur until all manganese IV oxides are depleted. In addition, bacterial Mn(IV) respiration appears to be restricted to areas where sulfate is nearly or completely absent.

Iron-Reducing to Sulfate-Reducing Conditions

Iron reduction continues until substrate or carbon limitations allow sulfate-reducing bacteria to become active. Sulfate-reducing bacteria then dominate until usable carbon or sulfate limitations impede their activity.

Sulfate-Reducing to Methanogenic Conditions

Once usable carbon or sulfate limitations occur, methanogenic bacteria are able to dominate.

The ambient redox condition of the aquifer is important when determining the contribution of microbial degradation to MNA mechanisms. In the case of petroleum hydrocarbons, because of their highly reduced condition, the preferred TEA for microbial processes would be oxygen (Brown et al., 1996; Clark et al., 1997). From a thermodynamic standpoint, this is the most favorable reaction mechanism. When the soluble portion of petroleum hydrocarbons, BTEX (benzene, toluene, ethylbenzene, xylenes), are the contaminants of concern, an inverse relationship between BTEX and dissolved oxygen concentrations

within a plume is indicative of the microbial metabolism of these compounds as well as other hydrocarbons in the mixture (Donaldson et al., 1992; Huesemann and Truex, 1996). Data available from various sites indicate that the natural attenuation of BTEX proceeds at higher rates under oxic conditions than normally achieved in anoxic environments (Fig. 5), with rate constants ranging from 0.3 to 1.3 percent per day when modeled as a first-order process (Chiang et al., 1989; Kemblowski et al., 1987; Salanitro, 1992; and McAllister and Chiang, 1994). Although anaerobic biodegradation of toluene and xylene under nitrate-reducing (Barbaro et al., 1992; Schocher et al., 1991), iron-reducing (Lovley et al., 1989; Lovley and Lonergan, 1990), sulfate-reducing (Beller et al., 1992a and b; Edwards and Grbić-Galić, 1992; Rabus et al., 1993), and methanogenic (Vogel and Grbić-Galić, 1986; Bouwer and McCarty, 1983; Edwards and Grbić-Galić, 1994) conditions have been extensively reported. Until recently, unequivocal biodegradation of benzene under strict anaerobiosis was not demonstrated (Edwards and Grbić-Galić, 1992; Lovley et al., 1994). According to Borden et al. (1997), even though accurate description of anaerobic biodegradation of individual BTEX constituents may not follow a simple first-order decay function, biodegradation of total BTEX seems to more closely approximate a first-order decay function.

Biodegradation of chlorinated solvents, depending on the degree of halogenation (Fig. 6), is fundamentally different from that of petroleum hydrocarbons and other oxidized chemicals (Wiedemeier et al., 1995). The preferred redox conditions for the effective degradation of these chemicals is anaerobic (exception is vinyl chloride, VC). Effective degradation of these compounds may occur only when redox conditions are below nitrate reducing.

Although under aerobic conditions, cometabolism of TCE by autotrophic bacterial populations, obtained from soil and ground water, have been demonstrated, it is generally accepted that this route of removal is limited only to low concentrations of TCE. The cometabolism of TCE proceeds in the presence of methane (Fogel et al., 1986; Henson et al., 1988; Wilson and Wilson, 1985), ammonia (Arciero et al., 1989), or toluene (Ensley, 1991; Mu and Scow, 1994; McCarty and Semprini, 1994) as cosubstrate. Due to the inherent toxicity of TCE to microorganisms responsible for degradative process (Alvarez-Cohen and McCarty, 1991a; Broholm et al., 1990), and because of the competitive inhibition between

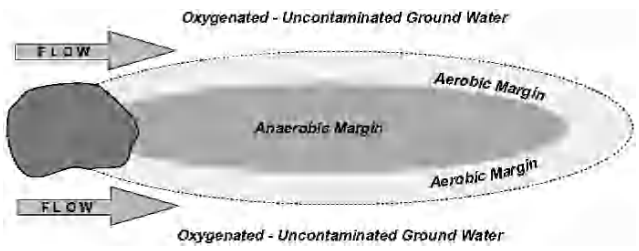


Figure 5. Plan view of a typical hydrocarbon plume undergoing natural attenuation. (Modified from *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*, p. 9-8, 1993, by Norris et al., EPA/600/R-93/124.).

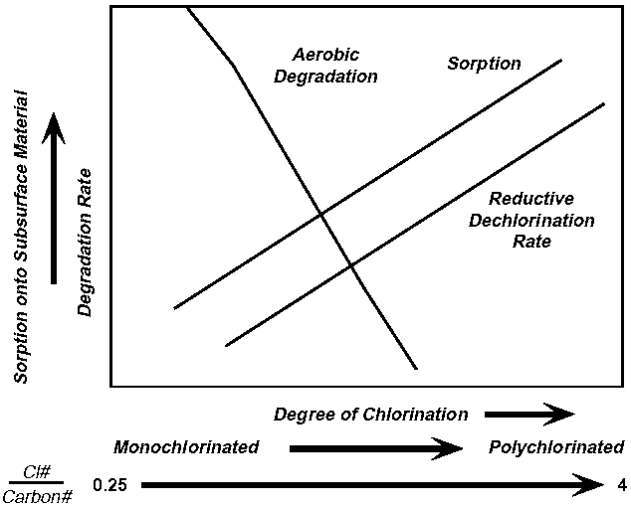


Figure 6. Relationships between degree of chlorination and anaerobic reductive dechlorination, aerobic degradation and sorption onto subsurface material. (Reprinted from *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*, p. 10–19, 1993, by Norris et al., EPA/600/R-93/124.).

a cosubstrate and the secondary substrate for oxygenase enzymes (Alvarez-Cohen and McCarty, 1991b; Hopkins et al., 1993), special attention to concentrations of TCE and its cosubstrate is warranted. Toxic or inhibitory effects of TCE are more serious than those of 1,1,1-TCA (Broholm et al., 1990).

Microcosm studies involving anaerobic biotransformation of PCE/TCE from environmental samples including sediments (Parsons et al., 1984), ground water (Wilson et al., 1983; Sewell and Gibson, 1991), and soil (Kleopfer et al., 1985) have been documented. Also, the reductive dechlorination of PCE and other chlorinated compounds under methanogenic conditions has been reported (Vogel and McCarty, 1985 and 1987b; Vogel et al., 1987; Freedman and Gossett, 1989; McCarty, 1988). Bagley and Gossett (1990) suggested that the ability of sulfate-reducing enrichment cultures for PCE dechlorination is apparently less than that of mixed methanogenic cultures. The main by-product of anaerobic biodegradation of chlorinated ethene is VC which is more toxic than the parent compounds PCE, TCE, and DCE (Chu and Jewell, 1993). It is noted that anaerobic reduction of VC to ethylene is a slow and inefficient process (Freedman and Gossett, 1989). Gantzer and Wackett (1991) determined that dechlorination of chlorinated ethenes proceed via first-order rate constants.

The oxidation-reduction (redox) potential is a relatively simple and inexpensive indicator of the redox state of an aquifer. If the redox is positive, one can assume that dissolved oxygen is present and the system has not been stressed by biological activity (Borden et al., 1995). If the redox potential is significantly negative, it can be assumed that processes favored under aerobic conditions, such as BTEX degradation, are occurring at a substantially reduced rate. Figure 7 suggests that the redox should be −400 mV or less and the dissolved oxygen should be below

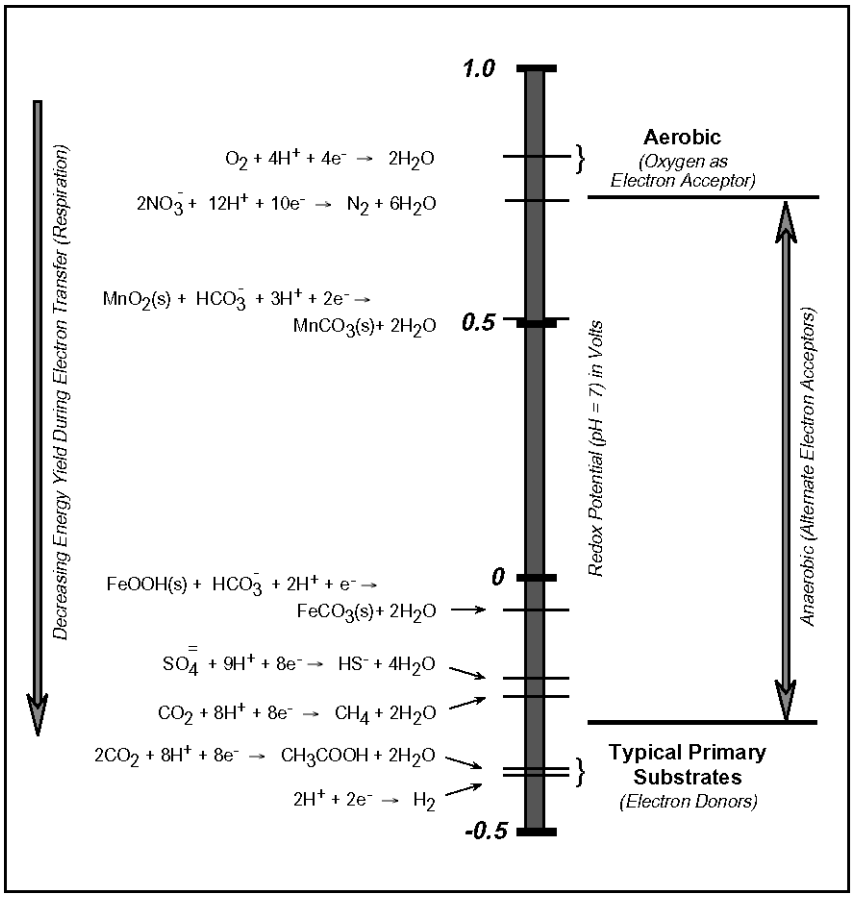


Figure 7. Important electron donors and acceptors in biotransformation processes. Redox potentials data were obtained from Stumm and Morgan (1981). (Modified from *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*, p. 8-3, 1993, by Norris et al., EPA/600/R-93/124.).

0.25 mg/l before anaerobic microbial reactions could take place for the more highly chlorinated compounds (i.e., PCE, PCA). It should be stressed that one normally does not attempt to determine the actual redox conditions for comparison between different sites, rather the differences between points within a plume. Furthermore, due to the lack of internal equilibrium (Morris and Stumm, 1967) and the mixed Eh potentials of natural aqueous systems, the use of any measured master Eh as an input in equilibrium hydrogeochemical model for predicting the equilibrium chemistry of redox reactions is misleading. Instead, measuring certain sensitive species such as oxygen, Fe(II), hydrogen sulfide, or methane as qualitative guides to the redox status of the water may generate better results (Lindberg and Runnells, 1984).

In anoxic waters, where low pH and Eh exist, the reduced form of manganese, Mn(II) is favored (Stumm and Morgan, 1981). Reduction of Fe(III) and Mn(IV), due to chemical processes or microbial metabolic reactions that couple the oxidation of organic matters to the reduction of these chemical species, has a major influence on the distribution of Fe(II) and Mn(IV) in aquatic sediments, submerged soil, and ground waters (Stone and Morgan, 1984; Burdige and Nealson, 1986; Ehrlich, 1987; DiRuggiero and Gounot, 1990; Lovley, 1991). Thus, measurable Fe(II) or Mn(II) may indicate suboxic conditions in the absence of detectable oxygen concentration (Higgo et al., 1996).

In addition to establishing background conditions away from the plume, dissolved oxygen, nitrate, manganese, iron, sulfate, and sulfide should be measured along the axis of the plume, as well as transverse to it, in order to characterize biological activity with respect to the redox state at those locations. This information will allow an estimation of the current redox state at various parts of the contaminated plume, thereby defining the types of reactions that may take place.

The rate of change in the concentration of these parameters can be useful as input to predictive models. This set of data will also characterize the abundance of the principal electron acceptors, oxygen, nitrate, and sulfate, to allow an estimate of how long natural attenuation will remain a viable remedial alternative.

Another approach that may be used to indicate the terminal electron acceptor process (TEAP) predominant in the areas of contamination is the hydrogen (H_2) concentration (Lovley and Goodwin, 1988). Hydrogen concentrations for the various terminal electron acceptors are shown in Table 2 (Chapelle et al., 1995).

Parameters that investigators should analyze for petroleum hydrocarbons include dissolved oxygen, nitrate, Fe(II), sulfate, redox potential, pH, Mn(IV), dissolved methane, and total petroleum hydrocarbons (ASTM, 1998). The majority of these parameters can be determined using field measurements, Hach™ kits, and/or CHEMetrics™ test kits. Since methane is produced after other TEAs

Table 2. Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process. (Data from Chapelle et al., 1995)

Terminal Electron Accepting Process	Hydrogen (H_2) Concentration (nanomoles per liter)
Denitrification	<0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Methanogenesis	5–20

(nitrate, iron, sulfate) are depleted, dissolved methane data is superior to contaminant data (Underground Storage Tank Technology Update, 1998). The parameters for chlorinated solvents may include: temperature, redox potential, DO, sulfide, Fe(II), methane, ethane/ethene, alkalinity, pH, sulfate, nitrate, chloride, dissolved organic carbon, and hydrogen. Since Fe(III) may be dissolved from aquifer matrix, Fe(II) is measured as proxy for biodegradation due to iron reduction. Although there may be a correlation between sediment redness and the hematite content of soil, when a soil sample represents a mixture of several iron species, the color is not a useful indicator (Heron et al., 1994).

The microbial activities of a site are thus determined by the dissolved organic carbon, presence of macro- and micronutrients and the TEA (Semprini et al., 1995). The presence and concentration of each will determine not only the activity, but the predominant population.

Different levels of QA/QC may be required for those analyses determined in the field versus those performed under laboratory conditions (U.S. EPA, 1996; Klusman, 1980; Shampine et al., 1992; Koterba et al., 1996). For example, dissolved iron and oxygen, redox, and temperature must be determined on-site (Shelton, 1994; Wood, 1981) using field test kits because of the deterioration that would normally occur between the time of sample collection and that of arrival at the laboratory. On the other hand, parameters such as metals, organics (Shelton and Capel, 1994; Fishman and Friedman, 1985), and bacteria can be properly preserved by cooling, capping, or chemical fixation, and thereby subjected to a higher level of QA/QC.

FACTORS AFFECTING THE DEMONSTRATION OF NATURAL ATTENUATION

Hydrogeology

State and federal agencies are increasingly relying on risk based corrective action (RBCA) and/or MNA for cleanup of contaminated sites (Brady et al., 1998). The American Society for Testing and Materials released on RBCA protocol two years ago (ASTM, 1998) and recently finalized an MNA protocol. The U.S. EPA has recently published a directive on MNA (U.S. EPA, 1999) and a protocol for chlorinated solvents (U.S. EPA, 1998a). Since RBCA and MNA incorporate no safety factors to reduce contaminant concentrations compared to active remediation technologies, these strategies rely solely on accurate and high quality hydrogeological site characterizations (Boulding, 1993a and b; U.S. EPA, 1997a) to demonstrate adequate public protection.

Adequate monitoring is one of the most important facets of proving that natural bioremediation is occurring in the subsurface. Many factors other than natural attenuation or bioremediation can have an effect on the observed concentration of contaminants at a monitoring well (Black and Hall, 1984). The infiltrating precipitation into a system may have a profound effect on contaminant concentrations, especially if the contaminants are light nonaqueous phase liquids (LNAPLs) such as petroleum hydrocarbons (Kemblowski and Chiang, 1990; Lenhard and Parker, 1990). High rates of infiltration may lower the apparent concentration of contaminants due to dilution. Pettyjohn (1982) has shown that there are actually two time periods after a precipitation event when dilution may have an effect on monitoring. The first is a few hours after a precipitation event where flow is through macropores or "wormholes" to the water table, and the second is a few days after with flow through the vadose zone. The time required for both of these events to occur will be a function of the number and size of the macropores, overall permeability of the unsaturated zone and depth to the water table. Monitoring during these events can result in an apparent decrease in the concentration of contaminants by dilution, or if contaminants are present in the vadose zone, an increase in concentrations due to their infiltration. Seasonal variations may also occur in flow paths within an aquifer (Schmidt, 1977). These variations may cause an apparent increase or decrease in concentration of contaminants due to dilution or plume movement. Although dilution is considered to be a part of natural attenuation, this reduction in concentration should not be attributed to degradation.

A major problem with monitoring wells is that a sample from the uncontaminated portion of the aquifer may be a composite of contaminated water from the plume drawn into the cone of depression along with clean water from the aquifer. This will result in an apparent increase in contamination. The reverse is also often possible if the monitoring well is pumped for an extended period prior to sampling, the amount of clean water coming into the well in relation to contaminated water will result in an apparent decrease in the concentration of the contaminants of interest. These problems are often exacerbated by using well screens that are too long (greater than 2 meters), inconsistent screened intervals, and inappropriate sampling methods (Church and Granato, 1996).

Pumping wells other than those designed for monitoring (such as those in an interdiction field, or water supply wells for municipalities or irrigation) may influence the movement of a plume as well as flow lines within an aquifer. Depending on when these wells were designed and constructed, how they are pumped, and how they affect plume movement, apparent decreases in concentration may be observed in monitoring wells (Martin-Hayden and Robbins, 1997; Martin-Hayden et al., 1991; Robbins, 1989; Robbins and Martin-Hayden, 1991).

Monitoring programs should be designed such that these concerns are taken into account (Zeeb et al., 1999).

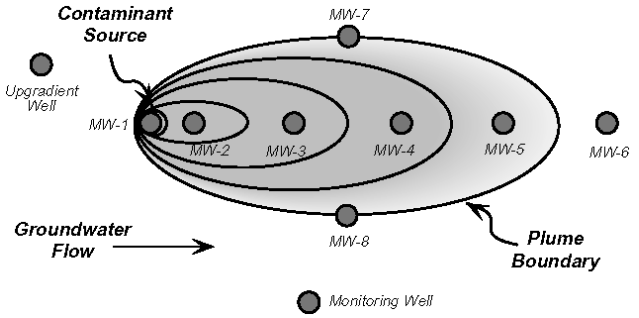


Figure 8. Recommended groundwater monitoring well network for demonstrating natural attenuation. (Reprinted from *A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water*, p. 166, 1994, by P.M. McAllister and C.Y. Chlang. Reprinted by permission of *Ground Water Monitoring & Remediation*, Westerville, OH, Copyright 1994. All rights reserved.).

A good monitoring program will require sampling (Puls and Barcelona, 1996) of not only monitoring wells which are completed into the plume, but also monitoring wells outside of the contaminated zone in order to establish background conditions (Fig. 8). Data from monitoring wells in the contaminated portion are then compared to background wells. The number and location of monitoring wells are not only determined by plume geometry and ground-water flow (ASTM, 1991), but by the degree of confidence required to statistically demonstrate that natural attenuation is taking place, to estimate the rate of attenuation processes, and to predict the time required to meet established remediation goals. These issues will be addressed in detail in the EPA guidance for long term monitoring (LTM) for MNA which is in preparation.

MNA Monitoring Well Network Considerations

RBCA and MNA both rely on sentinel wells for early warning signals of plume migration. The installation of monitoring wells (Aller et al., 1991) to adequately identify contaminant concentrations is of paramount importance in determining the overall contribution of biological processes to a reduction in either concentration or mass of contamination. Monitoring wells which are to be used to determine the contribution of natural bioremediation to site cleanup cannot be located until sufficient knowledge of the aquifer system is obtained (Zeeb et al., 1999). Information that must be obtained before installation include depth to water table, hydraulic conductivity (Molz et al., 1994) and gradient, direction of ground-water flow, storage coefficient or specific yield, vertical and horizontal conductivity distribution, direction of plume movement and the effects of any man-made or natural influences (i.e., lagoons or seeps) on the aquifer system. It is also important to determine if the hydraulic gradient is affected seasonally. Also, sentinel well screen depth and length are important. Often it is advantageous to use short screens to minimize averaging of vertical water quality differences (Martin-Hayden and Robbins, 1997).

The location, number (ASTM, 1995) and other pertinent data regarding monitoring wells (U.S. EPA, 1998b) for the evaluation of MNA should be determined on a site-specific basis. The design of the monitoring network will be determined by the size of the plume, site complexity, source strength, ground-water/subsurface water interactions, distance to receptors and the confidence limits each party involved wishes to place in the data obtained. By necessity, the denser the monitoring network, the greater the degree of confidence one may place in the data. The wells should be capable of monitoring singular flow paths within a plume's course and subsequent movement of contaminants along these flow paths. One way to determine natural attenuation is to determine the concentration of appropriate parameters at one location and sample the same volume of water for the same parameters at some distance downgradient. It is generally impractical to monitor flow paths within a plume with the exception of the plume axis which is the only flow line that can be located with any reasonable level of certainty.

A second way to monitor for natural attenuation assumes that the plume is in equilibrium. While less costly and less time-consuming than monitoring single flow paths for contaminants where a mass balance cannot be performed, the confidence level for data obtained is significantly less when plume equilibrium is assumed. Problems arise because plumes are never in complete equilibrium. Monitoring wells even a few feet apart differ significantly in observed concentrations of contaminants. It has been suggested that internal tracers such as trimethylbenzene (TMB), a biologically recalcitrant compound, can increase the confidence one might place in this method. One simply uses the difference between TMB concentrations at the upgradient and downgradient points to measure the observed loss which can be attributed to other factors such as dispersion. One must be cautioned, however, when using TMB as a conservative tracer due to its degradation under anaerobic conditions and the resulting production of aromatic acid intermediates (Fang et al., 1997).

To monitor the anaerobic degradation of chlorinated solvents, monitoring of singular flow paths may not be necessary, if a pseudo-mass balance can be performed. This method assumes that at each monitoring point either the parent chlorinated solvent or daughter product should be observed. Using PCE as an example at each monitoring point, samples are analyzed for PCE, TCE, DCE, VC, and ethene. The total concentration of analytes is compared on a molar basis. Changes in total molar concentrations are assumed to be losses due to flaws in the monitoring system. The pseudo-mass balance method does not account for physical loses due to dispersion, sorption, or dilution, therefore, one would also have to utilize some method, such as a conservative tracer, to account for these other processes. To place even greater confidence in data, the time frame for analysis must be sufficient to allow for differences in subsurface mobility of the various chlorinated solvents. They will not arrive at the downgradient monitoring point at the same time.

Often hazardous waste sites are monitored for natural attenuation using monitoring wells which have previously been installed, especially if plume equilibrium is assumed. This in itself presents a number of problems, especially

if the wells were installed without adequate knowledge of the subsurface and plume movement. If it can be demonstrated that contamination exists between these wells, by using tracer study for example, they can be used as appropriate monitoring points for assessing natural attenuation. Reinhard and Goodman (1984) used chloride as a reference to investigate the behavior of the trace organic compounds in leachate plumes of two sanitary landfills. Kampbell et al. (1995) and Wiedemeier et al. (1996) described the use of TMB to normalize for changes in BTEX concentration due to abiotic processes of dispersion, dilution, sorption, and volatilization.

It is also necessary to determine what contribution physical processes between sequential monitoring wells have on apparent reduction of chemicals. It may also be necessary to construct new monitoring wells which are offset to present wells or to perform borings near existing wells.

Statistical Validity of Data for MNA

Adequate monitoring is critical (Reinhard and Goodman, 1984), especially when considering natural attenuation as a remedial alternative. The number of sampling points (Barcelona et al., 1994 and 1985) and sampling rounds are often insufficient to establish statistically valid trends, given the natural variability in ground water quality, the variability due to pumping and sampling, and differences between analytical laboratories. Schmidt (1977) lists a number of conditions in which large fluctuations in water quality may be noted, indicating that minor changes in water chemistry may be related to sampling procedures. In order to minimize the effects of natural seasonal variations, sampling, and subsurface heterogeneity on ground water quality, any natural attenuation monitoring program (Gibbons, 1994; Gilbert, 1987) should be based on a detailed statistical evaluation of pertinent data (Hardin and Gilbert, 1993; McDonald and Erickson, 1994; O'Brien et al., 1991; O'Brien, 1997). Although it is recognized that intensive monitoring is expensive, increasing sampling points and frequencies, along with acceptable QA/QC procedures, will give more statistically reliable information. Caution should be exercised when drawing conclusions from limited data sets, especially when attempting to model complex situations.

The number of samples required for evaluating natural attenuation is intrinsically a function of a preselected confidence error and the variance of the data. Quarterly samples collected for a year or two, for example, may not be adequate for evaluating an overall reduction in the mass of contaminants from a particular monitoring well. Sampling frequencies such as this offer small windows for viewing contaminant reduction rates. Contaminant fronts may or may not have reached the monitoring points at the time of sampling, or as stated previously, any number of processes such as infiltration, dilution, and sorption may bias results when addressing only the bioremediation component of natural attenuation.

If the reduction of contaminant mass is to be determined by temporal trends (least squares analysis), for example, the statistical confidence is based on the variance of the data and the square root of the number of samples. In a least square analysis, the correlation coefficient (r) is a function of the degrees of freedom (df) which, in this case, is the number of observations minus two ($n - 2$). For example, if a well were sampled quarterly for two years, the degrees of freedom would be 6 ($8 - 2$) which requires a correlation coefficient of about 0.8 to demonstrate statistical significance at a 95 percent level of confidence (an r of 1.0 denotes a perfect correlation). The point is that one must sample with enough frequency, over a protracted period in order to obtain a statistically meaningful correlation between the reduction of contaminant mass and time.

MNA Degradation Rate Constant Considerations

Precision and accuracy in estimation of rate constants are essential to conclude how quickly the ground-water plume will be cleaned up following the source control (McNabb and Dooher, 1998). Reviews by Vogel et al. (1987a) and Howard et al. (1991) contain a compilation of chlorinated solvents rate constants. Experimental data on the neutral and base-catalyzed abiotic hydrolysis rates of chlorinated ethanes and ethenes was determined by Jeffers et al. (1989). Chapelle et al. (1996) integrated field and laboratory data to estimate rates of petroleum hydrocarbon biodegradation.

In the derivation of the rate constants, it is of considerable significance to calculate concentrations at the point of compliance, compare rates at the site to those in the literature to determine if the site is behaving like other sites, and predict changes caused by fluctuations in flow (Weaver et al., 1996). Although microcosms are used as an effective tool to determine the biodegradation potentials, the use of the microbiological laboratory data for calculation of rate constants may be inappropriate since they are not always representative of the degradative rate(s) under the field conditions (U.S. EPA, 1997b). Results from laboratory studies may significantly over- or underestimate biodegradation rates if environmental conditions in the laboratory differ from conditions in the field (Borden, 1994). Rifai (1997) also points out that, although useful in evaluating the biodegradation potential, microcosms can disrupt the normal structure of ecosystems and prevent the direct extrapolation of microcosm-determined biodegradation rates to field scale. If rate constants for attenuation of chlorinated contaminants are to be used for exposure assessments, it is necessary to estimate the residence time of the contaminants in the aquifer as accurately as possible (Molz and Boman, 1997). One should also be cautioned to not substitute literature biodegradation rates in the place of site specific values.

Often, first-order kinetics obtained from field studies are used to approximate the degradation mechanism. Wiedemeier et al. (1996) described two methods to estimate first-order rate constants: (1) the use of a conservative tracer, a biologically recalcitrant compound found in the dissolved contaminant plume; and (2) the interpretation of a steady state contaminant plume as proposed by Buscheck and Alcantar (1995). The later method is

founded on a one-dimensional steady state analytical solution to the advection-dispersion equation presented by Bear (1979).

Modeling as a Predictive Tool for MNA

MNA requires two types of models: (1) conceptual and (2) fate and transport. In order to understand ground water-flow and contaminant movement (Bear et al., 1992), the construction of a three-dimensional conceptual model of the site must be an integral part of any MNA Work Plan. A comprehensive conceptual model should be used as a clear and concise aid for the general understanding of the nature of the site, the acquired sampling results, and to indicate where additional sampling efforts should be directed. Once a conceptual model has been accepted, a period of monitoring is required to verify that the forecast of the conceptual model is adequate. Only when sufficient quantitative site characterization data are generated and the conceptual model is well developed, can an appropriate analytical or numerical fate and transport model be chosen for the site.

Care should be exercised when choosing the models to predict the fate and transport of contaminants in the subsurface. This may also include the use of screening models such as BIOSCREEN and BIOCHLOR (Newell et al., 1996 and 1998). Appropriateness of the model to the actual hydrogeologic situation, assumptions, limitations, and manner of application are all considerations (Corapcioglu and Baehr, 1987; Carey et al., 1988). The overall effectiveness of the model for predicting fate and transport of contaminants at a particular site depends on all of these factors. Caution should also be exercised when drawing conclusions from limited data sets, especially when modeling complex situations. The validity of the input data is critical in determining the accuracy of predictions made with the model.

Once a model is chosen, it may be applied using the site data (Hunt et al., 1988) and calibrated. Calibration is a process of careful modification of site hydrogeologic or contaminant transport parameters over numerous simulations to identify a set of parameters which generate simulation results which closely match field measured values of hydraulic head for the flow model and contaminant concentrations for the transport model. Calibration of the model results to observed values requires that an acceptable range of error be identified for each calibration target. This range will depend on the model purpose and also on the amount and reliability of the field data (Kresec, 1997). Once calibrated, the fate and transport model can then be used to predict the future extent and concentration of a dissolved contaminant plume by simulating the combined effects of advection, dispersion, sorption, and biodegradation (Rifai et al., 1989).

Many times during calibration, if a model does not fit observed concentrations, it is assumed that the biodegradation coefficient is the proper parameter to be adjusted. Using biodegradation to adjust a model without supporting field data should not be done until all abiotic mechanisms for reduction are explored. When using a model which incorporates a biodegradation term, care should be taken to verify that assumptions made about degradation rates and the amount and activity of biomass are valid for the site in question. Degradation rates are sensitive to a wide array of field conditions which have been discussed previously. Extrapolation of laboratory derived rates to a site can also lead to significant errors. Likewise, using models to derive degradation rates from limited field data where abiotic variables are not well defined can be misleading. Models can be useful tools in determining plume movement (Mercer, 1998) and the contribution of natural attenuation (Rifai et al., 1995) to reductions in contaminant mass provided that all model inputs are correct, particularly those associated with biodegradation rates. Kinetic constants derived from laboratory microcosms or other sites are generally not useful on a wide scale to predict overall removal rates. Site specific degradation rates should be developed and incorporated into a model.

SUMMARY

The behavior of a contamination plume, whether stable, shrinking, or expanding, is the primary evidence for the occurrence of natural attenuation. In the majority of the cases, historical data to indicate the status of a plume are not available. In these events, there are at least four basic conditions which must be present to confirm that natural attenuation processes are taking place. These include, but are probably not limited to:

1. The points of sampling must be on flow lines from the source of contamination or an upgradient point of observation. It must be demonstrated that the downgradient observations accurately reflect the abiotic and biotic processes which have occurred between the two points. Ideally, one would sample the same volume of water at the downstream point that was sampled earlier at the source or upgradient observation well. Since this is rarely practical, it must be assumed that the plume is in equilibrium with respect to natural attenuation processes between the two points of observation. If these conditions are not satisfied, any downgradient measurement of contaminant concentration must be lower than the true value, and therefore, exaggerate the effectiveness of natural attenuation. Confidence levels may be enhanced by 1) increasing the number of observation points and times at fixed frequencies, and 2) use of a conservative tracer.
2. There must be a reduction in contaminant mass or concentration. One could argue that natural attenuation results in a reduction in contaminant concentration by sorption, volatilization, or dilution, with the only loss of mass being that of volatilization to the atmosphere. Natural bioremediation, on the other hand, must result in a reduction of mass of the contaminants of concern by the eventual conversion to environmentally acceptable compounds.
3. Site geochemistry must assure that conditions are right for reduction of contaminant concentration,

such as the presence of mineral nutrients and electron acceptors, the state of redox, temperature, and pH.

4. Daughter products of contaminants must be present, perhaps with indicators of mineralization. For example, claims of intrinsic or natural bioremediation need to be supported by data including the relationship between the mass loss and the loss of oxygen. In addition to the biological utilization of oxygen, nitrate, and sulfate, these natural attenuation processes often result in the creation of by-products such as dissolved Fe(II), Mn(II), HCO_{3^-}, $CO_{3^=}$ and methane.

The use of MNA or passive remediation at contaminated ground-water sites is gaining attention both within the scientific and regulatory communities. The OSWER directive recommends that MNA be applied concurrently with or subsequently to active measures such as source control or active remedial technologies. Selection of MNA as a remedy or part of a remedy can be advantageous since it may minimize the transfer of contaminants to other media, is less intrusive to the environment, may be applied to all or part of a site, and overall remedial costs may be lower than for an active remedy. There are several factors which may limit the application of natural attenuation as a remedial alternative. They are: (1) the longer time frame that may be required to achieve remedial goals, (2) site characterization investigations that may be more extensive and costly, (3) the added responsibility for long-term monitoring and costs, (4) toxicity of byproducts, (5) potential for continued contaminant migration, and (6) required alternatives if natural attenuation fails to meet established goals.

Under proper conditions, MNA along with source removal, long-term monitoring, and land use restrictions might be selected over more expensive conventional technologies. There will be other sites where natural attenuation will not be acceptable as a remedial alternative because of regulatory constraints or the site conditions are not favorable for its application. In the end, the selection of a remedial technology at a specific site will be determined by time constraints in obtaining remediation objectives, the hydrogeology and geochemistry at the site, the contaminants of concern, regulatory constraints, and considerations of environmental exposure and cost.

DISCLAIMER

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QUALITY ASSURANCE STATEMENT

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve physical measurements and as such did not require a QA plan.

READING LIST

Aller, L., T.W. Bennett, G. Hackett, R.J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen, and J.E. Denne. 1991. *Handbook of Suggested Practices for the Design and Installation of Groundwater Monitoring Wells*. EPA/600/4-89/034. Environmental Monitoring Systems Laboratory, Las Vegas, NV. 398 pp.

Alvarez-Cohen, L., and P.L. McCarty. 1991a. Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture. *Appl. Environ. Microbiol.* **57**: 228–235.

Alvarez-Cohen, L., and P.L. McCarty. 1991b. Product toxicity and cometabolic competitive inhibition modeling of chloroform and trichloroethylene transformation by methanotrophic resting cells. *Appl. Environ. Microbiol.* **57**(4): 1031–1037.

Arciero, D., T. Vannelli, M. Logan, and A.B. Hooper. 1989. Degradation of trichloroethylene by the ammonia-oxidizing bacterium *Nitrosomonas europaea*. *Biochem. Biophys. Res. Commun.* **159**: 640–643.

Arneth. J.-D., G. Milde, H. Kerndorff, R. Schleyer. 1989. The 15 most frequently detected organic compounds in groundwater at waste disposal sites in Germany and the U.S. p. 399. In: P. Baccini (ed.), *The Landfill*. Springer-Verlag, New York, Inc., New York, NY.

ASTM. 1991. *Standard Guide for Selection of Aquifer Test Method in Determination of Hydraulic Properties by Well Techniques*. Standard D-4043-91. American Society for Testing and Materials, Philadelphia, PA.

ASTM. 1995. *Standard Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers*. Standard D-5092-90. American Society for Testing and Materials, Philadelphia, PA.

ASTM. 1998. *Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites*. E-1943-98. West Conshohocken, Pennsylvania.

Bagley, D.M., and J.M. Gossett. 1990. Tetrachloroethene transformation to trichloroethene and cis-1,2-aichloroethene by sulfate-reducing enrichment cultures. *Appl. Environ. Microbiol.* **56**(8): 2511–2516.

Barbaro, J.R., J.F. Barker, L.A. Lemon, and C.I. Mayfield. 1992. Biotransformation of BTEX under anaerobic denitrifying conditions: Field and laboratory observations. *J. Contam. Hydrol.* **11**: 245–277.

Barcelona, M.J., J.A. Helfrich, and E.E. Garske. 1985. Sampling tubing effects on groundwater samples. *Anal. Chem.* **57**(2): 460–464.

Barcelona, M.J., H.A. Wehrmann, and M.D. Varijen. 1994. Reproducible well purging procedure and VOC stabilization criteria for ground-water sampling. *Ground Water* **32**(1): 12–22.

Bear, J. 1979. *Hydraulics of Groundwater*. McGraw-Hill, New York, NY.

Bear, J., M.S. Beljin, and R.R. Ross. 1992. *Fundamentals of Ground-Water Modeling*. EPA/540/S-92/005. ORD, Washington, DC.

Beller, H.R., D. Grbić-Galić, and M. Reinhard. 1992a. Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process. *Appl. Environ. Microbiol.* **58**(3): 786–793.

Beller, H.R., M. Reinhard, and Grbić-Galić. 1992b. Metabolic by products of anaerobic toluene degradation by sulfate-reducing enrichment cultures. *Appl. Environ. Microbiol.* **58**(9): 3192–3195.

Blake, S.B., and R.A. Hall. 1984. *Monitoring petroleum spills with wells–Some problems and solutions*. pp. 305–310. In: *Proceedings of the Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring*. Dallas, TX, 23–25 May.

Borden, R.C. 1994. Natural Bioremediation of Hydrocarbon-Contaminated Ground Water. p. 177. In: R.D. Norris, R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward (eds.), *Handbook of Bioremediation*. Lewis Publishers, Boca Raton, FL.

Borden, R.C., C.A. Gomez, and M.T. Becker. 1995. Geochemical indicators of intrinsic bioremediation. *Ground Water* **33**(2): 180–189.

Borden, R.C., J.H. Melody, M.B. Shafer, and M.A. Barlaz. 1997. *Anaerobic biodegradation of BTEX in aquifer material*. EPA/600/S-97/003.

Boulding, J.R. 1993a. *Subsurface Characterization and Monitoring Techniques, A Desk Reference Guide, Volume I: Solids and Ground Water*. EPA/625/R-93/003a.

Boulding, J.R. 1993b. *Subsurface Characterization and Monitoring Techniques, A Desk Reference Guide, Volume II: The Vadose Zone, Field Screening and Analytical Methods*. EPA/625/R-93/003b.

Bouwer, E.J. 1994. Bioremediation of chlorinated solvents using alternate electron acceptors. p. 149. In: R.D. Norris, R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward (eds.), *Handbook of Bioremediation*. Lewis Publishers, Boca Raton, FL.

Bouwer, E.J., and P.L. McCarty. 1983. Transformation of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Appl. Environ. Microbiol.* **45**(4): 1286–1294.

Bouwer, E.J., B.E. Rittman, and R.L. McCarty. 1981. Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. *Environ. Sci. Technol.* **15**(5): 596–599.

Brady, P.V., M.V. Brady, and D.J. Borns. 1998. *Natural Attenuation - CERCLA, RBCA's, and the Future of Environmental Remediation*. Lewis Publishers, Boca Raton, FL. 245 pp.

Broholm, K., B.J. Jensen, T.H. Christensen, and L. Olsen. 1990. Toxicity of 1,1,1-trichlororethane and trichloroethene on a mixed culture of methane-oxidizing bacteria. *Appl. Environ. Microbiol.* **56**(80): 2488–2493.

Brown, R.A., R.E. Hinchee, R.D. Norris, and J.T. Wilson. 1996. Bioremediation of petroleum hydrocarbons: A flexible, variable speed technology. *Biorem. J.* **6**(4): 95–108.

Burdige, D.J., and K.H. Nealson. 1986. Chemical and microbiological studies of sulfide-mediated manganese reduction. *Geomicrobiol. J.* **4**(4): 361–387.

Buscheck, T.E.G., and C.M. Alcantar. 1995. *Regression techniques and analytical solutions to demonstrate intrinsic bioremediation*. In: *Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioreclamation*.

Carey, G.R., P.J. Van Geel, J.R. Murphy, E.A. McBean, and F.A. Rovers. 1998. Full-scale field application of a coupled biodegradation-redox model (BIOREDOX). pp. 213–218. In: G.B. Wickramanayake and R.H. Hinchee (eds.), *Natural Attenuation of Chlorinated Solvents*. Battelle Press, Columbus, OH.

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resour. Res.* **31**(2): 359–371.

Chapelle, F.H., P.M. Bradley, D.R. Lovley, and D.A. Vroblesky. 1996. Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods. *Ground Water* **34**(4): 691–698.

Chen, C., J.A. Puhakka, and J.F. Ferguson. 1996. Transformation of 1,1,2,2-tetrachloroethane under methanogenic conditions. *Environ. Sci. Technol.* **30**: 542–547.

Chiang, C.Y., J.P. Salanitro, E.Y. Chai, J.D. Colthart, and C.L. Klein. 1989. Aerobic biodegradation of benzene, toluene, and xylene in a sandy aquifer: Data analysis and computer modeling. *Ground Water* **27**(6): 823–834.

Christensen, T.H., P. Kjeldsen, H-J. Albrechtsen, G. Heron, P.H. Nielsen, P.L. Bjerg, and P.E. Holm. 1994. Attenuation of landfill leachate pollutants in aquifers. *Crit. Revs. Environ. Sci. Tech.* **24**(2): 119–202.

Chu, K.H., and W.J. Jewell. 1993. Treatment of tetrachloroethylene with an anaerobic attached film process. *J. Environ. Eng. Am. Soc. Civ. Engrs.* **2**: 155–162.

Church, P.E., and G.E. Granato. 1996. Bias in ground-water data caused by well-bore flow in long-screen wells. *Ground Water* **34**(2): 262–273.

Clark, D., D. Ours, and L. Hineline. 1997. Passive remediation for groundwater impacted with hydrocarbons. *Rem. Manage.* **1**: 50–45.

Corapcioglu, M.Y., and A.L. Baehr. 1987. A compositional multiphase model for groundwater contamination by petroleum products, 1. Theoretical considerations. *Water Resour. Res.* **23**(1): 191–200.

Davis, J.W., N.J. Klier, and C.L. Carpenter. 1994. Natural biological attenuation of benzene in ground water beneath a manufacturing facility. *Ground Water* **32**(2): 215–226.

Di-Ruggiero, J., and A.M. Gounot. 1990. Microbial manganese reduction mediated by bacterial strains isolated from aquifer sediments. *Microb. Ecol.* **20**: 53–63.

Donaldson, S.G., C.M. Miller, and W.W. Miller. 1992. Remediation of gasoline-contaminated soil by passive volatilization. *J. Environ. Qual.* **21**: 94–102.

Edwards, E.A., and D. Grbić-Galić. 1992. Complete mineralization of benzene by aquifer microorganisms under strictly anaerobic conditions. *Appl. Environ. Microbiol.* **58**: 2663–2666.

Edwards, E.A., and D. Grbić-Galić. 1994. Anaerobic degradation of toluene and o-xylene by a methanogenic consortium. *Appl. Environ. Microbiol.* **60**: 313–322.

Ehrlich, H.L. 1987. Manganese oxide reduction as a form of anaerobic respiration. *Geomicrobiol. J.* **5**(3): 423–431.

Ensley, B.D. 1991. Biochemical diversity of trichloroethylene metabolism. *Ann. Rev. Microbiol.* **45**: 283–299.

Fang, J., M.J. Barcelona, and C. West. 1997. The use of aromatic acids and phospholipid ester-linked fatty acids for delineation of processes affecting an aquifer contaminated with JP-4 fuel. pp. 65–76. In: R. Eganhouse (ed.), *Molecular Markers in Environmental Geochemistry*. ACS Symposium Series 671. Amer. Chem. Soc.

Fishman, M.J., and L.C. Friedman. 1985. Methods for determination of inorganic substances in water and fluvial sediments. p. 545. In: M.J. Fishman and L.C. Friedman (eds.), *Techniques*

of Water-Resources Investigations. U.S. Geological Survey, book 5, chap. A1.

Fogel, M.M., A.R. Taddeo, and S. Fogel. 1986. Biodegradation of chlorinated ethenes by a methane-utilizing mixed culture. *Appl. Environ. Microbiol.* **51**: 720–724.

Freedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. *Appl. Environ. Microbiol.* **55**: 2144–2151.

Gantzer, C.J., and L.P. Wackett. 1991. Reductive dechlorination catalyzed by bacterial transition-metal coenzymes. *Environ. Sci. Technol.* **25**: 715–722.

Gibbons, R.D. 1994. *Statistical Methods for Groundwater Monitoring*. John Wiley & Sons, New York, NY, 286 pp.

Gilbert, R.O. 1987. *Statistical Methods for Environmental Pollution Monitoring*. Van Nostrand Reinhold Co., New York, NY, 320 pp.

Hanson, R.S., and T.E. Hanson. 1996. Methanotrophic bacteria. *Microbiol. Rev.* **60**(2): 439–471.

Hardin, J.W., and R.O. Gilbert. 1993. *Comparing statistical tests for detecting soil contaminations greater than background*. PNL-8989. Pacific Northwest Laboratory, Richland, WA.

Henson, J.M., M.V. Yates, J.W. Cochran, and D.L. Shackleford. 1988. Microbial removal of halogenated methanes, ethanes, and ethylenes in an aerobic soil exposed to methane. *FEMS Microbiol. Ecol.* **53**: 193–201.

Heron, G., C. Crouzet, Alain C.M. Bourg, and T.H. Christensen. 1994. Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques. *Environ. Sci. Technol.* **28**: 1698–1705.

Higgo, J.J., P.H. Nielsen, and M.P. Bannon. 1996. Effect of geochemical conditions on fate of organic compounds in groundwater. *Environ. Geol.* **27**: 335–346.

Hopkins, G.D., L. Semprini, and P.L. McCarty. 1993. Microcosms and in-situ field studies of enhanced biotransformation of trichloroethylene by phenol-oxidizing microorganisms. *Appl. Environ. Microbiol.* **59**: 2277–2285.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Maylan, and E.M. Michalenko. 1991. *Handbook of Environmental Degradation Rates*. Lewis Publishers, Chelsea, MI.

Huesemann, M.H., and M.J. Truex. 1996. The role of oxygen diffusion in passive bioremediation of petroleum contaminated soils. *J. Hazard. Mater.* **51**: 93–113.

Hunt, J.R., N. Sitar, and K.S. Udell. 1988. Nongaseous phase liquid transport and cleanup, 1. Analysis of mechanisms. *Water Resour. Res.* **24**(8): 1247–1258.

Jeffers, P.M., L.M. Ward, L.M. Woytowitch, and N.L. Wolfe. 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propanes. *Environ. Sci. Technol.* **23**(8): 965–969.

Kampbell, D.H., T.H. Wiedemeier, and J.E. Hansen. 1995. Intrinsic bioremediation of fuel contamination in ground water at a field site. *J. Hazard. Mater.* **49**: 197–204.

Kemblowski, M.W., and C.Y. Chiang. 1990. Hydrocarbon thickness fluctuations in monitoring wells. *Ground Water* **28**(2): 244–252.

Kemblowski, M.W., J.P. Salanitro, G.M. Deeley, and C.C. Stanley. 1987. *Fate and transport of dissolved hydrocarbons in groundwater - a case study.* pp. 207–231. In: *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference*. Houston, TX, 17–19 November. NGWA: Dublin, OH.

Kennedy, L.G., and S.R. Hutchins. 1992. Applied geologic, microbiologic, and engineering constraints of in-situ BTEX bioremediation. *Remediation* **3**(1): 83–107.

Kleopfer, R.D., D.M. Easley, B.B. Hass, Jr., T.G. Deihl, D.E. Jackson, and C.J. Wurrey. 1985. Anaerobic degradation of trichloroethylene in soil. *Environ. Sci. Technol.* **19**: 277–280.

Klusman, R.W. 1980. *Sampling Designs for Biochemical Baseline Studies in the Colorado Oil Shale Region: A Manual for Practical Application*. U.S. Department of Energy. Report DOE/EV/10298-2. 180 pp.

Koterba, M., F. Wilde, and W. Lapham. 1996. *Ground-Water Data-Collection Protocols and Procedures for the National Water-Quality Assessment Program*. U.S. Geological Survey. Open-File Report 95-399. 113 pp.

Kresec, N., 1997. *Quantitative Solutions in Hydrogeology and Groundwater Modeling*. Lewis Publishers, CRC Press, Inc., Boca Raton, FL.

Lee, M.D. 1988. Biorestoration of aquifers contaminated with organic compounds. *CRC Crit. Rev. Environ. Control* **18**: 29–89.

Lenhard, R.J., and J.C. Parker. 1990. Estimation of free hydrocarbon volume from fluid levels in monitoring wells. *Ground Water* **28**(1): 57–67.

Lesage, S., R.E. Jackson, M.W. Priddle, and P.G. Riemann. 1990. Occurrence and fate of organic solvent residences in anoxic groundwater at the Gloucester landfill. *Canada Environ. Sci. Technol.* **24**(4): 559–566.

Lindberg, R.D., and D.D. Runnells. 1984. Ground water redox reactions: An analysis of equilibrium state applied to En measurements and geochemical modeling. *Science* **225**: 925–927.

Lovely, D.R. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol. Rev.* **55**(2): 259–287.

Lovely, D.R., and D.J. Lonergan. 1990. Anaerobic oxidation of toluene, phenol, and *p*-creosol by the dissimilatory iron-reducing organism GS-15. *Appl. Environ. Microbiol.* **56**: 1858–1864.

Lovely, D.R., and S. Goodwin. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reaction in aquatic sediments. *Geochim. Cosmochim. Acta.* **52**: 2993–3003.

Lovely, D.R., J.C. Woodward, and F.H. Chapelle. 1994. Stimulated anoxic biodegradation of aromatic hydrocarbons using Fe(III) ligands. *Nature (London)* **370**: 128–131.

Lovely, D.R., M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.J.P. Phillips, and D.I. Siegel. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. *Nature (London)* **339**: 297–299.

Martin-Hayden, J.M., and G.A. Robbins. 1997. Plume distortion and apparent attenuation due to concentration averaging in monitoring wells. *Ground Water* **35**(2): 339–346.

Martin-Hayden, J.M., G.A. Robbins, and R.D. Bristol. 1991. Mass balance evaluation of monitoring well purging: Part II. Field tests at a gasoline contamination site. *J. Contam. Hydrol.* **8**: 225–241.

Mayer, K.R., D. Grbić-Galić, L. Semprini, and P.L. McCarty. 1988. Degradation of trichloroethylene by methanotrophic bacteria in a laboratory column of saturated aquifer material. *Water Sci. Tech.* **20**(11/12): 175–178.

McAllister, P.M., and C.Y. Chiang. 1994. A practical approach to evaluating natural attenuation of contaminants in ground water. *Ground Water Monit. Rem.* **14**(2): 161–173.

McCarty, P.L. 1988. Bioengineering issues related to in-situ remediation of contaminated soils and groundwater. pp. 143–162. In: G.S. Omenn (ed.), *Biotic and Abiotic Transformation of*

Chlorinated Solvents in Ground Water. Environmental Biotechnology, Plenum, New York, NY.

McCarty, P.L. 1996. *Biotic and abiotic transformations of chlorinated solvents in ground water*. pp. 5–9. In: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*. EPA/540/R-96/509. Office of Research and Development, Washington, DC.

McCarty, P.L., and L. Semprini. 1994. Ground-water treatment for chlorinated solvents. p. 87. In: R.D. Norris, R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward (eds.), *Handbook of Bioremediation*. Lewis Publishers, Boca Raton, FL.

McDonald, L.L., and W.P. Erickson. 1994. Testing for the bioequivalence in field studies: Has a distributed site been adequately reclaimed? pp. 183–198. In: D.J. Fletcher and B.F.J. Manly (eds.), *Statistics in Ecology and Environmental Monitoring*. Otago Conference Series No. 2, University of Otago Press, Dunedin, New Zealand.

McNabb, W.W. Jr., and B.P. Dooher. 1998. A critique of a steady-state method for estimating contaminant degradation rates. *Ground Water* **36**(6): 983–987.

Mercer, J.W. 1998. Transport. and remediation of chemicals in groundwater. In: R.A. Myers (ed.), *Encyclopedia of Environmental Analysis and Remediation*. John Wiley & Sons, New York, NY.

Molz, F., and G. Boman. 1997. *Site characterization tools: Using a borehole flowmeter to locate and characterize the transmissive zones of an aquifer*. In: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*. EPA/540/R-97/504. ORD, Washington, DC.

Molz, F.J., G.K. Woman, S.C. Young, W.R. Waldrop. 1994. Borehole flowmeters: Field application and data analysis *J. Hydrol.* **163**: 347–371.

Morris, J.C., and W. Stumm. 1967. p. 270. In: W. Stumm, (ed.), *Equilibrium Concept in Natural Waters Systems*. Am. Chem. Soc., Washington, DC.

Mu, D.Y., and K.M. Scow. 1994. Effect of trichloroethylene (TCE) and toluene concentrations on TCE and toluene biodegradation and the population density of TCE and toluene degraders in soil. *Appl. Environ. Microbiol.* **60**(7): 2661–2665.

Newell, C.J., R.K. McLeod, J.R. Gonzales. 1996. *BIOSCREEN Natural Attenuation Decision Support System*. User's Manual. Version 1.3. EPA/600/R-96/087. ORD, Washington, DC.

Newell, C.J., A.P. Smith, C.E. Aziz, T.A. Khan, J.R. Gonzales, and P.E. Hass. 1998. BIOCHLOR: A planning-level natural attenuation model and database for solvent sites. pp. 237–242. In: G.B. Wickramanayake and R.E. Hinchee (eds.), *Natural Attenuation of Chlorinated and Recalcitrant Compounds*. Battelle, Columbus, OH.

Norris, R.D., R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward. 1993. *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*. EPA/600/R-93/124.

Nyer, E.K., and M.E. Duffin. 1997. The state of the art bioremediation. *Ground Water Monit. Rem.* **2**: 64–69.

O'Brien, R.F. 1997. Statistical issues when comparing a site to background. pp. 367–372. In: R. Hinchee (ed.), *In-Situ and On-Site Bioremediation*. Battelle Press, Columbus, OH.

O'Brien, R.F., B.K. Sinha, and W.P. Smith. 1991. A statistical procedure to evaluate cleanup standards. *J. Chemometrics* **5**(3): 249–261.

Parsons, F.Z., P.R. Wood, and J. DeMarco. 1984. Transformations of tetrachloroethylene and trichloroethylene in microcosms and groundwater. *J. AWWA.* **71**: 56–59.

Patel, R.N., C.T. Hou, A.I. Laskin, and A. Felix. 1982. Microbial oxidation of hydrocarbons: Properties of a soluble methane monooxygenase from a facultative methane-utilizing organism, *Methylobacterium* sp. strain CRL-26. *Appl. Environ. Microbiol.* **44**: 1130–1137.

Pettyjohn, W.A. 1982. Cause and effect of cyclic changes in ground-water quality. *Ground Water Monit. Rem.* **2**(1): 43–49.

Puls, R.W., and M.J. Barcelona. 1996. *Low-Flow (Minimal Drawdown) Sampling Procedures*. EPA/540/S-95/504. ORD, Washington, DC.

Rabus, R., R. Nordhaus, W. Ludwig, and F. Widdel. 1993. Complete oxidation of toluene under strictly anoxic conditions by a new sulfate-reducing bacterium. *Appl. Environ. Microbiol.* **59**: 1444–1451.

Reinhard, M., and N.L. Goodman. 1984. Occurrence and distribution of organic chemicals in two landfill leachate plumes. *Environ. Sci. Technol.* **18**: 953–961.

Rifai, H.S. 1997. Natural Aerobic Biological Attenuation. In: C.H. Ward, J.A. Cherry, and M.R. Scalf (eds.), *Subsurface Remediation*. Ann Arbor Press, Inc., Chelsea, MI.

Rifai, H.S., C.J. Newell, R. Miller, S. Taffinder, and M. Roundsaville. 1995. Simulation of natural attenuation with multiple electron acceptors. *Bioremediation* **3**: 53–58.

Rifai, H.S., P.B. Bedient, and J.T. Wilson. 1989. *BIOPLUME model for contaminant transport affected by oxygen limited biodegradation*. EPA/600/M-89/019.

Robbins, G.A. 1989. Influence of using purged and partially penetrating monitoring wells on contaminant detection, mapping and modeling. *Ground Water* **27**(2): 155–162.

Robbins, G.A., and J.M. Martin-Hayden. 1991. Mass balance evaluation of monitoring well purging: Part I. Theoretical models and implications for representative sampling. *J. Contam. Hydrol.* **8**: 203–224.

Salanitro, J.P. 1992. *Criteria for evaluating the bioremediation of aromatic hydrocarbons in aquifers*. Presented at the National Research Council (Water Science Technology Board) Committee on In-Situ Bioremediation: How Do We Know When It Works? Washington, DC, 26–29 October.

Salanitro, J.P. 1993. The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers. *Ground Water Monit. Rem.* **13**(4): 150–161.

Schmidt, K.D. 1977. Water quality variations for pumping wells. *Ground Water* **15**(2): 130–137.

Schocher, R.J., B. Seyfried, F. Vazquez, and J. Zeyer. 1991. Anaerobic degradation of toluene by pure cultures or denitrifying bacteria. *Arch. Microbiol.* **157**: 7–12.

Semprini, L., P.K. Kitanidis, D.H. Kampbell, and J.T. Wilson. 1995. Anaerobic transformation of chlorinated aliphatic hydrocarbons in a sand aquifer based on spatial chemical distributions. *Water Resour. Res.* **13**(40): 1051–1062.

Sewell, G.W., and S.A. Gibson. 1991. Simulation of the reductive dechlorination of tetrachloroethylene in anaerobic aquifer microcosms by the addition of toluene. *Environ. Sci. Technol.* **25**: 982–984.

Shampine, W.J., L.M. Pope, and M.T. Koterba. 1992. *Integrating Quality Assurance in Project Work Plans of the U.S. Geological Survey*. U.S. Geological Survey. Open-File Report 92–162. 12 pp.

Sharples, B.P.M. 1992. Oil pollution by the offshore industry contrasted with tankers: An examination of the facts. *J. Process Mech. Eng.* **206**: 3–14.

Shelton, L.R. 1994. *Field Guide for Collection and Processing Stream-Water Samples for the National Water-Quality Assessment Program*. U.S. Geological Survey. Open-File Report 94-455, Sacramento, CA. 44 pp.

Shelton, L.R., and P.D. Capel. 1994. *Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants for the National Water-Quality Assessment Program*. U.S. Geological Survey. Open-File Report 94–458. 20 pp.

Stone, A.T., and J.J. Morgan. 1984. Reduction and dissolution of manganese (III) and manganese (IV) oxides by organics. 1. Reaction with hydroquinone. *Environ. Sci. Technol.* **18**(6): 450–456.

Stumm, W., and J.J. Morgan. 1981. *Aquatic Chemistry*, 2nd ed. John Wiley & Sons, New York, NY.

Tiedje, J.M., and T.O. Stevens. 1988. The ecology of anaerobic dechlorination consortium. pp. 3–14. In: G.S. Omen (ed.) *Environmental Biotechnology: Reducing Risks from Environmental Chemicals through Biotechnology*. Plenum Press, New York.

U.S. EPA. 1996. *Draft Field Methods Compendium (FMC)*. OERP #9285.2-11. Office of Emergency and Remedial Response, Washington, DC.

U.S. EPA. 1997a. *Field Analytical and Site Characterization Technologies, Summary of Applications*. EPA/542/R-97/011. OSWER, Washington, DC.

U.S. EPA. 1997b. *Draft EPA Region 4 Suggested Practices for Evaluation of a Site for Natural Attenuation (Biological Degradation) of Chlorinated Solvents*.

U.S. EPA. 1998a. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. EPA/600/R-98/128. ORD, Washington, DC.

U.S. EPA. 1998b. *Field Sampling and Analysis Technologies Matrix and Reference Guide*. EPA/542/B-98/002.

U.S. EPA. 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. OSWER Directive, 9200.4-17P. Office of Solid Waste and Emergency Response, Washington, DC.

Underground Storage Tank Technology Update. 1998. *Four Critical Considerations in Assessing Contaminated Plumes. Implications for Site-Specific MNA/RBCA Assessments at Petroleum-Contaminated Plumes*. EPA/600/J-98/228.

Vogel, T.M. 1988. *Biotic and abiotic transformations of halogenated aliphatic compounds*. Ph.D. Thesis. Stanford University. Stanford, CA.

Vogel, T.M., and D. Grbić-Galić. 1986. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. *Appl. Environ. Microbiol.* **52**: 200–202.

Vogel, T.M., and P.L. McCarty. 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride and carbon dioxide under methanogenic conditions. *Appl. Environ. Microbiol.* **49**: 1080–1083.

Vogel, T.M., C. Criddle, and P. McCarty. 1987. Transformation of halogenated aliphatic compounds. *Environ. Sci. Technol.* **21**: 722–736.

Vogel, T.M., and P.L. McCarty. 1987a. Rate of abiotic formation of 1,1-dichloroethylene from 1,1,1-trichloroethane in groundwater. *J. Cont. Hydrol.* **1**: 299–308.

Vogel, T.M., and P.L. McCarty. 1987b. Abiotic and biotic transformation of 1,1,1-trichloroethane under methanogenic conditions. *Environ. Sci. Technol.* **21**: 1208–1213.

Weaver, J.W., J.T. Wilson, and D.H. Kampbell. 1996. *Extraction of degradation rate constants from the St. Joseph, Michigan Trichloroethene site*. p. 69. In: *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*. September 11–13, 1996, Dallas, TX. EPA/540/R-96/509.

Westrick, J.J., J.W. Mellow, and R.F. Thomas. 1984. The groundwater supply survey. *J. AWWA.* **76**: 52–59.

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*. United States Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, TX.

Wiedemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1996. Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in groundwater. *Ground Water Monit. Rem.* **16**(3): 186–194.

Wilson, J.T., J.F. McNabb, B.H. Wilson, and M.J. Noonan. 1983. Biotransformation of selected organic pollutants in groundwater. *Dev. Ind. Microbiol.* **24**: 225–233.

Wilson J.T., and B.H. Wilson. 1985. Biotransformation of trichloroethylene in soil. *Appl. Environ. Microbiol.* **49**: 242–243.

Wood, W.W. 1981. *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents*. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chap. D2. 24 pp.

Zeeb, P.J., N.D. Durant, R.M. Cohen. and J.W. Mercer. 1999. *Site Investigation Approaches to Support Assessment of Natural Attenuation of Chlorinated Solvents in Groundwater: Part 1, Sandy Aquifer*. Draft of Site Characterization Manual. U.S. EPA. ORD, Washington, DC.

GROUNDWATER VULNERABILITY TO PESTICIDES: STATISTICAL APPROACHES

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Groundwater vulnerability to pesticides is the potential for contamination of groundwater by pesticides from a nonpoint source or aerially distributed point sources. Due to widespread pesticide use and detection in groundwater, assessments that evaluate and estimate pesticide vulnerability have increasingly proven valuable during decisions regarding groundwater management, conservation, and remediation because of the significant costs of such actions. To predict groundwater vulnerability and understand factors that affect the transport of pesticides to groundwater resources, a variety of approaches have been developed that are broadly classified into three general categories: (1) overlay and index, (2) statistically based, and (3) process based. Often the selection of an appropriate approach for assessing groundwater vulnerability to

pesticides is determined by the type and scale of the problem and by the available resources. This article provides an overview of the approaches and methods of evaluation for assessing groundwater vulnerability to pesticides.

BACKGROUND

Pesticide vulnerability assessments have become increasingly important in managing groundwater resources because of widespread pollution of groundwater by various pesticides. Pesticides are synthetic organic chemicals used to destroy insects or other organisms harmful to agriculture or animals. A comprehensive review by Barbash and Resek (1) of the published information on the distribution and behavior of pesticides in groundwater suggests that the greatest potential for unintended adverse effects from pesticides is through contamination of the earth's hydrologic system. Pesticides from every chemical class have been detected in groundwater (1), including samples collected from major aquifers of the United States, as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The samples collected from 1992 to 1998 by NAWQA revealed that pesticides were found most frequently in shallow groundwater in urban (54% of wells) and agricultural areas (61%), where pesticide use is greatest (2).

Knowledge of pesticide vulnerability for specific groundwater resources can be of great value for preserving and sustaining water quality. A variety of approaches have been developed to predict groundwater vulnerability and understand factors that affect the transport of pesticides to groundwater resources. Many of these approaches have been used by water-resource managers to make informed decisions regarding the potential risk of groundwater contamination by pesticides. This article provides an overview of the approaches and methods of evaluation for assessing groundwater vulnerability to pesticides.

Vulnerability is the potential for [pesticide] contamination of groundwater from a nonpoint source or aerially distributed point sources. The National Research Council (3) defined groundwater vulnerability to contamination as "the tendency or likelihood for contamination to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer." Similarly, the U.S. Environmental Protection Agency (4) defined groundwater vulnerability as "the relative ease with which a contaminant applied on or near the land surface can migrate to the aquifer of interest under a given set of agronomic management practices, pesticide characteristics, and hydrogeologic sensitivity conditions." Many definitions conceptualize two distinct components of groundwater vulnerability (5): (1) *intrinsic susceptibility*, which is defined by the inherent properties of the hydrogeologic system (hydraulic conductivity, porosity, depth to water, and soil type) and the associated sources of water and stresses for the system (rates and sources of recharge and discharge); and (2) *specific vulnerability*, or simply *vulnerability*, which is defined by the proximity of contaminant sources, fate and transport properties of the contaminant, and other factors that could increase loads of specified contaminants to the aquifer, their eventual delivery to a groundwater resource, or both. As Rupert (6) noted, although multiple definitions have been used for the term "vulnerability," they all address the same underlying question: What is the potential for groundwater contamination?

To assess the vulnerability of a groundwater resource to pesticide contamination, the physical and chemical mechanisms that control pesticide movement into groundwater must be addressed. A complete discussion of all processes and factors responsible for the behavior and fate of pesticides from land surface to groundwater is beyond the scope of this article. For additional details on pesticide fate and transport, refer to Barbash and Resek (1), a literature review of pesticide transport and leaching to groundwater by Flury (7); and Hornsby et al. (8), which is a comprehensive database that lists the properties of pesticides in the environment.

APPROACHES TO GROUNDWATER VULNERABILITY ASSESSMENTS OF PESTICIDES

A variety of approaches are presently used for assessing groundwater vulnerability to pesticides, ranging from subjective, qualitative, and opinion-based to objective, quantitative, and scientifically defensible methods. The approaches for assessing groundwater vulnerability can be classified into three general categories: (1) overlay and index, (2) statistically based, and (3) process based. Note that selection of the appropriate approach for assessing groundwater vulnerability is primarily driven by the type and scale of the problem and by the available resources.

Overlay and Index Approach

The overlay and index, one of the earliest approaches, generates vulnerability indexes based on the aggregation, or overlay, of many variables or factors deemed important in a given hydrologic setting, such as well location, geology, soil, and depth to water. This approach often is used as an initial screening tool and has an advantage over other methods because the data needed for implementation are generally available on the appropriate scale of study. The most widely used overlay and index method is DRASTIC (9), which incorporates professional judgment to weigh factors and create an aggregate point rating of groundwater vulnerability. DRASTIC is defined by seven factors: depth to water, net recharge, aquifer media, soil media, topography, impact of vadose zone media, and hydraulic conductivity of the aquifer. DRASTIC and other approaches that are based on best professional judgment are subjective and thus inherently result in less scientifically defensible groundwater vulnerability assessments. Overlay and index methods are not usually calibrated to measured pesticide concentrations in the groundwater and can result in poor correlation with actual pesticide concentration measurements (10). In addition, the seven factors considered by DRASTIC may not be the most appropriate for all groundwater systems.

Statistical Approach

Statistical approaches rely on empirical observation of measured pesticide concentration or detection in

groundwater to establish relations with independent, or explanatory, variables. Explanatory variables represent the physical and chemical system of the land surface and subsurface, such as land use, soil taxonomy, lithology, depth to water, and pesticide application rates. The results of statistical models often express vulnerability as the probability of detecting pesticide concentrations within the groundwater of a specific area from which the empirical data were drawn. Although statistical models do not explicitly define underlying processes of pesticide fate and transport, important processes can be inferred based on proper selection of explanatory variables. An important assumption of statistical vulnerability models is that the area to which they are applied must be comparable to that in which they were developed (3). To address this assumption, statistical models rely on groundwater monitoring networks that are spatially representative of the area of interest.

The following sections outline two common statistical approaches used to assess groundwater vulnerability to pesticides: logistic regression and posterior probability distribution. Other statistically based approaches include cluster analysis (11), principal component analysis (11), and linear regression.

Logistic Regression. Logistic regression is a multivariate statistical approach that has been used extensively in the health sciences to predict a binary response in the dependent variable from measured explanatory variables, but recently, it has been used to estimate the probability of detecting pesticide concentrations in groundwater resources (6,12–17). Logistic regression is conceptually similar to multiple linear regressions because the relation between one dependent (response) variable and several independent (explanatory) variables is evaluated (18). However, logistic regression has an advantage over other generalized linear regression models because is does not require a normal sample distribution and censored (nondetect) values can be used. The concentrations of pesticides in groundwater generally are low; therefore, laboratory detection levels serve as a convenient threshold for establishing the binary response (i.e., detection of pesticides in groundwater samples versus nondetection of pesticides). The underlying assumption of logistic regression is that the natural logarithm of the odds ratio, which is the probability of being in a response category, is linearly related to the explanatory variables. The odds ratio is defined by the probability of exceeding the established threshold, expressed as

$$\text{Odds ratio} = \frac{p}{1-p} \tag{1}$$

where p is the probability of exceeding the threshold value.

The log of the odds ratio, or logit, transforms a variable constrained between 0 and 1 into a continuous variable that is a linear function of the explanatory variables (19). The logit transformation is

$$\log\left(\frac{p}{1-p}\right) = b_o + b_x \tag{2}$$

where b_o is the logistic regression constant and b_x is the vector of slope coefficients and explanatory variables. Predicted values of the response variable are converted back into probability units by using the logistic transformation; the logistic regression model takes the form

$$P = \frac{e^{(b_o+bX)}}{1+e^{(b_o+bX)}} \tag{3}$$

where P is the probability of the binary response event, often defined as detecting the pesticide of interest in groundwater, and e is the base of the natural logarithm.

An additional advantage of logistic regression is the user's ability for model validation using an independent set of pesticide concentration data. However, logistic regression, like other statistical approaches, has received criticism because the models do not represent the physical, chemical, and biological processes that affect groundwater vulnerability and process-based approaches. A detailed description of logistic regression analysis is presented by Hosmer and Lemeshow (18).

Posterior Probability Distribution. Using the posterior probability distribution method, Worrall and Kolpin (20) developed an approach for the direct assessment of groundwater vulnerability to pesticides based on a single observation of multiple contaminants. This method of direct assessment is independent of the compounds examined, and it has a direct probabilistic interpretation making it ideal for risk assessment. In addition, this method has the advantage that the measures of vulnerability are based on observation rather than expert opinion, indexes, or physical models (20). Furthermore, errors of the probabilistic interpretation can be easily quantified.

The posterior probability distribution method is a measure of the difference between two proportions (the proportion of detections in the region and the proportions of detections observed in a single observation well) (20). Because vulnerability is always calculated relative to the region as a whole, compounds that are either always detected or never detected add no discriminating information to the assessment. The proportion of detections of each compound is calculated for the entire data set, and the probability distribution for each of the proportions is determined based on the observed data. The posterior probability distribution can help identify differences between the proportions of detections in the well compared to that in the region and provides estimates of vulnerability of the area of the aquifer contributing to the well. Worrall and Kolpin (20) provide in-depth details regarding the posterior probability distribution methodology.

Although the posterior probability distribution method is advantageous because it can be used to determine a probabilistic measure of vulnerability based on empirical observation rather than expert opinion, this method relies on a number of significant assumptions that may not be reasonable for all groundwater systems (20).

Process-Based Approach

Process-based pesticide vulnerability models include a wide range of methods and depend primarily on

the extent to which they simulate subsurface solute-transport processes (21). These deterministic models require analytical or numerical solutions of mathematical equations that represent processes governing pesticide fate and transport. Although process-based models incorporate a more complete description of the physical, chemical, and biological processes that affect groundwater vulnerability, they may not necessarily provide more reliable estimates of pesticide vulnerability because of extensive data requirements needed to define the subsurface hydrogeology (3). Often, detailed data sets of the subsurface are not available or may result in predictions that are of little value if the parameters describing the system are ill-defined or if they vary significantly in time and space (22).

Process-based pesticide vulnerability assessments include complex and simple models. Complex pesticide vulnerability models can range from analytical solutions for one-dimensional transport through the unsaturated zone to coupled, unsaturated–saturated, two- or three-dimensional models (3). The Pesticide Root Zone Model (PRZM) (23) is one of the most commonly used complex models for pesticide vulnerability modeling. PRZM is a one-dimensional, deterministic-empirical/conceptual model that simulates soil–water movement by using an empirical drainage algorithm and solute transport with the advection-dispersion equation. PRZM has two distinct advantages over simple index models for estimating pesticide leaching: (1) concentrations are estimated with reference to depth and time, and (2) heterogeneity in the soil column and variability in recharge can be accounted for (24). Other complex process-based models include the Type Transfer Function (TTF), outlined by Stewart and Loague (25); the Leaching Estimation and Chemistry Model (LEACHM) (26); and Monte-Carlo simulations of deterministic models (27).

Advantages gained by using complex pesticide vulnerability models can be minimized by extensive data requirements, which have limited their use to local or field-scale evaluations. If data are unavailable, estimates are used that may introduce additional model uncertainty. Therefore, uncertainty can be reduced when using a simple method (28). Simple index-based process models have been used more routinely for large-scale and regional pesticide vulnerability modeling. Process-based index models are first-order approximations of pesticide vulnerability that describe the relation between how fast the pesticide leaches and how fast it can be degraded. The net result of these two processes determines what fraction of soil-applied pesticides potentially reaches groundwater (29).

Index models are conceptually simplified and are valid only under steady-state flow within a uniform homogeneous ideal medium. The models represent the important transport processes for pesticides, are most appropriately used as screening tools, and are intended for evaluation and comparison of pesticide behavior under constrained and limited conditions with the advantage of requiring few input data (21). The following sections describe index process models that have routinely been used to evaluate pesticide vulnerability of groundwater.

Attenuation Factor. The attenuation factor (AF) (30) is a simple index of residence time and degradation rate of a pesticide that is equivalent to the fraction of applied pesticide mass likely to leach past a reference depth. This index is a simple solution of the one-dimensional, advection-dominated transport equation and is defined as

$$\mathrm{AF} = e\left(\frac{-0.693\ d\mathrm{RF}\theta_{\mathrm{FC}}}{\mathrm{qt}_{1/2}}\right) \tag{4}$$

where d is the distance from the land surface to groundwater; RF is the retardation factor, which accounts for pesticide sorption effects; θ_{FC} is the volumetric water content at field capacity; q is the net groundwater recharge rate; and $t_{1/2}$ is the half-life of pesticide degradation. RF is defined as

$$\mathrm{RF} = \left(1 + \frac{\rho_{\mathrm{b}} f_{\mathrm{oc}} K_{\mathrm{oc}}}{\theta_{\mathrm{FC}}} + \frac{\theta_{\mathrm{g}} K_{\mathrm{H}}}{\theta_{\mathrm{FC}}}\right) \tag{5}$$

where ρ_{b} is the soil bulk density (g/cm^3), f_{oc} is the fraction of soil organic carbon on a mass basis, K_{oc} is the organic carbon sorption coefficient (mL/g), θ_{g} is the gas constant (unitless), and K_{H} is Henry's constant for the pesticide of interest (unitless).

The AF ranges from zero to one, where zero corresponds to a minimal threat of applied pesticide leaching and a value of one corresponds to all the applied pesticide mass reaching the groundwater.

Leaching Potential Index. The Leaching Potential Index (LPI) was developed by Meeks and Dean (31) and, similar to the AF, is derived from the advection-dispersion equation. The LPI is compound specific and includes information regarding adsorption and degradation parameters. The LPI is defined as

$$\mathrm{LPI} = \frac{1000\ t_{1/2} V}{0.693\ R\mathrm{F} d} \tag{6}$$

where V is the average linear vertical soil–water velocity (L/t).

Increases in LPI values reflect a direct relation between increases in pesticide vulnerability. It should be noted that the LPI is simply the inverse of the exponent in Equation 5 of the AF, and a factor of 1000 is arbitrarily included to increase the numerical values of the LPI (32).

Schlosser and McCray (28) conducted a sensitivity analysis by using the LPI to evaluate the relative importance of input-parameter variability on model-predicted vulnerability. Results indicated that the calculated vulnerabilities were most sensitive to organic carbon content, depth to groundwater, and vertical soil–water velocity.

Vulnerability Index. The Vulnerability Index (VI) (32) is a modified version of the LPI equation, defined as

$$\mathrm{VI} = \frac{200\ k\theta_{\mathrm{FC}}}{d\rho_{\mathrm{b}}(\mathrm{OM})}\left(\frac{t_{1/2}}{K_{\mathrm{oc}}}\right) F_{\mathrm{DGW}} \tag{7}$$

where k is the decay constant (day^{-1}); OM is the percentage of organic matter present in the soil; $(t_{1/2}/K_{\mathrm{oc}})$

is the leachability ratio, which is the measure of the pesticide's propensity to biodegrade ($t_{1/2}$) and to sorb to organic matter in the soil (K_{oc}); and F_{DGW} is a factor that accounts for the depth to groundwater.

The VI model is a practical approach to assessing many pesticides simultaneously by incorporating the leaching potential. The VI uses the leachability ratio to account for the leaching potential of multiple pesticides that have similar chemical properties. This method has a significant advantage over other index methods; by grouping pesticides according to their leachability ratio, vulnerability assessments are made for each group, rather than for each individual pesticide.

PESTICIDE VULNERABILITY MAPS

Pesticide vulnerability maps are spatial representations of models (i.e., overlay and index, statistical, or process-based) that identify areas of the aquifer that have a potential for pesticide contamination in the groundwater. Often, pesticide vulnerability maps are used to predict pesticide vulnerability of groundwater that has not been previously sampled. Many pesticide vulnerability assessments have incorporated the use of geographic information systems (GIS) for calculating pesticide vulnerability and visualizing the model over the study area. GIS is a modeling framework and tool designed for the analysis and display of spatial data. Many vulnerability studies use GIS because (1) a GIS can display and analyze the spatial variability of georeferenced variables important for the assessment, (2) a GIS can incorporate georeferenced measurements of pesticide concentration data, and (3) the digital display and data-manipulation ability of a GIS provides numerous advantages for creating maps of groundwater vulnerability to pesticide contamination.

UNCERTAINTY OF PESTICIDE VULNERABILITY ASSESSMENT

Uncertainty is unavoidable during estimation of pesticide vulnerability because of limitations in knowledge of contaminant behavior in the subsurface and significant limitations in the spatial databases used for assessments (3). Uncertainty in predictions reflect limitations due to (1) accurate spatial delineations of data and its transfer from real-world to digital data or maps; (2) spatial averaging and uncertainties of soil properties and other explanatory variables; (3) assumptions related to individual pesticide vulnerability approaches that often assume steady-state conditions or homogeneous conditions in the soil or unsaturated zone; (4) uncertainties from spatial interpolation from point estimates, if kriging or other interpolation methods are used; and (5) temporal variability of explanatory variables, such as land-use practices, may limit predictions of future vulnerability estimates for a given groundwater resource.

Increasingly, studies of pesticide vulnerability have acknowledged the inherent uncertainty in the assessment and have made attempts to quantify this uncertainty. Refer to the work of Freissinet et al. (33), Loague et al. (24), and Loague (34) for specific approaches to estimate and quantify uncertainty during pesticide vulnerability assessments.

BIBLIOGRAPHY

1. Barbash, J.E. and Resek, E.A. (1996). *Pesticides in Ground Water, Distribution, Trends, and Governing Factors*. Ann Arbor Press, Chelsea, MI.
2. Gilliom, R.J. (2001). Pesticides in the hydrologic system—what do we know and what's next? *Hydrological Processes* **15**: 3197–3201.
3. National Research Council. (1993). *Ground-Water Vulnerability Assessment: Predicting Relative Contamination Potential under Conditions of Uncertainty*. National Academy Press, Washington, DC.
4. USEPA (1993). *A Review of Methods for Assessing Aquifer Sensitivity and Ground Water Vulnerability to Pesticide Contamination*. EPA 813/R-93-002, Washington, DC.
5. Focazio, M.J., Reilly, T.E., Rupert, M.G., and Helsel, D.R. (2002). *Assessing Ground-Water Vulnerability to Contamination: Providing Scientifically Defensible Information for Decision Makers*. U.S. Geological Survey Circular 1224.
6. Rupert, M.G. (2003). *Probability of Detecting Atrazine/Desethyl-atrazine and Elevated Concentrations of Nitrate in Ground Water in Colorado*. U.S. Geological Survey Water-Resources Investigations Report 02-4269.
7. Flury, M. (1996). Experimental evidence of transport of pesticides through field soils—a review. *J. Environ. Qual.* **25**: 25–45.
8. Hornsby, A.G., Wauchope, R.D., and Herner, A.E. (1996). *Pesticide Properties in the Environment*. Springer-Verlag, New York.
9. Aller, L., Truman, B., Lehr, J.H., and Petty, R.J. (1985). *DRASTIC—A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings*. U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Office of Research and Development.
10. Rupert, M.G. (1999). *Improvements to the DRASTIC Ground-Water Vulnerability Mapping Method*. U.S. Geological Survey Fact Sheet 066-99.
11. Troiano, J., Johnson, B.R., Powell, S., and Schoenig, S. (1994). Use of cluster and principal component analyses to profile areas in California where ground water has been contaminated by pesticides. *Environ. Monitoring Assessment* **32**: 269–288.
12. Worrall, F. and Kolpin, D.W. (2004). Aquifer vulnerability to pesticide pollution—combining soil, land-use and aquifer properties with molecular descriptors. *J. Hydrol.* **293**: 191–204.
13. Rupert, M.G. (1998). *Probability of Detecting Atrazine/Desethyl-atrazine and Elevated Concentrations of Nitrate ($NO_2 + NO_3 - N$) in Ground Waters in the Idaho Part of the Upper Snake River Basin*. U.S. Geological Survey Water-Resources Investigations Report 98-4203.
14. Nolan, B.T., Hitt, K.J., and Ruddy, B.C. (2002). Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. *Environ. Sci. Technol.* **36**: 2138–2145.
15. Nolan, B.T. and Stoner, J.D. (2000). Nutrients in groundwaters of the conterminous United States, 1992–1995. *Environ. Sci. Technol.* **34**: 1156–1165.

16. Teso, R.R., Poe, M.P., Younglove, T., and McCool, P.M. (1996). Use of logistic regression and GIS modeling to predict groundwater vulnerability to pesticides. *J. Environ. Qual.* **25**: 425–432.
17. Eckhardt, D.A.V. and Stackelberg, P.E. (1995). Relation of ground-water quality to land use on Long Island, New York. *Ground Water* **33**: 1019–1032.
18. Hosmer, D.W. and Lemeshow, S. (1989). *Applied Logistic Regression*. John Wiley & Sons, New York.
19. Helsel, D.R. and Hirsch, R.M. (1992). *Statistical Methods in Water Resources*. Elsevier Science, New York.
20. Worrall, F. and Kolpin, D.W. (2003). Direct assessment of groundwater vulnerability from single observations of multiple contaminants. *Water Resour. Res.* **39**: 1345–1352.
21. Shukla, S., Mostaghimi, S., Shanholtz, V.O., and Collins, M.C. (1998). A GIS-based modeling approach for evaluating groundwater vulnerability to pesticides. *J. Am. Water Resour. Assoc.* **34**: 1275–1293.
22. Nolan, B.T. (1998). *Modeling Approaches for Assessing the Risk of Nonpoint-Source Contamination of Ground Water*. U.S. Geological Survey Open-file report 98-531.
23. Carsel, R.F., Smith, C.N., Mulkey, L.A., Dean, J.D., and Howise, P. (1984). *User's Manual for the Pesticide Root Zone Model (PRZM), Release 1*. USEPA, Washington, DC.
24. Loague, K., Bernknopf, R.L., Green, R.E., and Giambelluca, T.W. (1996). Uncertainty of groundwater vulnerability assessment for agricultural regions in Hawaii: Review. *J. Environ. Qual.* **25**: 475–490.
25. Stewart, I.T. and Loague, K. (2003). Development of type transfer functions for regional-scale nonpoint source groundwater vulnerability assessments. *Water Resour. Res.* **39**: 1359–1371.
26. Hutson, J.L. and Wagenet, R.J. (1992). *Leaching Estimation and Chemistry Model. Version 3, User Manual*. Res. Ser. No 92-3. Dept. of Soil, Crop and Atmospheric Sciences. Cornell University, Ithaca, NY.
27. Soutter, M. and Musy, A. (1998). Coupling 1D Monte-Carlo simulations and geostatistics to assess groundwater vulnerability to pesticide contamination on a regional scale. *J. Contam. Hydrol.* **32**: 25–39.
28. Schlosser, S.A. and McCray, J.E. (2002). Sensitivity of a pesticide leaching-potential index model to variations in hydrologic and pesticide-transport properties. *Environ. Geosciences* **9**: 66–73.
29. Rao, P.S.C. and Alley, W.M. (1993). Pesticides. In: W.M. Alley (Ed.). *Regional Ground-Water Quality*. Van Nostrand Reinhold, New York, pp. 345–377.
30. Rao, P.S.C., Hornsby, A.G., and Jessup, R.E. (1985). Indices for ranking the potential for pesticide contamination of groundwater. *Soil Crop Sci. Soc. Fl. Proc.* **44**: 1–8.
31. Meeks, Y.J. and Dean, J.D. (1990). Evaluating groundwater vulnerability to pesticides. *J. Water Resour. Plann. Manage.* **116**(5): 693–707.
32. Schlosser, S.A., McCray, J.E., Murray, K.E., and Austin, B. (2002). A subregional-scale method to assess aquifer vulnerability to pesticides. *Ground Water* **40**(4): 361–367.
33. Freissinet, C., Vauclin, M., and Erlich, M. (1999). Comparison of first-order analysis and fuzzy set approach for the evaluation of imprecision in a pesticide groundwater pollution screening model. *J. Contam. Hydrol.* **37**: 21–43.
34. Loague, K. (1991). The impact of land use on estimates of pesticide leaching potential: Assessments and uncertainties. *J. Contam. Hydrol.* **8**: 157–175.

GROUNDWATER—NATURE'S HIDDEN TREASURE

Environment Canada



Groundwater is an essential and vital resource for about a quarter of all Canadians. It is their sole source of water for drinking and washing, for farming and manufacturing, indeed, for all their daily water needs. Yet for the majority of Canadians—those who do not depend on it—groundwater is a hidden resource whose value is not well understood or appreciated.

Our image of Canada is of a land of sparkling lakes, rivers and glaciers. Groundwater, which exists everywhere under the surface of the land, is not part of this picture. Not surprisingly, therefore, concerns of Canadians about water quality focus primarily on surface waters—our lakes and rivers. The less visible, but equally important, groundwater resources have received less public attention, except in regions of Canada where people depend on them.

GROUNDWATER NEEDS PROTECTION

In recent years, however, a number of events affecting groundwater quality have contributed to a heightened public awareness and concern about the importance and vulnerability of the resource. Media reports about the contamination of wells from leaking gasoline storage tanks or dry cleaning solvents, and about the effects on groundwater of chemical leakage from landfill or industrial waste disposal sites have raised public concerns about

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groundwater quality. Early in 1990, chemical seepage, caused by the tire fire at Hagersville, Ontario, threatened to pollute groundwater supplies in that region. Newspaper reports alerted area residents and helped focus attention on the problem of groundwater pollution.

Even where we might not use it directly as a drinking water supply we must still protect groundwater, since it will carry contaminants and pollutants from the land into the lakes and rivers from which other people get a large percentage of their freshwater supply.

Groundwater and Geology

Groundwater is also important quite apart from its value as a resource or its close connection with surface water supplies. Engineers must consider groundwater when planning almost any kind of structure, either above or below the ground. Ignoring the effect of groundwater on slope stability can be both costly and dangerous. Geologists see groundwater as a major force in geological change. The fluid pressures exerted by groundwater, for example, play an important role in the occurrence of earthquakes. Geologists also know that the movement of water through underground geologic formations controls the migration and the accumulation of petroleum and the formation of some ore deposits.

WHAT IS GROUNDWATER?

It is sometimes thought that water flows through underground rivers or that it collects in underground lakes. Groundwater is not confined to only a few channels or depressions in the same way that surface water is concentrated in streams and lakes. Rather, it exists almost everywhere underground. It is found underground in the spaces between particles of rock and soil, or in crevices and cracks in rock. The water filling these openings is usually within 100 metres of the surface. Much of the earth's fresh water is found in these spaces. At greater depths, because of the weight of overlying rock, these openings are much smaller, and therefore hold considerably smaller quantities of water.

Groundwater flows slowly through water-bearing formations (aquifers) at different rates. In some places, where groundwater has dissolved limestone to form caverns and large openings, its rate of flow can be relatively fast but this is exceptional.

Many terms are used to describe the nature and extent of the groundwater resource. The level below which all the spaces are filled with water is called the *water table*. Above the water table lies the *unsaturated zone*. Here the spaces in the rock and soil contain both air and water. Water in this zone is called *soil moisture*. The entire region below the water table is called the *saturated zone*, and water in this saturated zone is called *groundwater*.

WHAT IS AN AQUIFER?

Although groundwater exists everywhere under the ground, some parts of the saturated zone contain more water than others. An *aquifer* is an underground formation of permeable rock or loose material which can produce useful quantities of water when tapped by a well. Aquifers come in all sizes. They may be small, only a few hectares in area, or very large, underlying thousands of square kilometres of the earth's surface. They may be only a few metres thick, or they may measure hundreds of metres from top to bottom.

GROUNDWATER—ALWAYS ON THE MOVE

Permeable material contains interconnected cracks or spaces that are both numerous enough and large enough to allow water to move freely. In some permeable materials groundwater may move several metres in a day; in other places, it moves only a few centimetres in a century. Groundwater moves very slowly through relatively *impermeable* materials such as clay and shale.

Groundwater scientists generally distinguish between two types of aquifers in terms of the physical attributes of the aquifer: porous media and fractured aquifers.

Porous media are those aquifers consisting of aggregates of individual particles such as sand or gravel. The groundwater occurs in and moves through the openings between the individual grains. Porous media where the grains are not connected to each other are considered *unconsolidated*. If the grains are cemented together, such aquifers are called *consolidated*. Sandstones are examples of consolidated porous media.

Fractured aquifers are rocks in which the groundwater moves through cracks, joints or fractures in otherwise solid rock. Examples of fractured aquifers include granite and basalt. Limestones are often fractured aquifers, but here the cracks and fractures may be enlarged by solution, forming large channels or even caverns. Limestone terrain where solution has been very active is termed *karst*. Porous media such as sandstone may become so highly cemented or recrystallized that all of the original space is filled. In this case, the rock is no longer a porous medium. However, if it contains cracks it can still act as a fractured aquifer.

Most of the aquifers of importance to us are unconsolidated porous media such as sand and gravel. Some very porous materials are not permeable. Clay, for instance, has many spaces between its grains, but the spaces are not large enough to permit free movement of water.

Groundwater usually flows downhill with the slope of the water table. Like surface water, groundwater flows toward, and eventually drains into streams, rivers, lakes and the oceans. Groundwater flow in the aquifers underlying surface drainage basins, however, does not always mirror the flow of water on the surface. Therefore, groundwater may move in different directions below the ground than the water flowing on the surface.

Unconfined aquifers are those that are bounded by the water table. Some aquifers, however, lie beneath layers of impermeable materials. These are called *confined aquifers*, or sometimes *artesian aquifers*. A well in such an aquifer is called an *artesian well*. The water in these wells rises higher than the top of the aquifer because of confining pressure. If the water level rises above the ground surface a *flowing artesian well* occurs. The *piezometric surface* is

the level to which the water in an artesian aquifer will rise.

Groundwater As a Source of Energy

Groundwater may be used as a source of heat. Ground source heat pumps are receiving increased attention as energy efficient commercial and residential heating/cooling systems. Although initial costs are higher than air source systems—due to the additional costs of the underground installations—the much greater energy efficiency of ground source systems makes them increasingly attractive.

Research into the use of geothermal water has been carried out in a number of institutions across Canada. The City of Moose Jaw has developed a geothermal heating system for a public swimming pool and recreational facility. Carleton University in Ottawa already uses groundwater to heat and cool its buildings. The Health Centre complex in Sussex, New Brunswick, has been utilizing an aquifer for thermal energy storage since 1995.

GROUNDWATER—A MAJOR LINK IN THE HYDROLOGIC CYCLE

Groundwater circulates as part of the hydrologic cycle. As precipitation and other surface water sources recharge the groundwater it drains steadily, and sometimes very slowly, towards its discharge point.

Groundwater does not stay underground forever, and it does not lie still waiting for us to draw it from a well. The *hydrologic cycle* is the series of transformations that occur in the circulation of water from the atmosphere onto the surface and into the subsurface regions of the earth, and then back from the surface to the atmosphere. Precipitation becomes surface water, soil moisture, and groundwater. Groundwater circulates back to the surface, and from the surface all water returns to the atmosphere through evaporation and transpiration.

When precipitation falls on the land surface, part of the water runs off into the lakes and rivers. Some of the water from melting snow and from rainfall seeps into the soil and percolates into the saturated zone. This process is called recharge (Fig. 2). Places where recharge occurs are referred to as *recharge areas*.

Eventually, this water reappears above the ground. This is called *discharge*. Groundwater may flow into streams, rivers, marshes, lakes and oceans, or it may discharge in the form of *springs* and flowing wells.

Groundwater discharge can contribute significantly to surface water flow. In dry periods, the flow of some streams may be supplied entirely by groundwater. At all times of the year, in fact, the nature of underground formations has a profound effect on the volume of surface runoff. While the rate of discharge determines the volume of water moving from the saturated zone into streams, the rate of recharge determines the volume of water running over the surface. When it rains, for instance, the volume of water running into streams and rivers depends on how much rainfall the underground materials can absorb. When there is more water on the surface than can be absorbed into the groundwater zone, it runs off into streams and lakes.

The *residence time* of groundwater, i.e., the length of time water spends in the groundwater portion of the hydrologic cycle, varies enormously. Water may spend as little as days or weeks underground, or as much as 10 000 or more years. Residence times of tens, hundreds, or even thousands of years are not unusual. By comparison, the average turnover time of river water, or the time it takes the water in rivers to completely replace itself, is about two weeks.

Groundwater and Permafrost

Most of the Northwest Territories is covered by either the Canadian Shield or permafrost (permanently frozen ground), both of which inhibit the flow of groundwater. The major exceptions include the Mackenzie Mountains in the western Northwest Territories and Yukon, and the limestone terrain southwest of Great Slave Lake, where soils, fractured rock, and glacial debris provide material that can store and release groundwater.

On a local scale, the seasonal development of a thawed "active layer" above the permafrost can provide permeable pathways for the subsurface movement of water and contaminants.

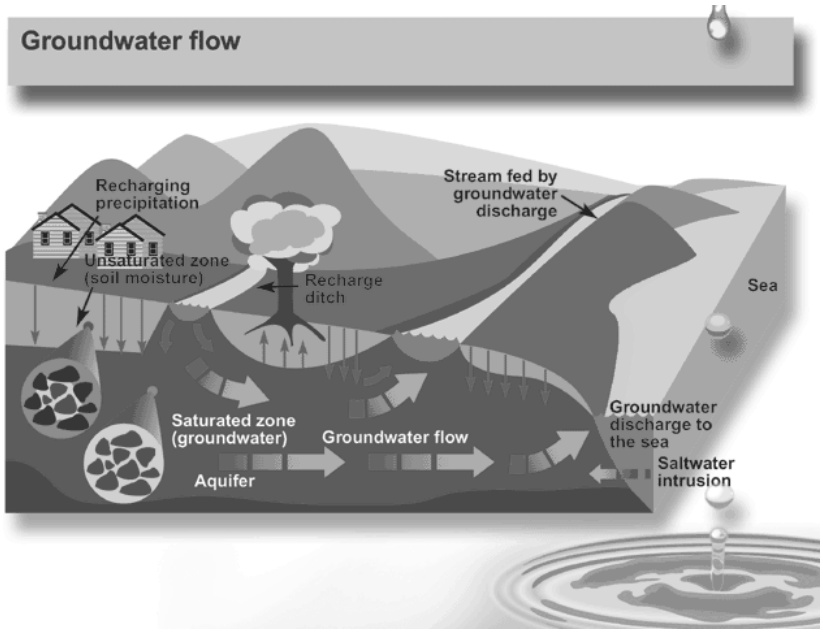
ALMOST NINE MILLION CANADIANS DEPEND ON GROUNDWATER

In Canada, 8.9 million people, or 30.3% of the population, rely on groundwater for domestic use. Approximately two thirds of these users live in rural areas. In many areas, wells produce more reliable and less expensive water supplies than those obtained from nearby lakes, rivers and streams. The remaining users are located primarily in smaller municipalities where groundwater provides the primary source for their water supply systems. For instance, 100% of Prince Edward Island's population and over 60% of the population of New Brunswick rely on groundwater to meet their domestic needs.

Furthermore, the predominant use of groundwater varies by province. In Ontario, Prince Edward Island, New Brunswick, and the Yukon, the largest users of groundwater are municipalities; in Alberta, Saskatchewan, and Manitoba, the agricultural industry for livestock watering; in British Columbia, Quebec and the Northwest Territories, industry; and in Newfoundland and Nova Scotia, rural domestic use. Prince Edward Island is almost totally dependent on groundwater for all its uses.

According to some estimates, the quantity of groundwater in the earth would cover the entire surface of the globe to a depth of 120 metres. By contrast, the volume of surface water in lakes, rivers, reservoirs and swamps could be contained in a depth of about one quarter of a metre.

It is extremely difficult to estimate the volume of groundwater on the entire planet. For example, a recent review of the literature revealed estimated figures ranging from 7 000 000 to 330 000 000 cubic kilometres. However,



all the estimates imply that if we do not include the water frozen in ice caps, glaciers and permanent snow, groundwater makes up almost the entire volume of the earth's usable *fresh* water. Yet, this supply is often not easily accessible, and it may be difficult and expensive to develop these water supplies in some regions. The quality of the groundwater source is also a significant determining factor when identifying its use.

GROUNDWATER QUALITY

We often think of water quality as a matter of taste, clarity and odour, and in terms of other properties which determine whether water is fit for drinking. For other uses different properties may be important. Most of these properties depend on the kinds of substances that are dissolved or suspended in the water. Water for most industrial uses, for instance, must not be corrosive and must not contain dissolved solids that might precipitate on the surfaces of machinery and equipment.

Pure water is tasteless and odourless. A molecule of water contains only hydrogen and oxygen atoms. Water is never found in a pure state in nature. Both groundwater and surface water may contain many constituents, including microorganisms, gases, inorganic and organic materials.

The chemical nature of water continually evolves as it moves through the hydrologic cycle. The kinds of chemical constituents found in groundwater depend, in part, on the chemistry of the precipitation and recharge water. Near coastlines, precipitation contains higher concentrations of sodium chloride, and downwind of industrial areas, airborne sulphur and nitrogen compounds make precipitation acidic.

One of the most important natural changes in groundwater chemistry occurs in the soil. Soils contain high concentrations of carbon dioxide which dissolves in the groundwater, creating a weak acid capable of dissolving many silicate minerals. In its passage from recharge to discharge area, groundwater may dissolve substances it encounters or it may deposit some of its constituents along the way. The eventual quality of the groundwater depends on temperature and pressure conditions, on the kinds of rock and soil formations through which the groundwater flows, and possibly on the residence time. In general, faster flowing water dissolves less material. Groundwater, of course, carries with it any soluble contaminants which it encounters.

Saltwater Intrusion

Saltwater intrusion can be a problem in coastal areas where rates of groundwater pumping are high enough to cause sea water to invade freshwater aquifers (Fig. 2). The problem can be avoided by appropriate well field design and by drilling relief wells to keep the salt water away from the fresh groundwater source. Some wells pumping saltwater in Prince Edward Island, are used as convenient water supplies for shellfish farms.

Scientists assess *water quality* by measuring the amounts of the various constituents contained in the water. These amounts are often expressed as milligrams per litre (mg/L), which is equivalent to the number of grams of a substance per million grams of water.

The suitability of water for a given use depends on many factors such as hardness, salinity and pH. Acceptable values for each of these parameters for any given use depend on the use, not on the source of the water, so that the considerations important for surface water (as mentioned in Freshwater Series No. A-3, entitled "Clean Water—Life Depends on It!") are equally applicable to groundwater.

The natural quality of groundwater differs from surface water in that:

a. for any given source, its quality, temperature and other parameters are less variable over the course of time; and,
b. in nature, the range of groundwater parameters encountered is much larger than for surface water, e.g., total dissolved solids can range from 25 mg/L in some places in the Canadian Shield to 300 000 mg/L in some deep saline waters in the Interior Plains.

At any given location, groundwater tends to be harder and more saline than surface water, but this is by no means a universal rule. It is also generally the case that groundwater becomes more saline with increasing depth, but again, there are many exceptions.

Leaking Underground Storage Tanks and Piping

Leaks of petroleum products have been increasing over the last two decades because underground steel tanks installed in large numbers in the 1950s and 1960s have become corroded. Before 1980, most underground tanks were made of steel. Without adequate corrosion protection, up to half of them leak by the time they are 15 years old.

Groundwater dissolves many different compounds, and most of these substances have the potential to contaminate large quantities of water. For example, one litre of gasoline can contaminate 1 000 000 litres of groundwater. This problem is particularly severe in the Atlantic provinces where there is a high usage of groundwater. In many cases, the problem is noticed long after the aquifer is contaminated, for example, when consumers start tasting or smelling gasoline.

As groundwater flows through an aquifer it is naturally filtered. This filtering, combined with the long residence time underground, means that groundwater is usually free from disease-causing microorganisms. A source of contamination close to a well, however, can defeat these natural safeguards. Natural filtering also means that groundwater usually contains less suspended material and undissolved solids than surface water.

DNAPLs

A type of contaminant that is especially troublesome is the group of chemicals known as *dense non-aqueous phase liquids*, or *DNAPL*s. These include chemicals used in dry cleaning, wood preservation, asphalt operations, machining, and in the production and repair of automobiles, aviation equipment, munitions, and electrical equipment. They can also be generated and released in accidents, e.g., the Hagersville "tire fire." These substances are heavier than water and they sink quickly into the ground. This makes spills of DNAPLs more difficult to handle than spills of petroleum products. As with petroleum products, the problems are caused by groundwater dissolving some of the compounds in these volatile substances. These compounds can then move with the groundwater flow. Except in large cities, drinking water is rarely tested for these contaminants.

HOW WE CONTAMINATE GROUNDWATER

Any addition of undesirable substances to groundwater caused by human activities is considered to be *contamination*. It has often been assumed that contaminants left on or under the ground will stay there. This has been shown to be wishful thinking. Groundwater often spreads the effects of dumps and spills far beyond the site of the original contamination. Groundwater contamination is extremely difficult, and sometimes impossible, to clean up.

Sources of Contamination That Can Cause Groundwater Contamination

Point sources

- On-site septic systems
- Leaky tanks or pipelines containing petroleum products
- Leaks or spills of industrial chemicals at manufacturing facilities
- Underground injection wells (industrial waste)
- Municipal landfills
- Livestock wastes
- Leaky sewer lines
- Chemicals used at wood preservation facilities
- Mill tailings in mining areas
- Fly ash from coal-fired power plants
- Sludge disposal areas at petroleum refineries
- Land spreading of sewage or sewage sludge
- Graveyards
- Road salt storage areas
- Wells for disposal of liquid wastes
- Runoff of salt and other chemicals from roads and highways
- Spills related to highway or railway accidents
- Coal tar at old coal gasification sites
- Asphalt production and equipment cleaning sites

Non-point (distributed) sources

- Fertilizers on agricultural land
- Pesticides on agricultural land and forests
- Contaminants in rain, snow, and dry atmospheric fallout

Source: Adapted from Cherry, p. 395.

Groundwater contaminants come from two categories of sources: *point sources* and distributed, or *non-point sources*. Landfills, leaking gasoline storage tanks, leaking septic tanks, and accidental spills are examples of point sources. Infiltration from farm land treated with pesticides and fertilizers is an example of a non-point source.

Among the more significant point sources are municipal landfills and industrial waste disposal sites. When either of these occur in or near sand and gravel aquifers, the potential for widespread contamination is the greatest.

In Ville Mercier, Quebec, for example, the disposal of industrial wastes into lagoons in an old gravel pit over many years rendered the water supplies of thousands of residents in the region unusable. Water had to be pumped from a well 10 kilometres away to replace the area's supply.

Other point sources are individually less significant, but they occur in large numbers all across the country. Some of these dangerous and widespread sources of contamination are septic tanks, leaks and spills of petroleum products and of dense industrial organic liquids.

Septic systems are designed so that some of the sewage is degraded in the tank and some is degraded and absorbed by the surrounding sand and subsoil. Contaminants that may enter groundwater from septic systems include bacteria, viruses, detergents, and household cleaners. These can create serious contamination problems. Despite the fact that septic tanks and cesspools are known sources of contaminants, they are poorly monitored and very little studied.

Contamination can render groundwater unsuitable for use. Although the overall extent of the problem across Canada is unknown, many individual cases of contamination have been investigated such as Ville Mercier in Quebec; the highway de-icing salt problem in Nova Scotia; industrial effluents in Elmira, Ontario; various pesticides in the Prairie provinces; industrial contamination in Vancouver, British Columbia; and so on. In many cases, contamination is recognized only after groundwater users have been exposed to potential health risks. The cost of cleaning up contaminated water supplies is usually extremely high.

Contamination problems are increasing in Canada primarily because of the large and growing number of toxic compounds used in industry and agriculture. In rural Canada, scientists suspect that many household wells are contaminated by substances from such common sources as septic systems, underground tanks, used motor oil, road salt, fertilizer, pesticides, and livestock wastes. Scientists also predict that in the next few decades more contaminated aquifers will be discovered, new contaminants will be identified, and more contaminated groundwater will be discharged into wetlands, streams and lakes.

Once an aquifer is contaminated, it may be unusable for decades. The residence time, as noted earlier, can be anywhere from two weeks or 10 000 years.

Furthermore, the effects of groundwater contamination do not end with the loss of well-water supplies. Several studies have documented the migration of contaminants from disposal or spill sites to nearby lakes and rivers as this groundwater passes through the hydrologic cycle, but the processes are not as yet well understood. In Canada, pollution of surface water by groundwater is probably at least as serious as the contamination of groundwater supplies. Preventing contamination in the first place is by far the most practical solution to the problem. This can be accomplished by the adoption of effective groundwater management practices by governments, industries and all Canadians. Although progress is being made in this direction, efforts are hampered by a serious shortage of groundwater experts and a general lack of knowledge about how groundwater behaves.

GROUNDWATER AND ENGINEERING

Groundwater can also have dramatic implications for engineering and geotechnical studies. The study of groundwater is essential for engineers who construct dams, tunnels, water conveyance channels, mines, and other structures. Groundwater must be considered whenever the stability of slopes is important, whether the slope is natural or constructed. Groundwater must also be taken into account when devising measures to control flooding. In all of these situations, groundwater flow and fluid pressure can create serious *geotechnical problems*.

Groundwater, for example, may create structural weaknesses in dams, or it may flow underground right around the structure as it did at the Jerome Dam in Idaho. Water flowed so efficiently through the rock formations surrounding the reservoir that the dam would hold no water, even though it was structurally sound.

In another case, when geological exploration was being carried out in preparation for the construction of the Revelstoke Dam in British Columbia, geologists and engineers were concerned about an old landslide on the bank of the proposed reservoir. They suspected that the water held in the reservoir could increase groundwater pressures enough to make the slide unstable. The solution was to increase drainage around the slide to ensure that groundwater pressures did not increase. In 1963, these same conditions at the Vaiont reservoir in Italy caused a slide which killed 2500 people.

Other problems result from the excessive use of groundwater. *Overdrafting* occurs when people draw water out of an aquifer faster than nature can replenish it. The most obvious problem created is a shortage of water. Overdrafting, however, can also create significant geotechnical problems. Although not an issue in Canada, at many locations around the world overdrafting has caused *land subsidence*. This can produce severe engineering difficulties. Parts of Mexico City, for instance, have subsided as much as 10 metres in the past 70 years, resulting in a host of problems in its water supply and sewerage system. Land subsidence may also occur when the water table is lowered by drainage. In the early 1970s, for example, an entire residential subdivision in Ottawa subsided when a collector sewer was constructed nearby. The subsidence seriously damaged the residents' property.

Groundwater and Wetlands

Wetlands, which provide a summer home to nearly all of North America's 45 million ducks and other waterfowl, often have very close connections with the groundwater system. Some wetlands, e.g., potholes in higher ground, may serve as important groundwater recharge areas. Others, especially those in low-lying areas, may be the receptors for significant amounts of groundwater discharge. Therefore, if the underlying groundwater is contaminated, detrimental consequences will be felt by the wildlife and all other resources dependent on that wetland.

SAFEGUARDING OUR GROUNDWATER SUPPLY

Groundwater is an essential resource. It exists everywhere under the Canadian landscape and is vitally connected to our rich surface water resources.

Contamination of groundwater is a serious problem in Canada. Industrial and agricultural activities are major sources of contaminants, but Canadian households are equally important sources.

Groundwater moves so slowly that problems take a long time to appear. Because of this, and because it is so expensive to clean up a contaminated aquifer (if it can be done at all), it is preferable by far to prevent contamination from happening in the first place. For example, leaking underground storage tanks can be replaced by tanks that will not corrode; landfills can be sited in locations where leachates will not contaminate underlying groundwater; and the impacts of spills of hazardous materials reduced by restricting access to recharge areas.

All levels of government in Canada are starting to take some of the actions necessary to protect our groundwater supplies, but there is a long way to go before these measures are fully effective. At the same time, universities and government research institutes are investigating what happens to water underground and what can be done to preserve it and even improve its availability to us. Both as a society and as individuals, we must keep in mind groundwater's susceptibility to contamination.

Groundwater is just as important as the sparkling lakes and rivers of our postcard image of Canada. This national treasure may be "hidden," but it must not be forgotten.

READING LIST

American Chemical Society. *Ground Water Information Pamphlet*. American Chemical Society, Department of Public Affairs: Washington, 1983. 14 pp.

American Institute of Professional Geologists. *Ground Water: Issues and Answers*. American Institute of Professional Geologists: Arvado, Colo., 1986. 24 pp.

Bowen, Robert. *Groundwater*. Elsevier Applied Science Publishers: London, UK, 1986. 427 pp.

Cherry, John A. "Groundwater Occurrence and Contamination in Canada." In M.C. Healey and R.R. Wallace, *Canadian Aquatic Resources*, eds., Canadian Bulletin of Fisheries and Aquatic Sciences 215: 387–426. Department of Fisheries and Oceans: Ottawa, 1987.

Coon, David, and Janice Harvey. *The Groundwater Pollution Primer*. Conservation Council, Fredericton, N.B., July 1987. 44 pp.

Federal-Provincial Advisory Committee on Environmental and Occupational Health. *Guidelines for Canadian Drinking Water Quality*, 4th ed., Health and Welfare Canada: Ottawa, 1989. 25 pp.

Freeze, R.Allen, and John A. Cherry. *Groundwater*. Prentice-Hall: Englewood Cliffs N.J., 1979. 604 pp.

Hess, Paul J. *Ground-Water Use in Canada, 1981*. National Hydrology Research Institute: Ottawa, 1986. NHRI Paper No. 28, IWD Technical Bulletin No. 140. 43 pp.

Johnston, L.M., and J.A. Gilliland. *"Ground Water—Why Worry?"* Unpublished Report, National Hydrology Research Institute, Saskatoon, Sask., 1987. NHRI Contribution No. 87008.

Keating, Michael. *To the Last Drop: Canada and the World's Water Crisis*. MacMillan: Toronto, 1986. 265 pp.

Laycock, A.H. "The Amount of Canadian Water and Its Distribution." In M.C. Healey and R.R. Wallace, *Canadian Aquatic Resources*, eds., Canadian Bulletin of Fisheries and Aquatic Sciences 215: 13–42. Department of Fisheries and Oceans: Ottawa, 1987.

McNeely, R.N., V.P. Neimanis, and L. Dwyer. *Water Quality Sourcebook: A Guide to Water Quality Parameters*. Inland Waters Directorate, Water Quality Branch: Ottawa, 1979. 89 pp.

Price, Michael. *Introducing Groundwater*. George Allen & Unwin: London, UK, 1985. 195 pp.

Speidel, David H., L.C. Ruedisili, and A.F. Agnew. *Perspectives on Water, Uses and Abuses*. Oxford University Press: New York, N.Y., 1988.

Todd, David Keith. *Groundwater Hydrology*, 2nd ed. John Wiley & Sons: New York, 1980. 535 pp.

U.S. Environmental Protection Agency. *EPA Ground Water Handbook*. Government Institutes, Inc.: Rockville, Md., 1989. 212 pp.

FRESHWATER SERIES A-5

Note: A resource guide, entitled Let's Not Take Water For Granted, is available to help classroom teachers of grades 5–7 use the information from the Water Fact Sheets.

PHARMACEUTICALS, HORMONES, AND OTHER ORGANIC WASTEWATER CONTAMINANTS IN U.S. STREAMS

HERBERT T. BUXTON
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United States Geological Survey

A recent study by the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS) shows that a broad range of chemicals found in residential,

This article is a US Government work and, as such, is in the public domain in the United States of America.

industrial, and agricultural wastewaters commonly occurs in mixtures at low concentrations downstream from areas of intense urbanization and animal production. The chemicals include human and veterinary drugs (including antibiotics), natural and synthetic hormones, detergent metabolites, plasticizers, insecticides, and fire retardants. One or more of these chemicals were found in 80 percent of the streams sampled. Half of the streams contained 7 or more of these chemicals, and about one-third of the streams contained 10 or more of these chemicals. This study is the first national-scale examination of these organic wastewater contaminants in streams and supports the USGS mission to assess the quantity and quality of the Nation's water resources. A more complete analysis of these and other emerging water-quality issues is ongoing.

BACKGROUND

Chemicals, used everyday in homes, industry and agriculture, can enter the environment in wastewater. These chemicals include human and veterinary drugs (including antibiotics), hormones, detergents, disinfectants, plasticizers, fire retardants, insecticides, and antioxidants. To assess whether these chemicals are entering our Nation's streams, the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS) collected and analyzed water samples from 139 streams in 30 states during 1999 and 2000. Streams were sampled that were considered susceptible to contamination from various wastewater sources, such as those downstream from intense urbanization or livestock production. Thus, the results of this study are not considered representative of all streams.

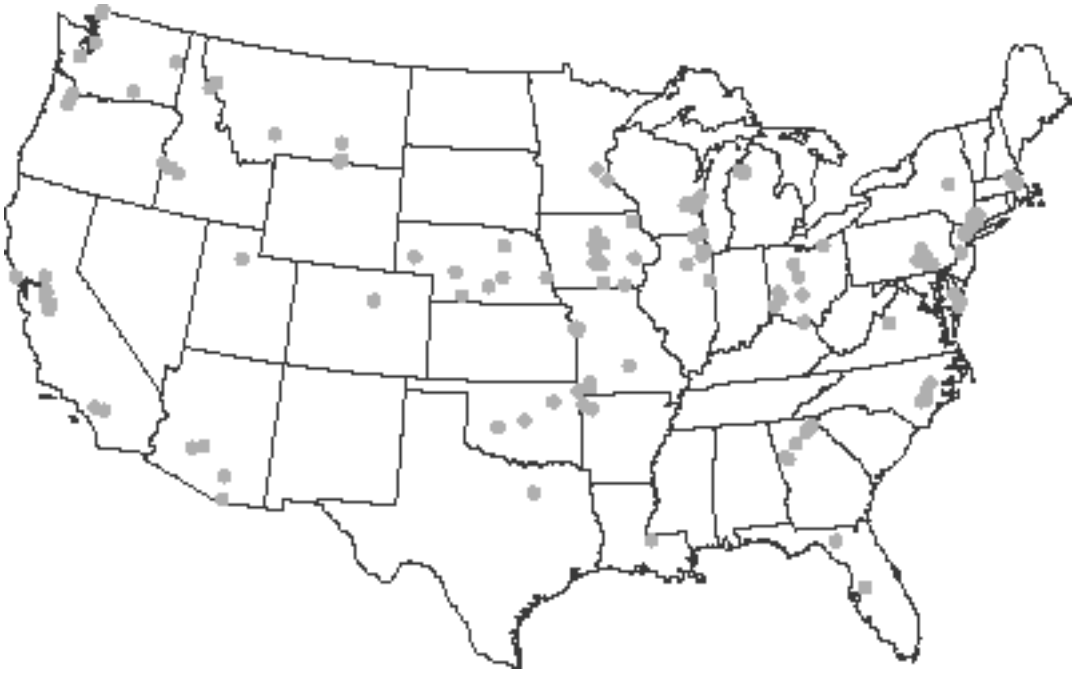
Although each of the 95 chemicals is used extensively, there is little information about the extent or occurrence of many of these compounds in the environment. Some may be indicators of certain classes of contamination sources, such as livestock or human waste, and some have human or environmental health implications. The results of this study are a starting point for investigation of the transport of a wide range of organic wastewater contaminants in the Nation's waters.

New laboratory methods were developed in several USGS research laboratories to provide the analytical capability to measure concentrations of 95 wastewater-related organic chemicals in water. Uniform sample-collection protocols and field and laboratory quality-assurance programs were followed to ensure that results are comparable and representative of actual stream conditions.

FINDINGS

One or more chemicals were detected in 80 percent of the streams sampled, and 82 of the 95 chemicals were detected at least once. Generally, these chemicals were found at very low concentrations (in most cases, less than 1 part per billion). Mixtures of the chemicals were common; 75 percent of the streams had more than one, 50 percent had 7 or more, and 34 percent had 10 or more.

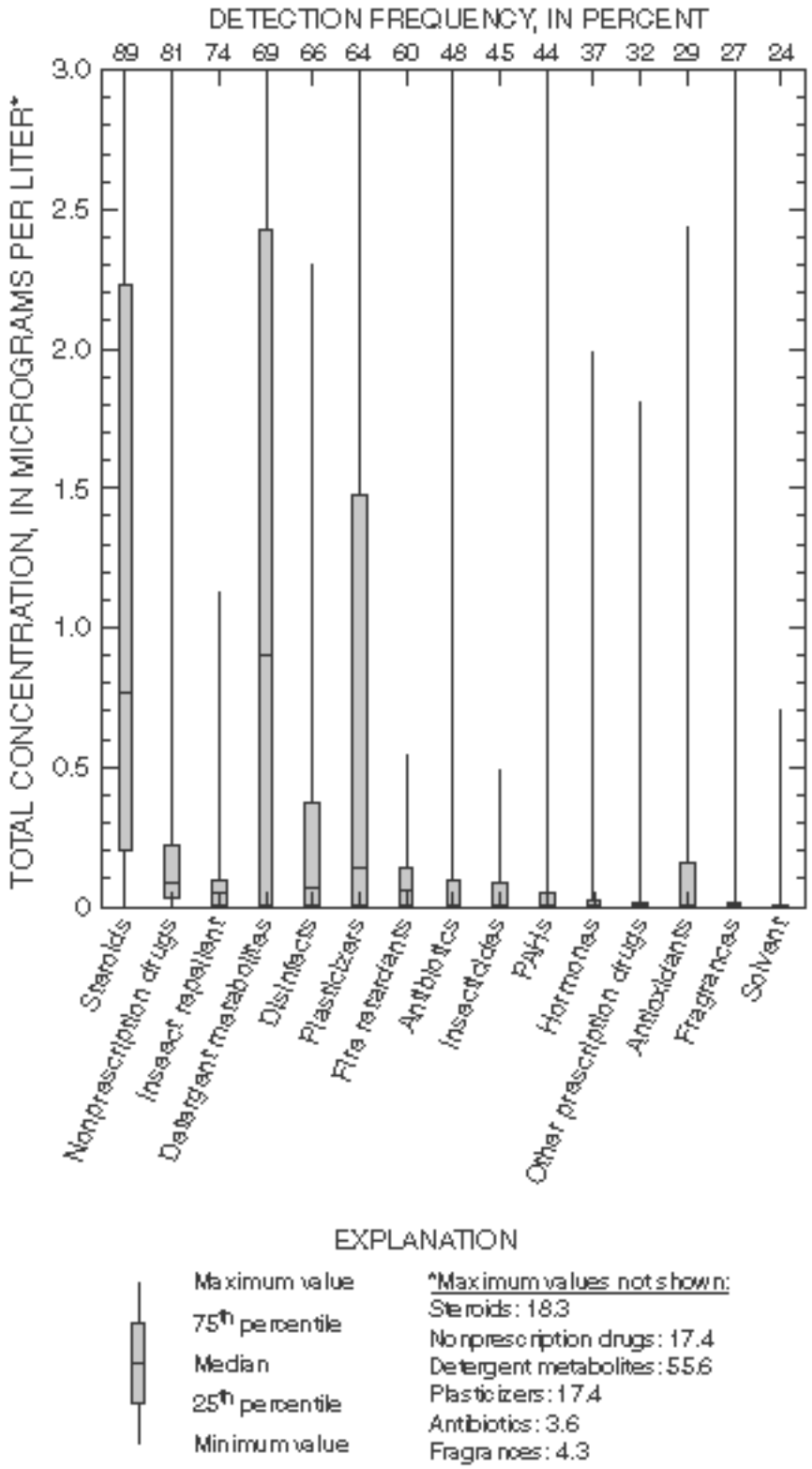
The most frequently detected chemicals (found in more than half of the streams) were coprostanol (fecal steroid), cholesterol (plant and animal steroid), N-N-diethyltoluamide (insect repellent), caffeine (stimulant), triclosan (antimicrobial disinfectant), tri (2-chloroethyl) phosphate (fire retardant), and 4-nonylphenol (nonionic detergent metabolite). Steroids, nonprescription drugs, and insect repellent were the chemical groups most frequently detected. Detergent metabolites, steroids, and plasticizers generally were measured at the highest concentrations.



Pharmaceuticals, hormones, and other organic wastewater contaminants were measured in 139 streams during 1999 and 2000.

HUMAN AND ENVIRONMENTAL EFFECTS

Knowledge of the potential human and environmental health effects of these 95 chemicals is highly varied; drinking-water standards or other human or ecological health criteria have been established for 14. Measured concentrations rarely exceeded any of the standards or criteria. Thirty-three are known or suspected to be



Steroids, nonprescription drugs, and an insect repellent were the three chemical groups most commonly detected in susceptible streams. Detergent metabolites, steroids, and plasticizers generally were found at the highest concentrations.

hormonally active; 46 are pharmaceutically active. Little is known about the potential health effects to humans or aquatic organisms exposed to the low levels of most of these chemicals or the mixtures commonly found in this study.

SIGNIFICANCE OF FINDINGS

This study suggests that mixtures of pharmaceuticals, hormones, and other wastewater contaminants can occur at low concentrations in streams that are susceptible to various wastewater sources. It provides methodology and guidance for future monitoring and assessment of these types of environmental contaminants, and establishes the needed foundation for setting priorities for further study of sources, pathways and effects.



Household chemicals can enter streams through wastewater discharges. A wastewater treatment facility near Atlanta, Georgia, is shown above. (Photograph by Daniel J. Hippe, U.S. Geological Survey).



Veterinary pharmaceuticals used in animal agriculture can enter streams through runoff or infiltration. A swine facility near the South Fork Iowa River, Iowa, is shown above. (Photograph by Doug Schnoebelen, U.S. Geological Survey).

FUTURE DIRECTIONS

Further analyses of these data, including relationships to specific source types, are ongoing. The Toxic Substances Hydrology Program is conducting research on the occurrence of organic wastewater chemicals in susceptible wells and drinking-water sources across the nation; assessments of antibiotics and antibiotic-resistant bacteria; the identification of wastewater indicators; and the development of new laboratory analytical capabilities, including sediment and fish tissue.

ADDITIONAL INFORMATION

These findings are based on "Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance," an article published in the March 15, 2002 issue of Environmental Science & Technology, v. 36, no. 6, pages 1202–1211. Data are presented in a companion USGS report, "Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000" (USGS Open-File Report 02-94). These and other reports, data, and maps can be accessed on the Internet at http://toxics.usgs.gov.

THE ENVIRONMENTAL IMPACT OF IRON IN GROUNDWATER

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Iron is a common constituent in soils and groundwater. It readily participates in subsurface redox reactions and under some conditions can cause taste, odor, and flow problems with drinking water wells and can precipitate and plug up *in situ* groundwater remediation systems. In other geochemical conditions, iron can aid in the remediation of certain chemicals undergoing chemical transformations associated with Redox reactions. Ferrous iron is used as a terminal electron acceptor for anaerobic bioremediation processes that play a dominant role in the natural attenuation process.

BACKGROUND

The average crustal abundance of iron is 5% by weight. The iron content of soils is typically in the range of 0.5% to 5% and is dependent on the source rocks from which the soil was derived, transport mechanisms, and overall geochemical history. Not only is iron common, but it is also reactive and readily reflects changes in surrounding Eh/pH conditions. This is particularly true in soil and groundwater systems that have been environmentally impacted with hydrocarbons. In groundwater systems, iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{+2}) or oxidized insoluble trivalent ferric iron (Fe^{+3}). The modern atmosphere has 21% oxygen, which causes most iron in shallow subsurface soils to be in the oxidized ferric state. Ferric hydroxide ($Fe(OH)_3$) is the direct result of ferrous iron oxidation and precipitation. With time, ferric hydroxide is mineralized. The principal forms of mineralized ferric iron found in soils are follows:

- Amorphous hydrous ferric oxide ($Fe_2O_3 \cdot XH_2O$)
- Maghemite (gamma-Fe_2O_3)
- Lepidocrocite (gamma-FeOOH)
- Hematite (alpha-Fe_2O_3)
- Goethite (alpha-FeOOH)

The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing Eh conditions has a solubility of 0.6 μg/L, which is three orders of magnitude greater than that of goethite. However, a high concentration of iron in groundwater is not rare. Obviously, other processes are at work.

IRON COMPLEXING

Ferrous iron is soluble as a cation, and ferric iron is not. However, ferric iron can form soluble complexes with many inorganic and organic ligands, including compounds that are the byproducts of the biodegradation of aromatic petroleum hydrocarbons (catechols, which are organic acids resulting from aromatic ring cleavage). The yellow/orange coloration of groundwater at some sites contaminated with petroleum hydrocarbons is caused by these ferric-catechol complexes.

It is important to remember that complexed ions typically react more slowly than do uncomplexed ions, which impacts the behavior of ferrous iron. Ferrous iron normally can be oxidized to ferric iron in minutes (see below for more details). Complexed ferrous iron may take months to complete the same reaction, which has profound implications for the fouling of groundwater injection systems. Humic acid, fulvic acid, and tannic acid are examples of noncontaminant organic complexes. Phosphate also serves as an effective complexing agent for iron.

IRON OXIDATION

The time required for uncomplexed ferrous iron to undergo oxidation to the ferric state is dependent on many factors, the dominant ones being: pH, temperature, dissolved oxygen level, and the presence of other soluble ions. The lower the pH and temperature, the longer the time required for completion of the oxidation reaction. Increasing dissolved oxygen decreases the time required for oxidation. For example:

At pH 7.0, 90% Fe^{+2} oxidation requires 1 hour at 21 °C and 10 hours at 5 °C.

At pH 8.0, 90% Fe^{+2} oxidation occurs in 30 seconds; at pH 6.0, it requires 100 hours.

The critical dissolved oxygen concentration is 2 mg/L. Below that ferrous iron oxidation occurs slowly.

The above reactions are often responsible for the iron fouling of air strippers treating iron-rich groundwater. These reactions can also foul screens in poorly designed recovery wells pumping that groundwater.

MICROBIOLOGY AND IRON

Iron readily undergoes reduction or oxidation, depending on surrounding conditions. As a consequence, many microbiological metabolic pathways use redox couples between ferrous and ferric iron. Organic material can be biodegraded with ferric iron as the terminal electron acceptor, which results in the production of reduced soluble ferrous iron. Anaerobic conditions are required as is the presence of ferric iron in a suitable form. As the crystallinity of the ferric iron mineral increases (as discussed above), the microbiological availability decreases. Or contrarily, iron fixing bacteria can oxidize ferrous iron to ferric iron, even under oxygen poor conditions, by many methods, including the extraction of carbon dioxide (for microbial energy systems) from ferrous bicarbonate leaving insoluble ferric hydroxide and the utilization of iron bearing organic acid complexes as a carbon source, leaving precipitated ferric hydroxide. Bacteria also reduce nitrate and oxidize ferrous iron to ferric iron. It is now thought that the Precambrian banded iron formations were the consequence of the mass utilization of ferrous iron in the ancient oceans shortly before oxygenation because photosynthesis took place. These are the reactions that are typically responsible for iron fouling of well screens, piping systems, and air strippers that remediate iron-rich groundwater.

IRON OXIDES AND *IN SITU* METAL/ORGANIC ADSORPTION

Amorphous hydrous ferric oxide can be described as an amphoteric ion exchange media, which means that as pH conditions change, it has the capacity to offer hydrogen ions (H^+) or hydroxyl ions (OH^-) for cation or anion exchange, respectively. As a rough rule of thumb, amorphous ferric oxide is capable of adsorbing 0.5 millimoles of ionic material per gram. Ionic material includes oxyanions of chrome, arsenic, or selenium; heavy metal cations; or ionized organic compounds. The dominant mechanism of interaction between iron oxides and soluble organic compounds is through carboxyl and hydroxyl functional groups on the organic, which is

particularly true for the organic acids that are the intermediate product of the biodegradation of petroleum hydrocarbons.

Sorption behavior is primarily related to pH (within the typical range of 5.0 to 8.0), and each ion has its optimum pH range for adsorption. Given the average concentration in soil, the iron in a cubic yard of soil is capable of adsorbing from 0.5 to 5 pounds of soluble metals as cations, anionic complexes, or a similar amount of organic biodegradation products.

SUMMARY

The reactions described above are complex. At any given location, it is difficult to determine the specific processes taking place. However, the overall effect is as follows: Impacting hydrocarbons provide a carbon source to stimulate aerobic microbial degradation, which consumes the readily available oxygen driving the system anoxic. In the anoxic state, soluble ferrous ions are generated by the action of iron reducing bactgeria and soluble ferrous and ferric complexes are formed. High levels of soluble iron is an indicative side effect of hydrocarbon contamination in groundwater.

The mobilized iron is then drawn into any installed groundwater recovery and treatment systems. There, oxygenation takes place changing redox conditions, and the elevated levels of soluble iron react and which causes fouling in the recovery and treatment systems. Adsorption and attenuation of contaminant transport is concurrently taking place on the residual solid iron oxide phases remaining in the soil matrix, which can extend the duration of a pump and treat effort. Or it can be exploited in a passive "funnel and gate" groundwater barrier remediation system.

The presence and form of naturally occurring iron in groundwater are indicators of complex reactions in the subsurface. Iron in high concentrations does affect drinking water quality. It can also be an important element in aiding or lowering the efficiency of *in situ* remediation of contaminants, depending on specific geochemical conditions. It is also a key element in the natual attenuation process. Therefore, iron data are valuable information that may greatly affect everything from groundwater quality to remedial operations.

GROUNDWATER AND COBALT: CHEMICAL BEHAVIOR AND TREATMENT

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HISTORY OF COBALT

Cobalt has been used as a pigment since 3000 B.C. The name "Kobald" may have come from the Erzgebirge region of Saxony, a silver mining region. Kobalds are mythical creatures like gnomes who frequented the mines causing trouble. The problems were due to interference of cobalt with silver smelting and causing respiratory illnesses in the miners. Before 1914 only oxides of cobalt were used; since then the metal has been used in a variety of ways, particularly as alloys and in the electronic component industry.

MINERAL COMMODITY

Cobalt, identified by Co in the periodic table, has an atomic weight of 58.9322. There are seven radioisotopes of cobalt. It is a solid at room temperature and has been classified as a transition metal. It is magnetic, hard, and brittle and has a metallic gray color. Cobalt will also exist as cobalt(II) and cobalt(III) and will form a number of organic and inorganic salts. Cobalt is not found as a discrete metal but as a solid solution with other elements in minerals. The similarity in ionic radii allows cobalt to substitute for iron, manganese, copper, and chromium. Cobalt metal is produced as a by-product of copper, nickel, and lead production, as it is not economically feasible to isolate cobalt on its own.

Worldwide, the background concentration range of cobalt in soil is 1–40 mg/kg and the average background concentration of cobalt in soil is 8 mg/kg (1). Many mineral species contain cobalt as an integral structural component. Cobalt salts are important for biological processes such as production of vitamin B_{12} and providing the blue-green color in broccoli and other vegetation. On average, humans contain 20 parts per billion (ppb) by mass of cobalt. Cobalt is also an important commercial, industrial, and military metal. Its uses are as follows:

- Cobalt salts are used for the production of brilliant and permanent blue colors in porcelain, glass, pottery, tiles, and enamels.
- For magnet, stainless, and high speed steel production.
- For electroplating, cemented carbides, and diamond tools.
- In the petroleum and chemical industry as catalysts.
- Cobalt compounds are used as paint pigments.
- Cobalt is combined with iron, nickel, and other metals to make corrosion- and wear-resistant alloys.
- Cobalt-60 is an artificial radioactive isotope used as a tracer and radiotherapy agent for cancer treatment and as a food preservation method, also called the food irradiation process.
- Cobalt is used in batteries, car tires, recording media, semiconductor ceramics, and most importantly in superalloys in jet turbines and gas turbine generators.

SOURCES OF COBALT

Mining of cobalt occurs primarily in twelve countries, most notably Canada, Russia, Democratic Republic of Congo, Zambia, and Australia, which also refine the cobalt ore.

The main countries that only refine cobalt include Finland, Norway, and Brazil.

PHYSICAL PROPERTIES

Cobalt is a shiny, gray, brittle metal with a close packed hexagonal (CPH) crystal structure at room temperature but which changes at 421 °C to a face centered cubic form. The metal is rarely used as a structural material in the pure form but almost always as an alloy or a component of another system. The density is 8.85 g/cm^3, the melting point is 1493 °C (2719 °F), the Curie point is 1121 °C, and the atomic number for cobalt is 27. Cobalt comes in two valence states: +2 and +3. For more information on physical and chemical properties, see Reference 2.

CHEMICAL REACTIONS

Cobalt is not particularly reactive with air. However, on heating the oxide Co_3O_4 is formed. If the reaction is carried out above 900 °C, the result is cobalt(II) oxide, CoO. Cobalt does not react directly with nitrogen (N_2).

$$3Co(s) + 4O_2(g) \rightarrow 2Co_3O_4(s),$$

$$2Co(s) + O_2(g) \rightarrow 2CoO(s).$$

Water has little effect on cobalt metal. The reaction between red hot cobalt metal and steam produces cobalt(II) oxide, CoO. Simple inorganic salts of cobalt are generally very soluble in water.

$$2Co(s) + O_2(g) \rightarrow 2CoO(s).$$

Cobalt metal reacts directly with halogens, producing cobalt(II) salts.

$$Co(s) + Br_2(l) \rightarrow CoBr_2(s) \quad \text{[green]},$$

$$Co(s) + Cl_2(g) \rightarrow CoCl_2(s) \quad \text{[blue]},$$

$$Co(s) + I_2(s) \rightarrow CoI_2(s) \quad \text{[blue-black]}.$$

Cobalt metal dissolves slowly in dilute sulfuric acid to form solutions containing the aqueous Co(II) ion together with hydrogen gas, H_2. In practice, Co(II) is present as the complex ion $[Co(OH_2)_6]^{2+}$ (see Reference 3).

$$Co(s) + H_2SO_4(aq) \rightarrow Co^{2+}(aq) + SO_4^{2-}(aq) + H_2(g),$$

COBALT ISOLATION

Numerous ores contain cobalt, but not many of these are of economic importance. These include the sulfides and arsenides linnaeite (Co_3S_4), cobaltite, (CoAsS), and smaltite, ($CoAs_2$). Normally the cobalt ore is "roasted" to form a mixture of metals and metal oxides. Treatment with sulfuric acid leaves metallic copper as a residue and dissolves out iron, cobalt, and nickel as the sulfates. Iron is obtained by precipitation with lime (CaO) while cobalt is produced as the hydroxide by precipitation with sodium hypochlorite (NaOCl):

$$2Co^{2+}(aq) + NaOCl(aq) + 4OH^-(aq) + H_2O \rightarrow 2Co(OH)_3(s) + NaCl(aq).$$

The trihydroxide $Co(OH)_3$ is heated to form the cobalt oxide and then reduced with carbon (as charcoal) to form cobalt metal (3).

$$2Co(OH)_3(\text{heat}) \rightarrow Co_2O_3 + 3H_2O,$$

$$2Co_2O_3 + 3C \rightarrow Co + 3CO_2.$$

FATE AND TRANSPORT

The geochemical behavior of cobalt generally follows the iron–manganese system. The cobalt concentration in soils is controlled by adsorption and coprecipitation reactions with manganese and iron oxide minerals. Cobalt-60 (^{60}Co) is an activation product of stable cobalt (^{59}Co). It is the isotope of primary importance to waste disposal and site remediation. ^{60}Co has a half-life of about 5.3 yr, relatively short compared to other radionuclides of environmental concern. It readily adsorbs to minerals and as such its mobility should be limited to soil and water systems near to the area in which it was released (2).

Co(II) is the stable valence state in water under most geochemical conditions. Co(III) is a strong oxidizing agent; hence it is not thermodynamically stable and will decompose under the conditions typical of natural water. Cobalt(III) will form strong complexes with organic ligands such as ethylenediamine-tetraacetic acid (EDTA) and NH_3 and exist in aqueous solution. These complexes affect cobalt's environmental mobility by increasing its solubility in aqueous solutions, decreasing its adsorption in soil, and stabilizing Co(III) in some sediment systems. Co(III) can be mobilized and reduced to Co(II) as a result of bacterial iron reduction. The solubility of Co(III) is a function of the composition of the media and buffers (see Fig. 1).

The migration and sorption of cobalt depends strongly on the pH of the medium. In acidic media, cobalt occurs in solution; an increase in pH will cause it to sorb to soil, sediments, and other precipitates such as manganese and iron oxides and clay minerals. Adsorption is minimal below a pH of 4. In the absence of organic complexants cobalt will adsorb (moderate to high) to minerals at near neutral and basic pH values. Humic acid will increase the adsorption of cobalt on all mineral sorbents by 10–60%. The highest cobalt adsorption due to humic acid will occur between pH 4.5 and 6.5. K_d for dissolved Co(II) ranges from 10^3 to 10^5 mL/g. Inorganic ligands such as cyanide in low concentrations can decrease cobalt adsorption on sediment significantly ($K_d < 2$ mL/g). The presence of other cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) in solution can decrease cobalt adsorption.

Adsorption on manganese minerals results in the surface-mediated oxidation of Co(II) to Co(III) by the reduction of surface Mn(IV) sites. This will occur at pH values of 4, 6, and 7. At pH 8 and 10, Co(II) adsorption resulted in the precipitation of something similar to cobalt

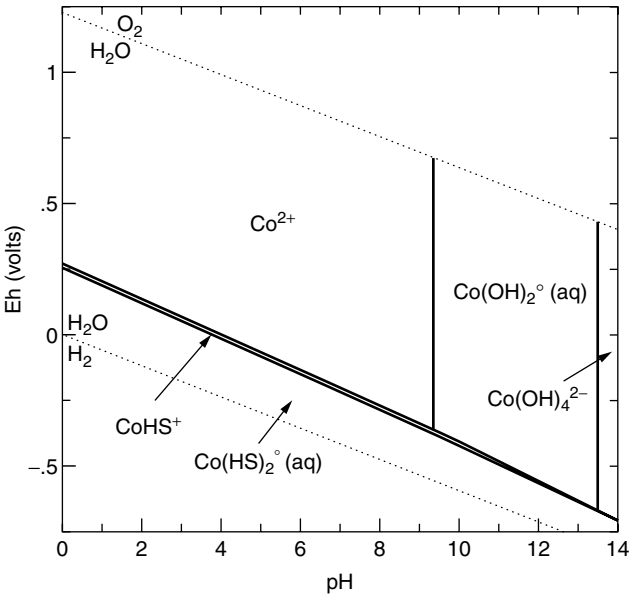


Figure 1. Eh–pH diagram showing the dominant aqueous complexes of cobalt (2). (Diagram was calculated at 25 °C and a concentration of 10–14.8 mol/L total dissolved cobalt in the presence of dissolved chloride, nitrate, sulfate, and carbonate).

hydroxide; this could explain the large range of K_d values reported in the literature (2).

HEALTH AND SAFETY

Exposure to very high levels of cobalt can cause serious health problems to the respiratory system and skin of humans and animals. Most typically, persons breathing air with high cobalt levels are at risk for lung problems, wheezing, asthma, and pneumonia. Cobalt has been found to be a sensitizer and as such dermatitis can occur on contact. Three cobalt compounds are classified as a human carcinogen on the PHS Category 1 Chemical Table maintained by the Los Alamos National Laboratory (2000). The three carcinogenic compounds include cobalt(II) arsenate, cobalt–chromium alloy (as Cr^{6+}), and beryllium–copper–cobalt alloy.

Research has shown that a high cobalt level is harmful to fetus development in pregnant animals. It is known to cause cancer in animals when placed under the skin or in the muscle. The lowest published lethal dose by oral application in rats is 1500 mg/kg, 250 mg/kg for intraperitoneal doses, and 25 mg/kg for intratracheal doses. Inhalation is the most hazardous exposure pathway of cobalt. When working with cobalt, goggles and gloves are recommended for personal protection. If cobalt powder is present, the area should be well ventilated and inert, as the powder can ignite spontaneously.

Several countries have determined different toxicity levels for cobalt.

In Ontario, the cobalt toxicity limit in soil is 40 parts per million (ppm) (4). In Sweden the limit is 30 ppm (5) and in Quebec the agricultural soil standard is 15 ppm.

PERSISTENCE IN GROUNDWATER

Cobalt will exist in groundwater as Co(II) or Co(III) depending on the pH. Under most geochemical conditions, Co(II) is the stable valence state in water. Co(III) is not thermodynamically stable and decomposes under Eh–pH conditions common for most natural waters. However, the presence of certain complexing ligands can stabilize Co(III) relative to reduction and allow it to persist in aqueous solutions. Cobalt will be retarded in groundwater due to its large K_d values (2).

COBALT CONTAMINATION

Cobalt is naturally occurring in the environment and is found in a variety of places, including plants, soil, dust, and seawater. Anthropogenic releases are by way of burning coal and oil and fuel exhaust from cars, trucks, airplanes, and many industrial processes that use any of the numerous cobalt compounds. Most sites with cobalt contamination have occurred due to mining operations. Cobalt contamination is generally greatest in the soil around mine sites due to the leaching acids in the tailings. Cobalt contamination is usually coupled with high arsenic and nickel contaminations and is rarely the contaminant of major concern due to its low toxicity. Cobalt-60 contamination does occur when storage tanks leak or disposal practices are inadequate. Contamination by ^{60}Co is generally of less concern than other radionuclides based on its short half-life. ^{60}Co is highly sorbed on sandy soils and relatively immobile. When ^{60}Co is complexed with EDTA, the cobalt mobility increases.

COBALT REMEDIATION TECHNIQUES

Remediation of cobalt-contaminated sites can be carried out via removal of the soil and groundwater. Cobalt is most hazardous to the human respiratory system. Cobalt fumes can be generated when cutting or torching cobalt-containing metals. Cobalt mists occur when groundwater or process water containing dissolved cobalt is sprayed through a nozzle, such as a process washing system or a bathroom shower.

To reduce the mobility of cobalt dust from contaminated soil, the stockpiles are usually covered with clean soil, plastic sheeting, sod, or pavement. Because cobalt is mobile in an acidic medium, the upper layers of contaminated soil can be tilled with lime to reduce the pH and prevent toxicity to plants. The soil can also be covered with a thick layer of crushed limestone. The limestone layer will raise the pH in the vadose zone and prevent further leaching of the soluble cobalt.

Phytoaccumulation is one of the biological techniques used to remediate soils close to the surface contaminated by cobalt. Phytoaccumulation is done using nonfood crops to absorb metals from the soil into the stems and leaves. There are several plants that are hyperaccumulators; they can absorb large amounts of metals in their root structures (comparative to other plants and the concentration of

metal in the ground). The cobalt is transported to the leaf and stalk biomass. Ultimately, the plant containing the cobalt is harvested for disposal or reclamation of the cobalt. There are 26 known plants that are hyperaccumulators of cobalt. There are also high accumulator plants that will take metal out of the soil in larger quantities than normal plants. Cobalt will exist as an oxalate compound in leaves, and as such it is readily extracted using accumulator plants. Accumulator plants are metal specific and will contain about 100 times more of a toxic element than normal plants. Phytoaccumulation can be enhanced using EDTA, citric, or oxalic acids on the soil (1).

For conventional remediation of cobalt in the groundwater, pump and treat or natural attenuation is used. At low pH, the cobalt is mobile. The contaminated water can be removed and treated with a strong base to reduce its solubility. Treatment with sodium hypochlorite (NaOCl) will cause precipitation of cobalt trihydroxide. The movement of cobalt-containing acidic plume within an aquifer matrix causes the pH to rise due to the presence of carbonate materials, which allows cobalt to be sorbed to the soil. High dissolved oxygen content will cause manganese oxides in the soil to precipitate and increase cobalt sorption, thus reducing the amount of soluble cobalt in the aquifer. Where monitored natural attenuation is the chosen remediation method, the down-gradient surface water body will be the location at which remediation is complete as the adsorbed cobalt will be remobilized with the migration of the plume. Only when the plume has traveled to a source with adequate dissolved oxygen will the iron and manganese oxides precipitate with sorbed cobalt.

Cobalt-contaminated groundwater can be treated *in situ* with a combination of methods that will allow the pH to be raised sufficiently to immobilize the cobalt and by providing enough dissolved oxygen to allow manganese oxides to precipitate and enhance cobalt sorption. Geochemical fixation using calcium polysulfide (pH 11.3–11.5) would significantly raise the pH in an aquifer. Extraction wells can be placed down-gradient to remove the acidic plume or in the middle.

BIBLIOGRAPHY

1. Suthersan, S.S. (2002). *Natural and Enhanced Remediation Systems*, CRC Press/Lewis Publishers, Boca Raton, FL.
2. Krupka, K.M. and Serne, R.J. (2002). *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments*, Report PNNL-14126; Pacific Northwest National Laboratory, December, Chap. 3; pp. 3.1–3.19.
3. Web Elements (WE) (2004). Available: http://www.webelements.com/webelements/elements/text/Co/.
4. Ontario Ministry of the Environment (OME) (2001). Fact sheet: cobalt in the environment. Available: http://www.ene.gov.on.ca/cons/.
5. Swedish Environmental Protection Agency (SEPA) (2002). Assessment of contamination level. Available: http://www.internat.naturvardsverket.se/

GROUNDWATER AND CADMIUM: CHEMICAL BEHAVIOR AND TREATMENT

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Cadmium occurs naturally in ores containing other elements such as oxygen (cadmium oxide), sulfur (cadmium sulfate, cadmium sulfide), and chlorine (cadmium chloride) or compounds (cadmium carbonate). Cadmium is usually extracted during the production of other metals such as zinc, lead, and copper. A primary use for cadmium is in rechargeable nickel–cadmium and solar batteries, which are sold worldwide. Cadmium does not corrode easily and is also used in metal plating and coating operations including transportation equipment and various industrial machinery as well as plastics manufacturing. It is used in numerous pigments, in baking enamels, and in photographic processes as well as in television and monitor screen phosphors. Cadmium is released into the environment through industrial waste streams and landfills. Cadmium is relatively mobile in surface and groundwater and has a United States Environmental Protection Agency (U.S. EPA) Maximum Contaminant Level Goal (MCLG) of 5 parts per billion (ppb) in drinking water (1). The World Health Organization has set the provisional tolerable daily intake of cadmium at 60–70 μg/day (2).

PHYSICAL AND CHEMICAL CHARACTERISTICS

In ancient times cadmium was known as "calamine" and was often confused with zinc carbonate. In 1817, cadmium was discovered by the German chemist Friedrich Strohmeyer from an impurity in zinc carbonate ($ZnCO_3$), also called calamine. The impurity glowed with a yellow color and was identified as a new element, cadmium. Cadmium most often occurs in small quantities associated with zinc ores, such as sphalerite (ZnS). Greenockite (CdS) is the only mineral of any consequence bearing cadmium. Cadmium is a poisonous metal. The oxidation state of cadmium is +2.

The most common forms of cadmium are Cd^{2+}, cadmium–cyanide complexes, or cadmium hydroxide solid sludge (3). Cadmium hydroxide [$Cd(OH)_2$] and cadmium carbonate ($CdCo_3$) solids are most common at high pH, whereas the cadmium ion (Cd^{2+}) and aqueous cadmium sulfate species are the dominant forms at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid cadmium sulfate [CdS(s)] is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate, and other anions, although solubility will vary with pH and other geochemical factors (4).

Naturally occurring cadmium is composed of 6 stable isotopes; 27 radioisotopes have been characterized with the most stable being Cd-113 with a half-life of 7.7 quadrillion years, Cd-109 with a half-life of 462.6 d, and Cd-115 with a half-life of 53.46 h. All of the remaining radioactive

isotopes have half-lives that are less than 2.5 h and the majority of these have half-lives that are less than 5 min. This element also has 8 metastates with the most stable being Cdm-113 ($t_{1/2}$ 14.1 y), Cdm-115 ($t_{1/2}$ 44.6 d), and Cdm-117 ($t_{1/2}$ 3.36 h). The isotopes of cadmium range in atomic weight from 96.935 amu (Cd-97) to 129.934 amu (Cd-138).

Almost all cadmium is obtained as a by-product in the treatment of zinc, copper, and lead ores. It is a soft, bluish-white metal that is easily cut with a knife and is similar in many respects to zinc. It is a component of some of the lowest melting alloys and therefore is used in bearing alloys with low coefficients of friction and great resistance to fatigue. It is also used extensively in electroplating and in many types of solder, for standard EMF cells, for Ni–Cd rechargeable batteries, and as a barrier to control nuclear fission. Cadmium compounds are used in black and white television phosphorus and in blue and green phosphorus for color television and computer monitor tubes. It forms a number of salts, of which the sulfate is most common with the sulfide being used as a yellow pigment.

SOURCES OF CADMIUM

Environmental Exposure

Numerous human activities result in the release of significant quantities of cadmium to the environment. The relative importance of individual sources varies considerably from country to country. The major sources of anthropogenic cadmium release can be divided into three categories. The first is made up of those activities involved in the mining, production, and consumption of cadmium and other nonferrous metals. The second category consists of inadvertent sources where the metal is a natural constituent of the material being processed or consumed. Sources associated with the disposal of materials that had earlier received cadmium discharges or discarded cadmium products make up the third category. As a minor impurity in a variety of phosphate fertilizers, cadmium is introduced into the environment through direct application onto agricultural lands. The amount of cadmium impurities that are contained within phosphate fertilizers varies with the mining district.

Atmospheric Cadmium

The average global total emission of the metal from human sources in 1983 was 7570 tons (5) and represented about half the total quantity of cadmium produced in that year. In comparison, the worldwide emission of lead from human activities was about 10% of the total lead produced in 1983 (5). In both the European Economic Community (EEC) and on a worldwide scale (6), about 10–15% of total airborne cadmium emissions arise from natural processes, the major source being volcanic action. Nonferrous metal production, which accounts for about 75% of the total anthropogenic cadmium emissions worldwide, accounts for only 25% in the EEC. This is primarily a result of the extensive emission controls due to legislation and regulation in developed countries.

In addition, of the two basic methods of zinc production—thermal smelting and electrolyte refining—only the former releases significant atmospheric cadmium emissions. In recent years, electrolytic refining has assumed the major share of the world's production of zinc and cadmium and has largely replaced thermal processes in Europe. The once important vertical and horizontal retort smelters, which emit large quantities of atmospheric cadmium, have been phased out in most developed countries but are still in operation in several developing countries (7).

Other industries that employ thermal processes, for example, iron production, fossil fuel combustion, and cement manufacture, all release airborne cadmium, the metal being a natural component of the raw materials. The cadmium content of these materials is generally relatively low but due to the significant consumption of the raw material, significant cadmium is released into the environment. In addition, the elevated temperatures employed result in the volatilization of cadmium and release into the atmosphere. Municipal refuse is a common cadmium waste-related source, the cadmium being derived from discarded nickel–cadmium batteries and plastics that contain cadmium pigments and stabilizers. The incineration of refuse is also a major source of atmospheric cadmium release worldwide.

Sewage sludge receives cadmium from industrial sources, particularly from the discharges of plating operations and pigment works. One disposal option, the incineration of sewage sludge, is a relatively minor source of airborne cadmium, reflecting the small quantities of sludge disposed of in this manner.

Steel production can also be considered as a waste-related source, as large quantities of cadmium-plated steel scrap are recycled by this industry, at least in developed countries. As a result, steel production is responsible for considerable emissions of atmospheric cadmium.

Aquatic Cadmium

Nonferrous metal mines represent a major source of cadmium release to the aquatic environment. Contamination can arise from mine drainage water, wastewater from the processing of ores, overflow from the tailings pond, and rainwater runoff from the general mine area. The release of these effluents to local water sources can lead to extensive contamination of aquatic environments. The cadmium content of the ore body and climatic and geographical conditions, as well as mine management policies, all influence the quantities of cadmium released from individual sites. Aquatic inputs of cadmium are not restricted to active mine sites, and abandoned mining operations are also sources of continuing contamination of aquatic environments.

Cadmium is a natural constituent of rock phosphates and deposits from some regions of the world contain markedly elevated levels of the metal. The manufacture of phosphate fertilizer results in a redistribution of the cadmium in the rock phosphate between the phosphoric acid product and the gypsum waste. In many cases, the gypsum is disposed of by dumping in coastal waters, which leads to considerable cadmium inputs. Some countries,

however, recover the gypsum for use as a construction material and thus have negligible cadmium discharges.

Acidification of soils and lakes may result in enhanced mobilization of cadmium from soils and sediments and lead to increased levels in surface and groundwaters (2). The corrosion of soldered joints or zinc-galvanized plumbing by acidic waters can dissolve cadmium and produce increased levels of the metal in drinking water.

Terrestrial Cadmium

Solid wastes from a variety of human activities are disposed of in landfill sites, resulting in large cadmium inputs at the national and regional levels when expressed as a total tonnage (8,9). Of greater potential environmental significance are the solid wastes from both nonferrous metal production and from the manufacture of cadmium-containing articles, as well as the ash residues from refuse incineration. All three waste materials are characterized by elevated cadmium levels and as such require disposal to controlled sites to prevent the mobilization of the cadmium in groundwater.

Cadmium soil contamination is a characteristic feature around nonferrous metal mines and smelters, particularly in the case of those handling zinc ores. Contamination from mining is generally local but may be widespread in areas of high mineral content. Shipham, England, in the United Kingdom, is a site of extreme soil cadmium contamination. Between 1650 and 1850 the village of Shipham was the site of a major zinc mine. Once the mining stopped, the area was flattened and developed for agriculture and housing. Cadmium levels in agricultural and garden soils are some of the highest ever reported worldwide (10).

The application of municipal sewage sludge to agricultural soil as a fertilizer can also be a significant source of cadmium. Large increases in soil cadmium concentration have resulted in the past from the application of contaminated sludge in both North America and Europe. Even today, the high application rates used for sewage sludge result in relatively large cadmium inputs, a value of 80 g/ha having been estimated for the United Kingdom (9). On a national or regional basis, however, these inputs are much smaller than those from either phosphate fertilizers or atmospheric deposition.

TERRESTRIAL IMPACTS

Large cadmium concentrations in terrestrial environments are commonly a result of solid wastes disposed of in landfill sites, ashes from fossil fuel combustion, waste from cement manufacture, and the disposal of municipal refuse and sewage sludge. The solid wastes from both nonferrous metal production and the manufacture of cadmium-containing articles, as well as the ash residues from refuse incineration, are the main contributors to cadmium contamination in terrestrial environments. These three waste materials are characterized by elevated cadmium levels and as such require disposal to controlled sites to prevent the contamination of the groundwater.

The agricultural application of phosphate fertilizers represents a direct input of cadmium to arable soils. The cadmium content of phosphate fertilizers varies widely and depends on the origin of the rock phosphate that is the main component in fertilizers, particularly in third world countries. The application of municipal sewage sludge to agricultural soils as a fertilizer can also be a significant source of cadmium.

Impact on Water Bodies

Rivers contaminated with cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, by the dumping of dredged sediments, or through flooding. Cadmium compounds are able to leach through soils to groundwater. When cadmium compounds do bind to the sediments of rivers, they can be more easily bioaccumulated or redissolved when sediments are disturbed, such as during flooding. Its tendency to accumulate in aquatic life is great in some species. Much of the cadmium entering fresh waters from industrial sources is rapidly adsorbed by particulate matter, where it may settle out or remain suspended, depending on local conditions. This can result in low concentrations of dissolved cadmium even in rivers that receive and transport large quantities of the metal.

Health Risks

Cadmium and solutions of its compounds are toxic. In comparing the various standards available, exposure to cadmium dust is most common in workplaces, such as battery manufacturing plants, industrial facilities and metal fabricators having metal soldering and welding fumes, and coal plants. The cadmium dust levels should not exceed 0.01 mg/m^3 (8-h time-weighted average, 40-h week). The ceiling concentration (maximum), for a period of 15 min, should not exceed 0.14 mg/m^3. Cadmium oxide fume exposure (8-h day, 40-h week) should not exceed 0.05 mg/m^3, and the maximum concentration should not exceed 0.05 mg/m^3. Cadmium stays in the body for a very long time and concentrations in the body can build from years of low exposure (1).

Effects on Humans/Mammals. The United States Department of Health and Human Services (DHHS) has determined that cadmium and cadmium compounds may reasonably be anticipated to be carcinogens (1). Apart from the gastrointestinal tract and the lungs, the organ most susceptible to chronic cadmium exposure is the kidney. Cadmium is a cumulative poison; its ready solubility in weak acids is an important precondition for its absorption in the organism: 5% of cadmium is resorbed via the gastrointestinal tract and accumulated in liver and kidneys. In Asia, "Itai-Itai" disease is caused by high cadmium concentrations in rice.

Lung cancer is one potential result of chronic inhalation of fine-particle cadmium compounds, particularly cadmium oxide, which readily dissolves in the body. Ingestion of the compounds in food results from the fact that plants and fish absorb and retain cadmium, and hazardous levels can be reached when consuming food from areas where cadmium contamination has been generated at industrial sites or by the use of phosphate fertilizers. Adverse health

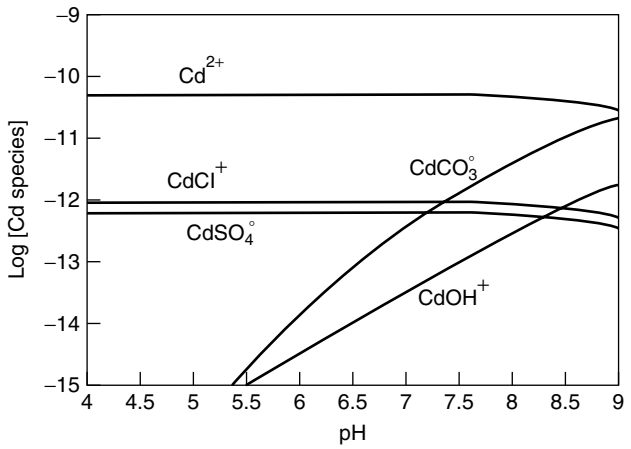


Figure 1. Inorganic cadmium speciation in soil water.

results from long-term, high level ingestion of cadmium include kidney damage and kidney stones, and debilitating effects on bones and the skeletal structure (1).

Effects on Plants. Cadmium reduces the photosynthesis and transpiration rate while increasing the respiratory rate. Small cadmium concentrations in the soil are sufficient to produce marked damage such as shortening of the shoot axis and intensive yellowing of older leaves. Absorption not only takes place via the roots but also through shoots and leaves. In addition to yield shortfalls, the main hazard results from the contamination of (accumulation in) crop plants since this is how cadmium as a cumulative poison enters the food chain.

GEOCHEMISTRY OF CADMIUM

In nature cadmium exists in the +2 oxidation state and forms a number of aqueous complexes, particularly with dissolved carbonate. The concentration of cadmium in the environment may be controlled by either adsorption or precipitation/coprecipitation processes. The concentration and extent to which cadmium is present in soils vary greatly with type of minerals, oxidation state of the system, and presence of competing cations in solution. Cadmium concentrations in uncontaminated soils are usually less than 1 mg/kg. However, higher concentrations may be present as a result of human activities or by the weathering of parent materials with high cadmium concentrations (i.e., cadmium-rich igneous rocks).

CADMIUM SPECIES AND CONDITIONS

Cadmium forms soluble complexes with inorganic and organic ligands resulting in an increase of cadmium mobility in soils. As the pH increases between 6 and 8.2, cadmium carbonate species [$CdHCO_3$ and $CdCO_3$ (aq)] assume greater significance. At pH values between 8.2 and 10, most of the cadmium in solution is expected to exist as the neutral complex $CdCO_3$(aq). The species $CdSO_4$(aq), $CdHCO_3$, $CdCl^{2+}$, and $CdOH^+$ are also present, but at much lower concentrations (Fig. 1).

CONDITIONS FOR THE DISSOLUTION AND PRECIPITATION OF CADMIUM

At pH values less than 7.5, most cadmium minerals are more soluble than cadmium concentrations found in oxic soils (10^{-7} M), indicating that cadmium at these concentrations is not likely to precipitate. At pH levels greater than 7.5, the solubilities of $Cd_3(PO_4)^2$ or $CdCO_3$ may control the concentrations of cadmium in soils. $CdCO_3$ precipitates in calcareous soils (pH > 7.8), whereas in neutral or acidic soils, adsorption is the predominate process for removal of cadmium from solution. The activity of dissolved cadmium in cadmium-amended soils was lowest in calcareous soils. Cadmium may coprecipitate with calcium to form carbonate solid solutions, $(Ca,Cd)CO_3$. This may be an important mechanism in controlling cadmium concentrations in calcareous soils. Although cadmium itself is not sensitive to oxidation/reduction conditions, its concentration in the dissolved phase is generally very sensitive to redox state. The concentrations of dissolved cadmium greatly increase when reduced systems are oxidized, such as when dredged river sediments are land filled or rice paddies are drained.

The following mechanisms appear to be responsible for this increase in dissolved cadmium concentrations:

1. Very insoluble cadmium species in rocks or soils (e.g., greenockite) dissolve as sulfide [S(II)] that is oxidized to sulfate [S(VI)].
2. Organic materials binding cadmium are decomposed through oxidation, releasing cadmium into the environment. This mechanism appears to be important only in environments in which moderate to high organic matter concentrations are present. Dissolved cadmium concentrations greatly increased when the sediments were incubated under oxidizing conditions (Eh > 350 mV).
3. Pyrites that may be present in soils or sediments get oxidized when exposed to air. The pyrite oxidizes to form $FeSO_4$, which generates high amounts of acidity when reacted with water. The decrease in the pH results in the dissolution of cadmium minerals and increase in the dissolved concentration of cadmium.

SORPTION AND DESORPTION OF CADMIUM IN SOILS

At high solution concentrations of cadmium (>10 mg/L), the adsorption of cadmium often correlates with the cation exchange capacity of the soil. During cation exchange, cadmium generally exchanges with adsorbed calcium and magnesium. At low solution concentrations of cadmium, surface complexation to calcite (11) and hydrous oxides of aluminum and iron (12) may be the most important adsorption mechanism. Both Cd^{2+} and possibly $CdOH^+$ may adsorb to aluminum and iron oxide minerals.

As with other cationic metals, cadmium adsorption exhibits pH dependency. The effect of pH on cadmium adsorption by soils, sediment, and iron oxides is influenced by the solution concentration of cadmium and the presence

of competing cations or complexing ligands. In lower pH environments, these metals, based on their propensity to adsorb, would rank as follows: Pb > Cr > Zn > Cd. This order is inversely related to the pH at which hydrolysis of these metals occurs.

Competition between cations for adsorption sites strongly influences the adsorption behavior of cadmium. The presence of calcium, magnesium, and trace metal cations reduces cadmium adsorption by soils and manganese oxides and aluminum oxides. The extent of competition between cadmium and other ions depends on the relative energies of interaction between the ions and the adsorbing surface, the concentrations of the competing ions, and solution pH (12,13). The addition of copper or lead, which are more strongly adsorbed, slightly reduces cadmium adsorption by iron and aluminum oxides, suggesting that copper and lead are preferentially adsorbed by different surface sites (14). In contrast, zinc almost completely displaces cadmium.

FATE AND TRANSPORT

Cadmium can enter the environment in several ways. It can enter the air from the burning of coal and household waste and from metal mining and refining processes. It can enter water from disposal of wastewater from households or industries. Fertilizers often contain some cadmium, which results in cadmium entering the soil. Spills and leaks from hazardous waste sites can also result in excessive amounts of cadmium entering the soil or water. Cadmium may attach to small particles, which may be transported in the air as a result of an industrial process (i.e., metallurgy, zinc/lead smelting). Cadmium does not break down in the environment but may form complexes, ligands, and compounds that facilitate transportation of cadmium ions. Most cadmium stays where it enters the environment for a long time. Some of the cadmium that enters water will bind to soil but some will remain in the water. Cadmium in soil can enter water or be taken up by plants. Fish, plants, and animals take up cadmium from the environment.

Cadmium in Water

About 67–75% of the cadmium in surface water and groundwater is adsorbed on suspended matter. It can be remobilized from sediment by complexing agents. Aquatic life tends to be vulnerable to increases in cadmium concentration. Fish toxicity is dependent among other things on the calcium content of the water. Generally, high calcium content in water reduces the toxic effect of cadmium on fish. It has been noted that biological self-purification of surface water and groundwater is impaired when cadmium concentrations are in excess of 0.1 mg/L.

Cadmium in Air

Cadmium is stable in air since it forms an oxide layer.

Cadmium in the Soil

The cadmium retention capacity is a function of the number of exchangeable alkalis. There is hardly any dilution because of the adsorption on organic soil components. The accumulation horizon for cadmium is in the rhizosphere (roots). The minimum availability is at pH 6.5. Cadmium absorption by plants increases with a decreasing pH of the soil.

Cadmium in Organisms

Excessive cadmium concentrations in the environment will affect all organisms. In humans, 50% of the accumulated amount of cadmium is found in the liver and the kidneys. Cadmium is primarily excreted in urine [2 mg/d on average (0.2–3.1 mg/L)]. The biological half-life of cadmium in the human body is between 15 and 25 years (measured in the kidneys) (15). Humans consume roughly one-third of the cadmium to which they are exposed in animal foodstuffs and two-thirds in vegetable foodstuffs. Smoking significantly increases the cadmium impact.

METHODS OF REMEDIATION

There are several ways to deal with soil contaminated with toxic heavy metals such as cadmium. The following sections detail some of the more common remediation options for cadmium-contaminated soil and water.

Capping

Capping systems are used to provide an impermeable barrier to surface water infiltration to contaminated soil for prevention of further release of contaminants to the surrounding surface water or groundwater. A variety of materials are available for use in capping systems and choice of materials is site specific because local soils are often incorporated into parts of the cap. Synthetic membranes such as high density polyethylene are also available for incorporation into capping systems. Surface water controls, such as ditches and dikes, are usually included to help control drainage from the cap. Multilayered capping systems may also include a hard cover and/or a layer of topsoil to separate the underlying layers from the ground surface. Revegetation is promoted in order to reinforce the topsoil, to reduce soil erosion and runoff velocity, and to help remove water from the soil by evapotranspiration.

Subsurface Barriers: Pump and Treat

Subsurface barriers may be used to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site. These barriers are designed to reduce the movement of contaminated groundwater from the site, or to restrict the flow of uncontaminated groundwater through the contaminated site. Vertical barriers are commonly used to restrict the lateral flow of groundwater. For effective isolation of the contaminated matrix, the barrier should extend and key into a continuous, low permeability layer, such as clay or competent bedrock, below the contaminated area. If an impermeable layer is not available, a groundwater extraction system must be used to prevent transport of contaminants under the barrier and this contaminated

water must be treated after extraction. Subsurface barriers are often implemented in conjunction with a capping system to control surface water infiltration. The use of circumferential barriers can prevent the escape of contamination from the site by using an infiltration barrier and collection system to create a hydraulic gradient in the inward direction.

Solidification, Stabilization, and Removal

The usual methods of dealing with soils contaminated with heavy metals are solidification, stabilization, and removal. The most commonly used method is solidification. Solidification involves a process in which the contaminated matrix is stabilized and fixated or encapsulated into a solid material by the addition of a chemical compound such as cement. The metal contaminants are chemically and/or physically bound to the matrix and are not obliterated but are contained in such a way that leaching into the environment is prevented or reduced. Removal is the process of physically removing the metal-contaminated soil from the current site and discarding the waste into a designated contaminated site. Stabilization, also referred to as fixation, usually uses a chemical reaction to convert the waste to a less mobile form. The general approach for solidification/stabilization treatment processes involves mixing or injecting treatment agents into the contaminated soils. Inorganic binders, such as cement, fly ash, or blast furnace slag, are commonly used. The dominant mechanism by which cadmium is immobilized is by precipitation of hydroxides or sulfides within the solid matrix.

ex situ Vitrification

The mobility of metal contaminants, particularly cadmium, can be decreased by high temperature treatment of the contaminated area, which results in the formation of vitreous material, usually an oxide solid. Most soils can be treated by vitrification with cadmium commonly being treated with *ex situ* vitrification. Typical stages in *ex situ* vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product.

Bioremediation

Bioremediation is the use of microorganisms to control, precipitate, or destroy contaminants. Enhanced bioremediation of soil involves the delivery of oxygen for aerobic bioremediation or a carbon source (molasses, corn syrup, milk, cheese whey, lactic acid, propane, etc.) for anaerobic bioremediation. For cadmium, anaerobic and reducing conditions are more likely to contribute toward precipitating the cadmium as a sulfide or hydroxide than are oxidizing conditions. More information about metals stabilization and phytoremediation are described in Reference 16. For enhanced bioremediation, cadmium concentrations must be carefully evaluated so as not to be toxic to the microbial populations. Bench testing with the appropriate treatment chemicals can optimize pH, Eh, and other factors in the laboratory.

Phytoremediation

Phytoremediation is defined as the use of green plants to remove heavy metals and contaminants from the soil (16). The plants take up the toxic metals or isotopes through their roots and transport them to the stems or leaves. There are plants that tolerate excessive concentrations of metals in soils by absorbing, translocating, and storing the metals in a nontoxic way. Many of these plants have evolved on metal-rich soils. Research over the last two decades has shown that certain specialized plants have the ability to accumulate up to 3% (by dry weight) of heavy metals and up to 25% (by dry weight) in sap/latex with no apparent damage to the plant. Alpine pennycress (*Thlaspi caerulescens*) can be used for the removal of zinc and cadmium. Research has indicated that the pennycress plant typically absorbed 3–4% of the cadmium contamination from the soil (in some cases as much as 9%). Willow is another plant that proved able to absorb cadmium but never more than 1% of the soil content. Consequently, soil could advantageously be cleaned of cadmium by pennycress, possibly in combination with willow.

In Situ Electrokinetic Remediation

An emerging remediation technology, which in laboratory experiments has indicated substantial results in the removal of heavy metal contaminants particularly cadmium, is electrokinetic remediation (4). While bench tests conducted at the Naval Air Weapons Station at Pt. Mugu, California did not give statifactory results in the removal of cadmium and chromium contamination from the site, the technology holds some promise. Electrokinetic remediation is an *in situ* process in which an electrical field is created in a soil matrix by applying a low voltage direct current (DC) to electrodes placed in the soil.

The current density is generally on the order of milliamperes per square centimeter (mA/cm^2) or an electric potential difference on the order of a few volts per centimeter across electrodes placed in the ground. The electrodes can be placed in either a vertical or horizontal array. When direct current is applied to the electrodes, an electrical field develops between the anodes and cathodes. The application of the electric field has several effects on the soil, water, and contaminants. These effects include electromigration, electroosmosis, changes in pH, and electrophoresis. Electromigration refers to the movement of cations and anions under the influence of the electrical field. Cations (positively charged ions) tend to migrate toward the negatively charged cathode, and anions (negatively charged ions) migrate toward the positively charged anode. These ions concentrate in the solutions near the electrodes or may undergo reactions at the electrodes, which may plate the metals onto the electrodes or liberate gaseous compounds. The electrokinetic remediation system was designed to extract the metal contaminants via electromigration of the contaminant ions and concentration of the ions in the electrode wells. The majority of these contaminants were expected to remain in solution with only minimal plating occurring on the electrodes. Once metal contaminant

concentrations had built up in the electrode well, processing of the electrolyte fluid would be conducted to extract the metal contaminants and return the processed electrolyte fluid back to the wells for continued use. This would have minimized the volume of waste generated by the process.

Precipitation/Flocculation/Sedimentation

Cadmium precipitation has been described in the literature (4). This process is the most common method of removing cadmium from soils. In precipitation reactions chemicals are added to transform dissolved cadmium constituents to form insoluble cadmium precipitates. Metals are precipitated as hydroxides, sulfides, and carbonates by adding appropriate precipitant and adjusting the pH to favor insolubility. Precipitation can be used to remove most metals and many anionic species (phosphates, sulfates, fluorides). Better removal efficiencies can be achieved with sulfite precipitation, but hydroxide precipitation, using lime or caustic, is more practiced, due to lower cost and better availability of the materials such as lime. This may change with newer chemicals such as calcium polysulfide (CaS_5). Precipitation reactions require rapid mixing, while flocculation reactions require slow, gentle mixing to encourage particle contact. After the contaminated product has reacted in the precipitation tank, it flows into the flocculation tank. In a flocculation reaction, alum, lime, ferric chloride, or polyelectrolytes are added to the inflow to reduce the repulsive forces between the precipitated particles. These particles aggregate, forming large flocs of material, which can be settled out in a sedimentation tank. For *in situ* methods, sulfur-based reducing chemicals such as calcium polysulfide, sodium metabisulfate, and ferrous sulfate can be used to precipitate cadmium and other metals. The resultant precipitate is cadmium sulfide (CdS).

CONCLUSIONS

Cadmium usage will continue to grow, especially in the area of rechargeable batteries and solar cells. The health effects of cadmium are well understood, so exposures are minimized through regulations. With recycling programs handling more spent batteries than in the past, cadmium emissions into the air and land should decline over time.

BIBLIOGRAPHY

1. ATSDR (1999). Agency for Toxic Substances and Disease Registry. *Toxological Profile for Cadmium,* U.S. Department of Health and Human Services, Public Health Service. Available: http://www.atsdr.cdc.gov/toxprofiles/tp5.html; updated July.
2. World Health Organization (WHO) (1992). *Environmental Health Criteria 134—Cadmium*, International Programme on Chemical Safety (IPCS) Monograph, Geneva, Switzerland.
3. Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C., Tixier, J.S. Jr., Brauning, S.E., Gavaskar, A.R., and Royer, M.D. (1995). *Remedial Options for Metals–Contaminated Sites*. Lewis Publishers/CRC Press, Boca Raton, FL.
4. Evanko, C.R. and Dzombak, D.A. (2000). Remediation of metals-contaminated soil and groundwater. In: *McGraw-Hill Standard Handbook of Environmental Science, Health and Technology*, J. Lehr (Ed.). McGraw-Hill New York, pp. 14.100–14.134.
5. Nriagu, J.O. and Pacyna, J.M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **333**: 134–139.
6. Nriagu, J.O. (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* **279**: 409.
7. International Lead and Zinc Study Group (ILZSG) (1988). *World Directory: Lead and Zinc Mines and Primary Metallurgical Works*. Chameleon Press, London.
8. Hutton, M., Wadge, A., and Milligan, P.J. (1988). Environmental levels of cadmium and lead in the vicinity of a major refuse incinerator. *Atmos. Environ.* **22**: 411–416.
9. Hutton, M. and Symon, C. (1986). The quantities of cadmium, lead, mercury and arsenic entering the United Kingdom environment from human activities. *Sci. Total Environ.* **57**: 129–150.
10. Thornton, I. (1988). The Shipham report. An investigation into cadmium contamination and its implications for human health. Metal content of soils and dusts. *Sci. Total Environ.* **75**: 21–39.
11. McBride, M.B. (1989). Reactions controlling heavy metal solubility in soils. *Adv. Soil Sci.* **10**: 1–56
12. Benjamin, M.M. and Leckie, J.O. (1981). Competitive adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *J. Colloid Interface Sci.* **79**: 410–419.
13. Sposito, G. (1984). *The Surface Chemistry of Soils*. Oxford University Press, Oxford.
14. Benjamin, M.M. and Leckie, J.O. (1980). Adsorption of metals at oxide interface: effects of the concentrations of adsorbate and competing metals. In: *Contaminants and Sediments*. Vol. 2. R.A. Baker (Ed.). Ann Arbor Science Publishers, Ann Arbor, MI, pp. 305–322.
15. Großklaus, X. (1989).
16. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*, Lewis Publishers/CRC Press, Boca Raton, FL.

READING LIST

United States Environmental Protection Agency (USEPA), 2004, EPA Ground Water & Drinking Water Consumer Factsheet on Cadmium, http://www.epa.gov/OGWDW/index.html.

World Health Organization (WHO), (1984) Guidelines for drinking-water quality: Health criteria and other supporting information, Geneva, World Health Organization, Vol. 2, pp. 84–90.

GROUNDWATER MODELING

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INTRODUCTION

Since the early beginnings with applications for the oil industry (1), computer models have become an

indispensable tool to study aquifers, to understand the interaction of different processes affecting the biogeochemistry and/or the heat distribution, to predict the effect of changes, and to solve practical groundwater problems. Examples are aquifer characterization, capture zone delineation, pumping and recharge well design and management, watershed simulation, groundwater pollution, potential hazards and remediation, acid mine drainage, natural attenuation, geo- and hydrothermics, and saltwater intrusion.

Computer software codes are available today for the modeler to set up groundwater models. Some codes are equipped with user-friendly interfaces and can be used for simulations of flow, as well as mass and heat transport. Some are even capable of including reactions between various chemical or biochemical species. Only a few specific programs can be mentioned here in detail. An extended description of codes is given elsewhere (2,3). Some topics have to be left out also. Multiphase flow is not considered, and modeling of sorption and biogeochemistry could only be mentioned in the context of reactive transport, just to list some topics.

DIFFERENTIAL EQUATIONS

A quantitative description of groundwater flow, transport, and reaction processes is obtained via differential equations. In three dimensions flow equations can be formulated as

$$S\frac{\partial h}{\partial t} = \left\{ \begin{array}{ll} \nabla \cdot T\, \nabla h & \text{for the confined aquifer} \\ \nabla \cdot \mathbf{K} h\, \nabla h & \text{for the unconfined aquifer} \end{array} \right\} + Q \tag{1}$$

with storativity S, transmissivity T, and the tensor of hydraulic conductivities $\mathbf{K}$. The tensor $\mathbf{K}$ allows us to take into account the direction-dependent conductivity. In the case of an isotropic porous medium, the tensor reduces to a scalar conductivity value K, which may change from one location to the other in order to consider different hydrogeological strata or inhomogeneities. In the term Q all types of sinks and sources are gathered. The value of Q is positive for sources of fluid and negative for sinks. Unknown is the variable of piezometric head h. Sometimes pressure p is used as an unknown variable, which is the more appropriate variable in cases in which water density changes (4).

The flow differential equations are derived from the principle of water mass conservation and from Darcy's law (2). The differential equations for the steady state are obtained when the storage term on the left side of differential equation 1 is omitted. More details are given elsewhere (5–7).

The general differential equation for mass transport in three-dimensional space is

$$\frac{\partial}{\partial t}(\phi c) = \nabla \phi\, \mathbf{D} \cdot \nabla c - \nabla(\mathbf{v}c) + q \tag{2}$$

with porosity ϕ, the vector of Darcy velocity $\mathbf{v}$, and the dispersion tensor $\mathbf{D}$. With the dispersion tensor $\mathbf{D}$ it is possible to account for direction-dependent dispersive processes, as they are mostly observed in porous media. The dispersion tensor depends on the parameters of molecular diffusivity D_m and longitudinal as well as transversal dispersivity, α_L and α_T. The term on the left side of the equation represents storage, the first two terms on the right side dispersion and advection. In the term q different additional processes can be taken into account, like decay, degradation, or production. Unknown is the concentration c of a chemical species. For more details see References 4, 8, and 9. In order to describe multispecies systems, the transport equations for the different species are combined by reaction terms:

$$\frac{\partial}{\partial t}(\phi \mathbf{c}) = \nabla \phi\, \mathbf{D} \cdot \nabla \mathbf{c} - \nabla(\mathbf{v}\mathbf{c}) + \mathbf{S}^T\mathbf{c} + q \tag{3}$$

$\mathbf{S}$ denotes the reaction matrix, in which all equilibrium reactions are gathered. In the given notation all unknown concentrations are gathered in a vector $\mathbf{c}$. In order to handle the system described by Equation 3, the equations are rearranged by linear operations, which makes the reaction term $\mathbf{S}^T\mathbf{c}$ vanish. In addition to the remaining transport equations, the equilibrium conditions for the reaction have to be taken into account (10,11). Sorption can be treated similarly, but instead of solving the equilibrium state equation directly, often a retardation parameter R is used as an additional coefficient on the left side of the transport equation (see References 2 and 3).

The heat transport equation is given by

$$(\rho c)^* \frac{\partial}{\partial t} T = \nabla \cdot \lambda\, \nabla T - (\rho c)_f \mathbf{v} \cdot \nabla T + H \tag{4}$$

with heat capacity $(\rho c)_f$ of the fluid as well as thermal conductivity λ and heat capacity $(\rho c)^*$ of the saturated porous medium (2,4,12). In the term H, all types of heat sources can be gathered. Sometimes direction-dependent dispersion processes are taken into account in heat transport; then a tensor has to be used, as in the mass transport equation 2. Unknown in Equation 4 is the temperature T.

Table 1 provides an overview of the types of processes and equations, their unknown variables, and parameters. While in the simplest case a model can be related uniquely to one of the three given types, some model concepts are complex. Transport models are often based on a flow model, which calculates the necessary velocity field $\mathbf{v}$. Even more complex is the coupled situation, when one of the transport variables has an influence on flow. The most prominent example is density-driven flow, in which the effect of salinity and/or temperature on the density is taken into account; see Reference 4. The complexity increases further when, for example, the effect of temperature on kinetic reaction rates in mass transport is to be considered.

BOUNDARY AND INITIAL CONDITIONS

Before the computer is engaged, the first task of the modeler is to specify the *model region*. The model region can be one, two, or three dimensional, depending on the situation to be modeled. The extent of the model region, more specifically its boundaries, has to be chosen appropriately, in order to formulate *boundary conditions*.

Table 1. Overview of Types of Models, Unknown Variables, and Parameters

Type	Unknown Variable	Parameters[a]
Flow	Head, h, or pressure, p	S, T, K, Q, ρ
Mass transport	Concentration(s), c	ϕ, D_m, α_L, α_T, q, R
Heat transport	Temperature, T	$(\rho c)^*$, $(\rho c)_f$, λ, H

[a]See text for description of parameters. The list of parameters is not complete; neither are all of them necessary in all cases.

The boundary of a one-dimensional model consist of two points, the boundary of a two-dimensional area consists of closed lines, and the boundary of a three-dimensional volume is given by surfaces.

In order to complete the mathematical formulation of the problem, boundary conditions have to be formulated. At the boundaries additional information about the behavior of the system is necessary, as the variation of the unknown variable is free outside the model region, while in the interior it is fixed in all directions by the differential equation. There are three major types of boundary conditions, which are listed in Table 2.

Some typical examples for boundary conditions in field situations are given as illustration. When a river or a lake is perfectly connected to groundwater (no clogging layer), the water table of the surface water body is taken as a first-type boundary condition for flow (see Fig. 1); the concentration or temperature of the surface water can be used as first-type boundary conditions for mass or heat transport. Interfaces to nearly impermeable strata in the subsurface are also appropriate boundaries: Neumann conditions are specified for both flow and mass transport, representing no-flow for water and solute. For transport the Neumann conditions represent no dispersive flux, but in combination with a no-flow condition for water there is no advective flux across that boundary either. More complex types of boundary conditions, in which heads and fluxes are combined, are described elsewhere (7,13).

In transient simulations, that is, when the system changes with time, *initial conditions* for the unknown variable have to be specified by the modeler additionally. The task, in mathematical terms, is to solve the *initial and boundary problem* for the differential equation. For this task analytical solutions are sought or numerical models are applied.

Analytical solutions are mostly given by an explicit equation, which is valid for all locations in the model region and all time instants (6). For the evaluation and illustration of such solutions usually a computer is used. Finally, the analytical methods also depend on discretization, that is, the use of discrete time and space values instead of a continuum. But in *numerical methods* the discretization is already applied in the solution process.

Table 2. Overview of Types of Boundary Conditions

Type	Name	Known Value, to be Specified as Condition
First	Dirichlet	Unknown variable
Second	Neumann	Derivative of unknown variable normal to the boundary
Third	Cauchy or Robin	Combination of unknown variable and its derivative

DISCRETIZATION

The major step in groundwater modeling by numerical methods is discretization. The term discretization means that an aquifer or a part of it is divided into a *grid* of small pieces, which are called blocks, volumes, elements, or cells, depending on the *method of discretization*; see below. In one-dimensional models a grid size of 1000 is already a fine model; in two-dimensional cases such a grid size is still small. In three-dimensional models grids containing more than a million unknowns are not uncommon nowadays.

Grids may look very different. A grid may consist of regular rows and columns of blocks: such a regular grid is shown in Fig. 1. It may consist of irregularly shaped triangles as shown in the upper left part of Fig. 3. In fact, these are the major types of grids, connected to the methods of finite differences (FD) and finite elements (FE), but other forms are possible also: irregular rectangular grids, regular triangular grids, grids containing triangles, and other forms of geometries (14). The term grid is not only valid in two dimensions: it consists of intervals in one dimension and prisms or tetrahedrons in three dimensions.

All discretization methods are constructed to calculate approximate solutions for the initial and boundary value problem. Finer grids usually guarantee better approximations. On the other hand, finer grids require more computer space and much longer execution time on the computer. Based on available computer facilities and experience, the modeler usually decides on the grid resolution. Only advanced software tools provide the user with the ability to check the model accuracy by adaptive grids (15).

There are different numerical discretization methods, by which computer algorithms are derived from differential equations. Most important are *finite differences* (FD), *finite elements* (FE), and *finite volumes* (FV).

Using the FD method, derivatives (differential quotients) in the differential equations are approximated by difference quotients. For first and second order derivatives in the x-direction, the simplest central stencils are given by

$$\frac{\partial f}{\partial x} \approx \frac{f_{i+1} - f_{i-1}}{2\Delta x} \quad \text{and} \quad \frac{\partial^2 f}{\partial x^2} \approx \frac{f_{i+1} - 2f_i + f_{i-1}}{\Delta x^2} \tag{5}$$

where the f-values denote function values at the grid nodes: that is, f_i is the approximate value of the function at node i, f_{i-1} at the previous node, and f_{i+1} at the following node. In that way, the differential equation delivers a condition for each block or node of the grid; altogether a system of equations is obtained for the values of unknown functions at the nodes.

Using the FE technique, the solution of the differential equation is approximated by a combination of shape

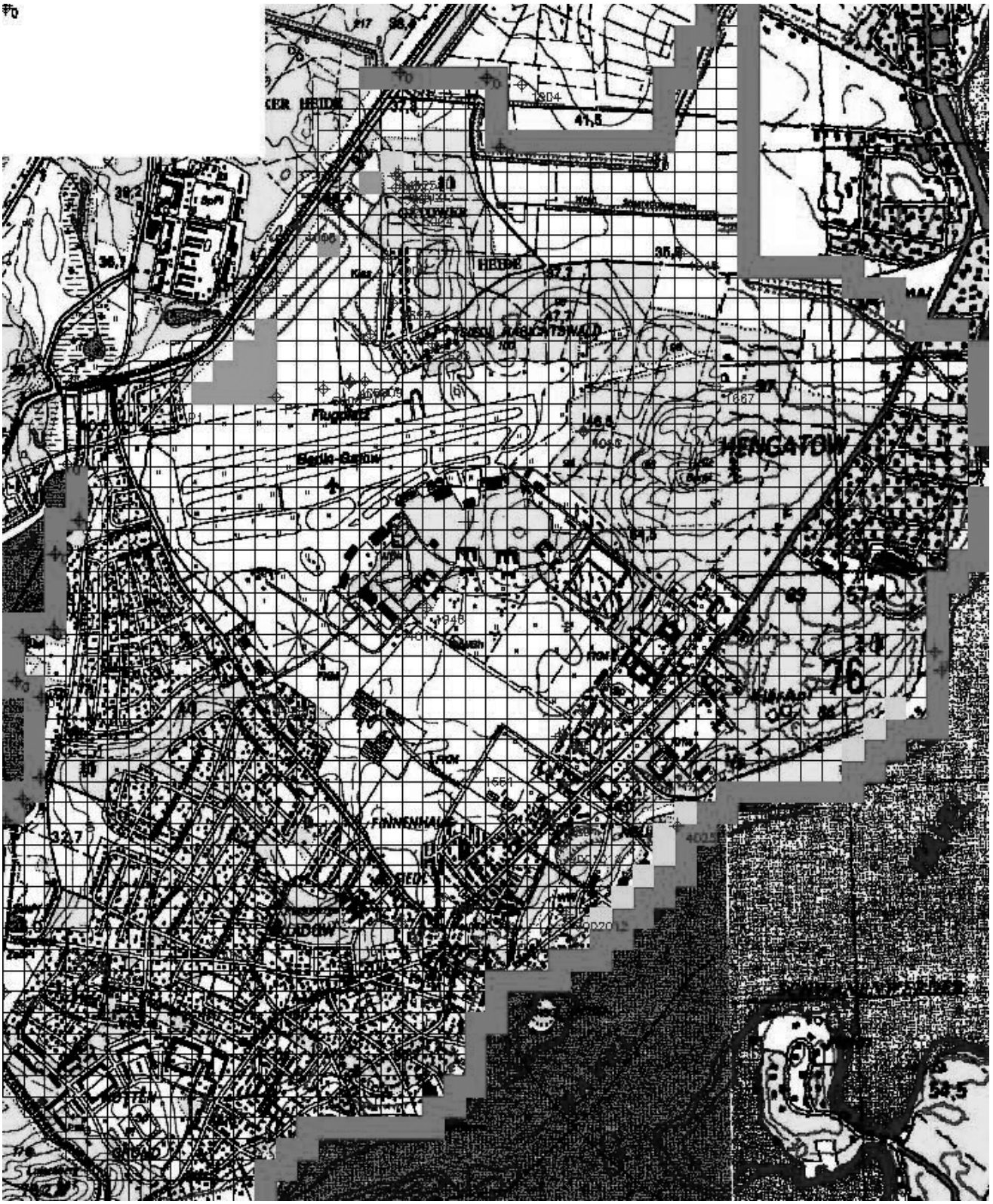


Figure 1. Regular finite volume grid for a horizontal model region. A map is depicted, underlying a regular FV grid, from which only active blocks are shown; boundaries of the model region are shorelines of lakes (west and east) and creeks (north), a water divide (northwest), and a streamline (southwest). Blocks with first-type boundary condition are dark colored pumping wells are light colored, and abandoned landfills as sources of contaminants are gray.

functions, which depend on the element type. For the most common triangular elements, the prescribed shape functions are linear within each element: in the two-dimensional situation the unknown function $f(x, y)$ is approximated by

$$f(x, y) = a_{\alpha 0} + a_{\alpha 1}x + a_{\alpha 2}y \quad \text{within element } \alpha \qquad (6)$$

The so-called weak form of the differential equation delivers conditions for the coefficients $a_{\alpha j}$ for all elements in the form of a linear or nonlinear system (14). FEFLOW (16) is a popular FE groundwater code, using prisms for single layers, while in the mathematical FEMLAB code (14) more general tetrahedrons can be used.

The method of finite volumes (FV) is derived from a mass or energy balance for all volumes of the grid. In the two-dimensional rectangular volume ij, for example, the balance can be noted as

$$\frac{\partial V}{\partial t} = Q_{i-} + Q_{i+} + Q_{j-} + Q_{j+} + Q \qquad (7)$$

where V denotes the volume or mass in the block, Q_{i-}, Q_{i+}, Q_{j-}, Q_{j+} the fluxes across the block edges, and Q other sources or sinks for water volume, mass, or energy in the volume. For further illustration of the technique, the flow equation 1 is considered: replacing the four flux terms in Equation 7 by using Darcy's law leads to a system of equations for the heads at the block centers. The popular MODFLOW code (13) is implemented following this strategy. Under certain conditions the FV technique delivers the same algorithm as the FD method.

The discretization of time is mostly implemented by a time-stepping approach; that is, starting from the initial condition the numerical simulation proceeds in time steps. For each time step, the discretized form of the left side of the differential equation is solved.

Concerning specific modeling situations, the basic techniques may deliver poor results; that is, they may produce bad approximations or results that do not resemble the solution at all, or they may even not converge. A very prominent example problem is transport in advection-dominated flow, for which standard methods deliver unrealistic oscillations or numerical diffusion (3,14). For this specific problem *operator splitting*, using different discretization methods for the different terms on the right side of the transport equation 2, has turned out to be a successful strategy to obtain accurate results even for small time steps (see References 2, 3, and 11).

Independent of the discretization method, a system of equations for the values of the unknown functions at the grid nodes is obtained. The task to find an approximation for the solution of the differential equation is thus transformed to the task of solving a linear or nonlinear system of equations. For the latter task, various solution techniques have been developed in numerical mathematics, which are included in modeling software tools.

PREPROCESSING, SOFTWARE, AND SOLUTION

The entire task of modeling can be divided into three steps: preprocessing, processing, and postprocessing. Processing means the execution of the mathematical solution algorithm for the system of equations (the *solver*), for which different alternatives are available. Taking into account several input parameters, in a model run the solver delivers values for the unknown variable in question on the grid. Depending on the discretization method, values are calculated at the nodes of the grid or at block centers.

Input parameters are prepared during preprocessing. Common software tools allow different preprocessing tasks, concerning the specification of input data. Data fields of distributed parameters can be calculated. For these calculations the user interfaces are equipped with interpolation tools, varying from simple nearest neighbor to complex krigging schemes.

The solvers are special numerical algorithms for the solution of large systems of linear or nonlinear equations. Several solvers and variants are included in most modeling codes. The default values for these solvers (often of conjugate gradient type) are usually appropriate for a wide range of model setups, but sometimes it may be necessary to change a solver parameter or switch to another solver type, in order to obtain a correct and fast solution.

User-friendly shells often not only offer the alternative to use different solvers of one processing program, but allow the user to choose different programs, for which the input data are prepared automatically. Visual MODFLOW (17), GMS (18), and PMWIN (19) are such shells, which are currently used. Operations with the values, which have been delivered by the solver, are gathered under postprocessing, which is dealt with next.

POSTPROCESSING: RESULTS AND VISUALIZATION

There are various ways to visualize large numerical data sets, delivered by a solver, in a form that provides direct insight to the hydrogeological situation. The most common output are head contours, shown as a surface plot, as a pattern of contours with or without fill pattern (see Fig. 2). When several layers of aquifers are modeled, contour plots are generally different from one layer to the other. In three-dimensional models, contour plots can be shown for layers and also for cross sections.

Very informative are flowpaths or flowlines, that is, the travelpaths of particles in the calculated flow field. Start positions have to be chosen by the modeler, and the trace of the particles is followed by a numerical algorithm (2,20). The direction can be either forward or backward in time: the path is traced forward to future positions or back to its origin. Traveltimes can be visualized as so-called isochrones, lines of equal traveltime. In transient simulations, the flowpath usually changes with time, while in steady-state flow the flowpaths are constant. In the latter case, one may speak of streamlines. In three-dimensional models it may be sufficient to depict flowpaths in one picture, in which crossovers are allowed (Fig. 2). Some modeling software delivers the very instructive three-in-one plots with one view from the top and two views in vertical cross sections, as in PMPATH (19).

With streamline plots, it is possible to visualize not only flow direction but also velocities. When streamline

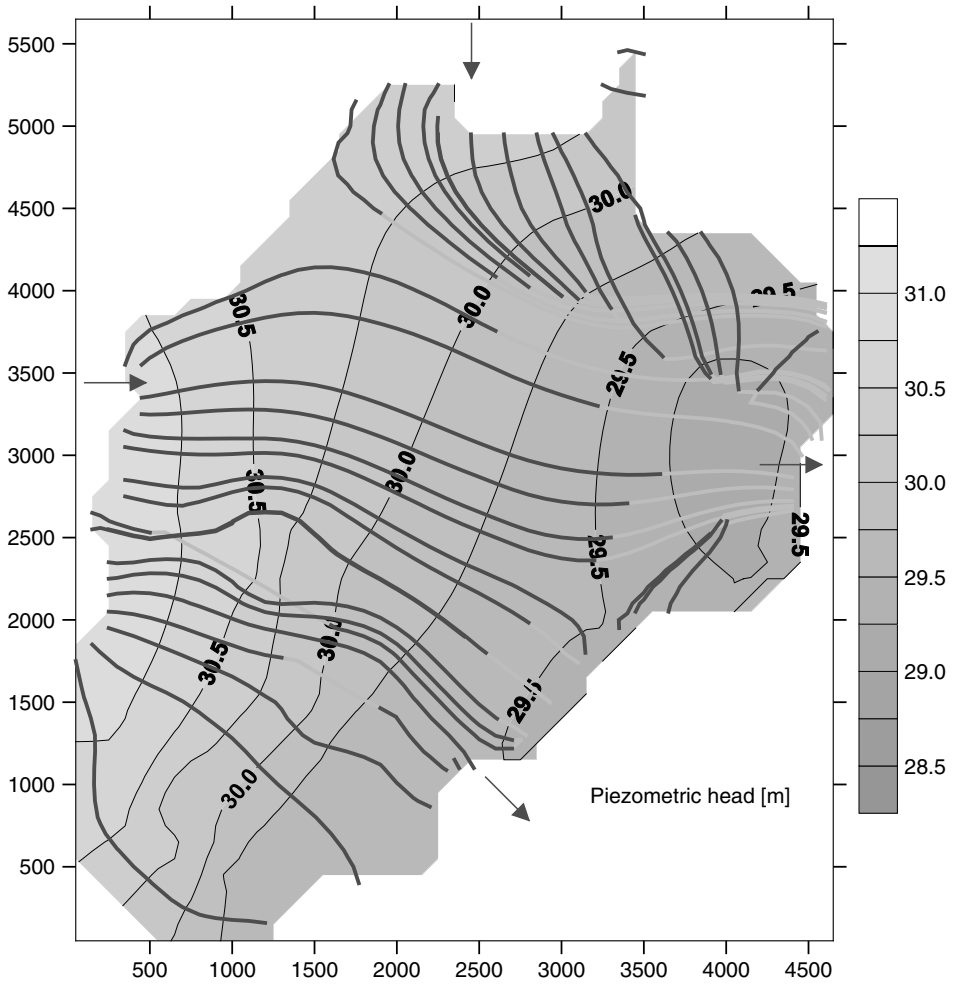


Figure 2. Head contour and flow-path plot, calculated using MODFLOW (13) and PMWIN (19).

levels are equidistant, streamlines become dense, where velocities are high; as the distance widens, the velocities are low. See the bottom left of Fig. 3 as an example.

Vector plots of velocities are also informative, as depicted in the top right of Fig. 3. Not only is the direction shown by the vectors, but the velocity can also be visualized by scaling the length of the vector with the size of the velocity. A problem with such a representation is that in most groundwater problems velocities change by several orders of magnitude within the model region; that is, some vectors become very large, while others are hard to recognize. The alternative is to scale the length of the vectors with the logarithm of the velocity.

In transport models, distributions of concentration or heat are depicted by plots of filled or unfilled contours, representing isohalines in the case of salt and isotherms in the case of temperature. An example for a steady-state concentration is given in the bottom right of Fig. 3. The transient behavior at certain locations of interest within the model region can be captured by breakthrough curves, as implemented in PMWIN (19).

Another important postprocessing tool is the calculation of a budget, for example, of fluid mass for flow models, of component mass in the case of mass transport, and of energy in the case of heat transport. Such budgets are extremely useful for the entire model region or for parts of it. Some programs allow a graphical representation of the different budget terms in a histogram (16).

PARAMETER ESTIMATION

There is an increasing demand for and use of parameter estimation in groundwater models. While the usual modeling task, as described so far, is termed *direct modeling*, parameter estimation is performed by *inverse modeling*. While in direct modeling of groundwater flow (for example) hydraulic conductivity (for example) is an input variable and piezometric head is the unknown variable, their role is exchanged in inverse modeling. However, direct modeling is part of the inverse modeling task.

After each direct modeling run, the performance of the model is evaluated. The performance measure usually is the mean deviation between measured and modeled values. Special algorithms are applied to change the input data set in a way that is likely to increase the performance. Levenberg-Marquard and Gauss-Newton are algorithms of that type, which are applied in all fields of parameter estimation. Various programs offer different types of assistance to the modeler to perform inverse

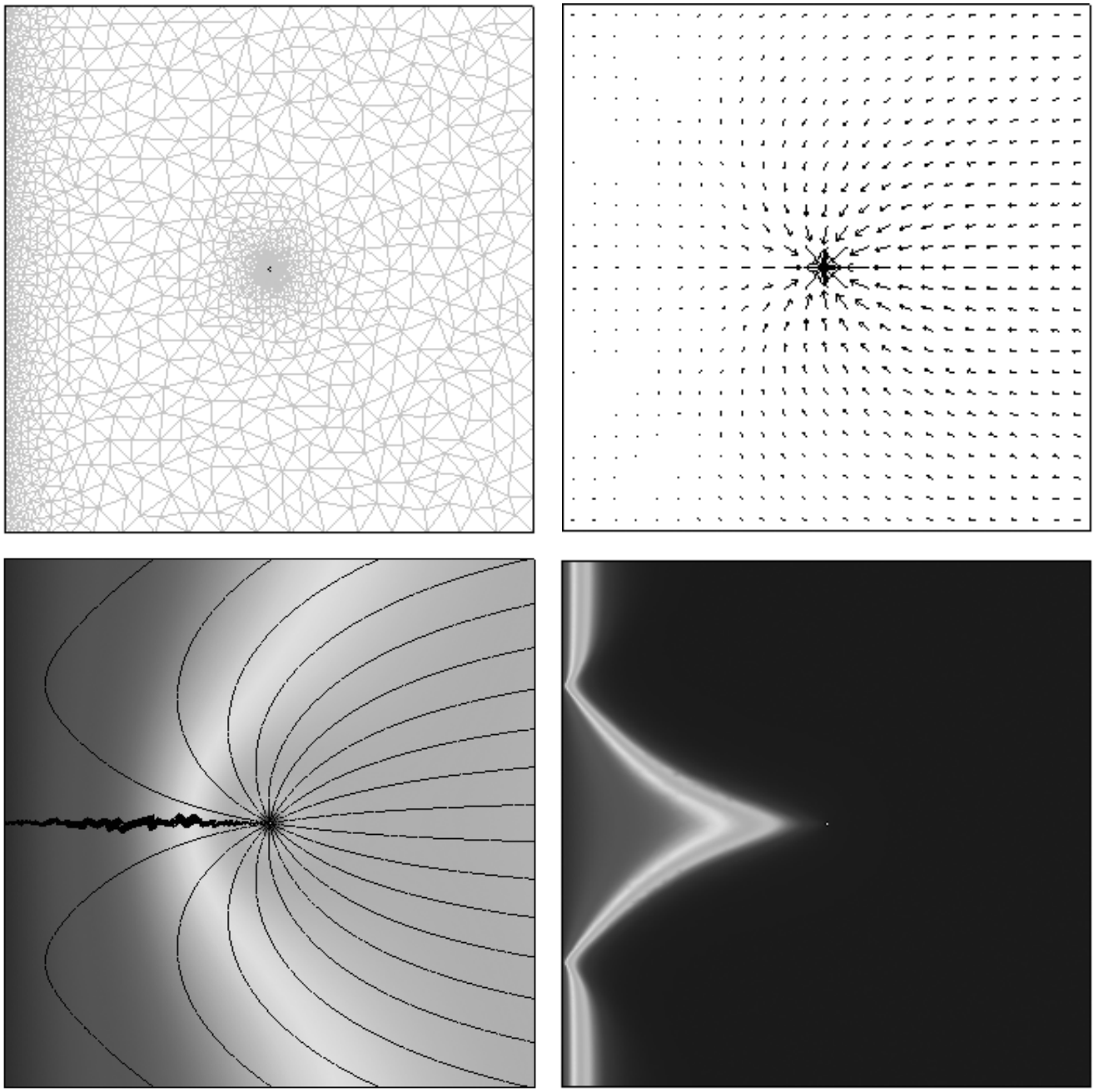


Figure 3. Finite element grid (top left), velocity vector plot (top right), head and streamline plot (bottom left), and concentration plot (bottom right) for bank filtration. The bank is located on the left boundary, the well in the middle of the depicted model region; water pumped at the well is a mixture of bank filtrate and groundwater. Simulated and visualized by FEMLAB (15).

modeling (16,19). In most cases the groundwater models are connected with general-purpose parameter estimation codes, like PEST (21) or UCODE (22).

CONCLUSION

Groundwater modeling has become a broad field in the few decades since its early beginnings. Only major features could be mentioned in a short introduction. Available software tools vary in many aspects and are in permanent development. The treated topics can thus be only a guideline for users searching for appropriate tools for specific applications. The reader may consult References 2 and 3 for more details.

Acknowledgments

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BIBLIOGRAPHY

1. Peaceman, D.W. (1977). *Fundamentals of Numerical Reservoir Simulation*. Elsevier, Amsterdam.
2. Holzbecher, E. (2002). *Groundwater Modeling—Computer Simulation of Groundwater Flow and Pollution*, FiatLux Publ., Fremont. CD-ROM. Available: http://envirocomp.org.
3. Holzbecher, E. and Sorek, S. (2004). Numerical models of groundwater flow and transport. In: *Encyclopedia of Hydrological Sciences*. M. Anderson (Ed.). John Wiley & Sons, Hoboken, NJ.
4. Holzbecher, E. (1998). *Modeling Density-Driven Flow in Porous Media*. Springer, Heidelberg.
5. Bear, J. and Verruijt, A. (1987). *Modeling Groundwater Flow and Pollution*. Reidel Publ., Dordrecht.
6. Strack, O.D.L. (1989). *Groundwater Mechanics*. Prentice Hall, Englewood Cliffs, NJ.
7. Anderson, M.P. and Woessner, W.W. (1991). *Applied Groundwater Modeling*. Academic Press, San Diego, CA.
8. Zheng, C. and Bennett, G.D. (1995). *Applied Contaminant Transport Modeling*. Van Norstrand Reinhold, New York.
9. Sun N.-Z. (1995). *Mathematical Modeling of Groundwater Pollution*. Springer, New York.
10. Saaltink, M.W., Ayora, C., and Carrera, J. (1998). A mathematical formulation for reactive transport that eliminates mineral concentrations. *Water Resource Res.* **34**(7): 1649–1656.
11. Holzbecher, E. (2005). Reactive transport—concepts and numerical approaches. In: *Transport Phenomena in Porous Media III*. D.B. Ingham and I. Pop (Eds.). Elsevier, Dordrecht.
12. de Marsily, G. (1986). *Quantitative Hydrogeology*. Academic Press, San Diego, CA.
13. Harbaugh, A.W., Banta, E.R., Hill, M.C., and McDonald, M.G. (2000). *MODFLOW-2000, the U.S. Geological Survey Modular Ground-Water Model—User Guide to Modularization Concepts and the Ground-Water Flow Process*. U.S. Geological Survey Open-File Report 00-92.
14. Huyakorn, P.S. and Pinder, G. (1983). *Computational Methods in Subsurface Flow*, Academic Press, New York.
15. FEMLAB, *Version 3.1, COMSOL AB, Tegnérgatan 23*, SE-111 40 Stockholm, Sweden.
16. FEFLOW, *WASY Inst. for Res. Planning and Systems Res.*, Waltersdorfer Str. 105, D-12526 Berlin, Germany.
17. Visual MODFLOW, *Waterloo Hydrogeologic, Inc.*, 460 Phillip Street, Suite 101, Waterloo, Ontario, N2L 5J2, Canada.
18. GMS, *Environmental Modeling Systems, Inc.*, 1204 W. South Jordan Pkwy, Suite B, South Jordan, UT 84095, USA.
19. Chiang, W.-H. and Kinzelbach, W. (2003). *3D-Groundwater Modeling with PMWIN—A Simulation System for Modeling Groundwater Flow and Pollution*, p. 346.
20. Pollock, D.W. (1988). Semianalytical computation of path lines for finite difference models. *Groundwater* **26**(6): 743–750.
21. Doherty, J. (2002). *PEST—Model Independent Parameter Estimation*. Watermark Numerical Computing, Corinda, Australia.
22. Poeter, E.P. and Hill, M.C. (1998). *Documentation of UCODE, a Computer Code for Universal Inverse Modeling*. U.S. Geological Survey Water-Resources Investigations Report 98-4080.

GROUNDWATER AND BENZENE: CHEMICAL BEHAVIOR AND TREATMENT

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Benzene (C_6H_6) is a clear, colorless, highly flammable aromatic hydrocarbon liquid. As an important ingredient for making plastics, rubber, resins, and synthetic fabrics like nylon and polyester, benzene is one of the most commonly used industrial chemicals in the world. It is also used as a solvent in printing, paints, and dry cleaning. It is also a major component of gasoline. The wide ranging industrial applications of benzene make it widely distributed, particularly in the case of petroleum products, of which it is a primary constituent. Benzene is highly toxic to humans and the environment. Because of its severe toxic effects, both in the short and long term, benzene use has been under strict regulations for many years. Nonetheless, widespread contamination of benzene has occurred in the environment, and, therefore, significant regulatory efforts in the United States and other nations are being enacted to limit or eliminate potential impacts.

HISTORY

In 1825, Michael Faraday began a number of experiments in distillation. Among the products he worked on was crude oil, from which he extracted a colorless gas-phase compound. Faraday lit the gas compound and it burned. For decades the benefits of what Faraday called "bicarburet of hydrogen" were unknown. In 1834 Eilhard Mitscherlich isolated the same gas-phase compound by heating benzene carboxylic acid ($C_6H_5CO_2H$), also called benzoic acid, with lime (CaO). He derived the chemical formula C_6H_6 and named the compound "benzin." In 1846, A. W. Hoffman isolated the same product, later called benzene, in large quantities by distilling coal (1).

CHEMICAL STRUCTURE

The molecular structure of benzene baffled scientists for many years, although the empirical formula was known. None of the proposed molecular structures at the time supported the chemical properties observed. In 1865, Friedrich August Kelule proposed a ring structure. It is now known that benzene, like all aromatic hydrocarbons, contains a cyclohexane type of ring structure that has alternating single and double bonds.

This unique molecular structure of benzene (C_6H_6), a volatile, colorless, and flammable hydrocarbon, made it incompatible or reactive with strong oxidizers, many fluorides, perchlorate, and nitric acid. It is slightly soluble in water [580–1780 ppm (~0.06–0.17%)] and has a boiling point of 80 °C and a freezing point of 5.5 °C. Benzene has a characteristic sweet odor, with an odor threshold of 2.7–12 ppm in air.

PRODUCTION AND USES

For a long time, benzene could only be extracted from coal; however, with the rise of crude oil use, its importance increased significantly. From the start of the twentieth century, benzene saw extraordinary growth in its applications in an abundance of industrial areas, including chemical, petroleum, agricultural, and pharmaceutical manufacturing. Benzene has been given a list of trade names by product producers, including Benzol 90, Pyrobenzol, Polystream, Coal naptha, and Phene (2).

Benzene first saw major industrial production during World War I, where it was produced specifically for the rubber industry as well as for the production of toluene, a major component of explosives. Eventually, benzene began finding uses in other industrial processes such as the manufacture of artificial leather, rubber goods, and rotogravure printing industries, and as a starting material in organic synthesis.

Benzene has been released into the air primarily from fumes and exhaust through incomplete vehicular combustion. Other air sources of benzene include the release of fumes from the production and use in manufacturing of other chemicals (2). Vapor emissions of benzene can be detected from carpet glue, textured carpet, and furniture wax (3).

Benzene is also an important component of gasoline. Benzene has been released into the subsurface through leaking fuel tanks, primarily gasoline. Discharges into water come from industrial effluents and losses during spills (2).

HAZARDOUS EFFECTS

Benzene has been recognized since 1900 as a toxic substance capable of producing acute and chronic nonmalignant effects in humans. When benzene vapors are inhaled, the benzene diffuses rapidly through the lungs and is quickly absorbed into the blood. Acute circulatory failure resulting in death within minutes often accompanies exposure to benzene concentrations as high as 20,000 ppm. Other acute effects of exposure to milder, though still high (250–500 ppm), concentrations of benzene include vertigo, nervous excitation, headache, nausea, and breathlessness. As a result of its toxicity, benzene's history has been one of regulation. In 1946, the American Conference of Governmental Industrial Hygienists recommended a threshold limit value for benzene exposure of 100 ppm. This value was reduced to 50 ppm in 1947, to 35 ppm in 1948, to 25 ppm in 1963, and to 10 ppm in 1974. The American National Standards Institute adopted a threshold limit value of 10 ppm in 1969, which OSHA adopted in 1971 without rulemaking under the authority of 29 U.S.C.A. § 655(a). This standard, codified in 29 C.F.R. § 1910.1000 Table Z-2, was based on the nonmalignant toxic effects of benzene exposure and not on any possible leukemia hazard (4).

The U.S. Congress passed the Safe Drinking Water Act (SDWA) in 1974. The law requires the U.S. EPA to determine safe levels of chemicals in drinking water, which do or do not cause health problems. These nonenforceable levels are based on possible health risks and exposures are called Maximum Contaminant Level Goals (MCLG). The MCLG for benzene is zero, as this level would not cause any harm to humans. The EPA set the enforceable Maximum Contaminant Level (MCL) for benzene at 5 μg/L or 5 parts per billion (ppb). This is the lowest level to which water systems can be reasonably required to remove benzene prior to serving the water. All community or public water supplies in the United States must abide by these regulations (2).

The carcinogenic nature of benzene was known from as early as the 1920s (5) and since then numerous medical studies have confirmed linkages between human exposure to benzene and the occurrence of leukemia. Since then, a number of U.S. health authorities [e.g., the Occupational Safety and Health Association (OSHA), the National Institute of Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH)] have set benzene exposure risk standards (at levels not exceeding 0.1 ppm per day) (6). Short-term exposure above the MCL could cause temporary nervous system disorders, immune system depression, and anemia. Long-term lifetime benzene exposure at levels above the MCL has the potential to cause chromosome aberrations and cancer (2).

CONTAMINATION AND EXPOSURE

Benzene has been found in at least 813 of the 1430 National Priorities List sites identified by the U.S. EPA. Industrial sites and gasoline service stations are the main sites of benzene contamination (7). Human exposure to benzene may result from such factors as industrial and motor vehicle emissions, tobacco smoke, industrial factories working environments, and hazardous waste disposal sites. Benzene is capable of passing into the air from soil and water sources. The largest issue is benzene contamination from leaking underground storage tanks (LUSTs) into groundwater, which may impact drinking water sources.

Remedial Measures

Environmental contamination of pure benzene is unlikely since benzene is often used as an ingredient with other compounds. Most benzene contamination occurs when other more common chemicals, such as gasoline, having benzene as a main constituent, are released into the environment. Examples of such products include petroleum fuel hydrocarbons (gasoline, diesel, and kerosene), industrial solvents, detergents, and pesticides, among others compounds (7). At present, there are a number of major contamination sites containing elevated levels of benzene and benzene-based products. In many of these cases, the contamination poses a threat to sources of groundwater utilized for human consumption.

Benzene does not readily sorb to soil and therefore may be transported large distances from its source depending on groundwater velocity and hydraulic conductivity. The potential environmental impact of subsurface benzene contamination is dependent on many factors. Under optimal

subsurface conditions, benzene is biodegradable. Benzene is relatively easy to oxidize with chemical oxidants such as ozone, potassium permanganate, sodium persulfate, and hydrogen peroxide. Benzene has been extracted from the subsurface using soil vapor extraction in the vadose zone and groundwater pump and treat systems. Common aboveground treatment methods for benzene include thermal and catalytic oxidizers, granular activated carbon, biofilters, and advanced oxidation processes. Aerobic bioremediation and enhanced natural attenuation work well with benzene. Suthersan (8) describes various gasoline and benzene bioremediation methods.

Extraction technologies such as soil vapor extraction (SVE) for the vadose zone and groundwater extraction with pumps and aboveground treatment of benzene have been used for decades. A good summary of various technologies for benzene vadose zone and groundwater treatment is Reference 9.

BIBLIOGRAPHY

1. Online Lawyer Source (OLS) (2003). The history of benzene. Available: http://www.onlinelawyersource.com/benzene/history.html.
2. United States Environmental Protection Agency (U.S. EPA) (2004). Consumer factsheet on benzene. Available: http://www.epa.gov/safewater/contaminants/dw_contamfs/benzene.html.
3. National Safety Council (2004). Available: http://www.nsc.org/library/chemical/benzene.htm.
4. Environmental Law Reporter (2004). American Petroleum Institute v. Occupational Safety and Health Administration. Available: http://www.elr.info/litigation/vol8/8.20790.htm.
5. Boston-Lawyer-Referral.com (BLR) (2004). Benzene cancer cases. Available: http://www.boston-lawyer-referral.com/pgs/benzene_cancer_14.html.
6. Acute myelogenous leukemia (AML). (2004). A history of benzene standards: benzene and acute myelogenous leukemia story. Available: http://www.acute-myelogenous-leukemia.com/html/risk.html.
7. Agency for Toxic Substances and Disease Registry (ATSDR) (2004). ToxFAQs™ for benzene. Available: http://www.atsdr.cdc.gov/tfacts3.html#bookmark02.
8. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL.
9. Testa, S.M. and Winegardner, D.L. (2000). *Restoration of Contaminated Aquifers: Petroleum Hydrocarbons and Organic Compounds*, 2nd Edn. CRC Press, Boca Raton, FL.

GROUNDWATER AND NITRATE: CHEMICAL BEHAVIOR AND TREATMENT

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Nitrate is a naturally occurring substance, which is an essential ingredient for the growth of plants. Human activities can contribute to higher levels of nitrate in the ground and surface waters. The major source of excess nitrogen is nitrate fertilizers for agricultural, lawn, and other garden uses. Nitrates are sourced from nitrates in nitrate fertilizers, the storage or use of animal manure, leaky septic systems, leaky sanitary sewer pipelines, and improper disposal of treated wastewater containing high nitrate levels. Through storm runoff and leaching processes, nitrates have become dissolved in stormwater runoff or infiltration waters. These sources of dissolved nitrates have created significant impacts on worldwide surface water and groundwater resources.

INTRODUCTION

Besides nitrate-based fertilizers, other sources of nitrates include animal manure from feedlots, dairies, and poultry farms; septic tanks; rainwater (acid rain); and sewage sludge. Human exposure to nitrates can occur through certain foods, such as cured meats and vegetables, and through tobacco smoke (1).

HISTORY

Daniel Rutherford in Scotland discovered nitrogen in 1772. In 1905 the world's first production of nitrogen fertilizer [Nrgessalpeter (calcium nitrate)] was done at a test facility in Nottodon, Norway. Production was based on the Birkeland Eyde invention using hydroelectric power to extract nitrogen from the air.

The German physical chemist Fritz Haber invented a process in 1909 that directly combines nitrogen from the air with hydrogen from a hydrocarbon source under extremely high pressure (200–400 atm) and moderately high temperatures (400–650 °C) to make ammonia (NH_3). The process initially used coal and later natural gas as a source of hydrogen and as a source for the considerable energy required. For his efforts, Haber received the Nobel Prize in Chemistry in 1918. It was an industrial chemist, Carl Bosch, who took the Haber method and designed a large scale process using a catalyst and high pressure methods. Those efforts were rewarded with a jointly shared Nobel Prize in 1931 with Friedrich Bergius for high pressure studies. The discovery and feasibility of the Haber–Bosch process (also called the Haber Ammonia Process and the Synthetic Ammonia Process) were dependent on the newly discovered sources of energy from coal and petroleum, which made the production of ammonia economically feasible. In 1928, ammonia-based production replaced the Birkeland Eyde technology both at the Nottodon and Rjukan facilities. Calcium nitrate based on ammonia from Rjukan nitrogen–phosphorus–potassium (NPK) production using a newer nitrophosphate process, started in the mid-1930s and gained importance in the mid-1960s.

PROPERTIES OF NITRATES

Nitrates, chemical compounds containing the nitrate (NO_3) radical, are salts or esters of nitric acid (HNO_3)

formed by replacing the hydrogen with a metal (e.g., sodium or potassium) or a radical (e.g., ammonia or ethyl). Some important inorganic nitrates are potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), silver nitrate ($AgNO_3$), and ammonium nitrate (NH_4NO_3). Calcium nitrate is also used in fertilizers. The presence of nitrate in the soil is of great importance, since it is from these compounds that plants obtain the nitrogen necessary for their growth. Nitrogen-fixing bacteria are important in keeping soil supplied with nitrates.

Nitrate is present in various compounds: nitrate (NO_3), nitrate-nitrogen (NO_3-N), nitrite (NO_2), nitrate plus nitrite (NO_3+ NO_2). Each represents a different measurement of nitrogen's impact on health.

Persistence in Groundwater

Nitrate occurs naturally in the subsurface in small quantities. Due to large inputs of agricultural fertilizers and runoff from manure, the level of nitrate in groundwater has in risen significantly in some locations. Nitrate in groundwater can be reduced by denitrification, resulting in nitrogen gas (2). Commonly available activated carbon, filtration, and standard water softeners do not remove nitrate-nitrogen from water.

Taste and Odor

Nitrate is odorless and colorless, so it can be detected only through a water test.

Health Risk

The main health threat from nitrate is methemoglobinemia, or blue baby syndrome. Infants less than six months old do not have the enzyme needed to break down nitrates. Excess nitrogen in the system interferes with the blood's ability to carry oxygen, resulting in a bluish tint to the skin. This condition is rare but can be fatal.

There is no conclusive evidence that nitrates can cause cancer in adults. However, there is some evidence that high levels of nitrate consumed over a long period may be toxic. Maximum contaminant levels (MCLs) are standards that provide a minimal level of risk to health from consuming a contaminant over the course of a lifetime. Lifetime exposure to nitrate levels above MCL can cause diureses, increased starchy deposits, and hemorrhaging of the spleen (3).

A water test for nitrate is suggested for households with infants, pregnant women, nursing mothers, or elderly people. It is recommended that new water supplies should be tested to determine the baseline nitrate concentration. In addition, if a water supply has never been tested for nitrate, it should be tested. If excess nitrate is found in a water supply, then the water should be treated, or an alternative source of potable water should be secured (4).

REGULATORY ISSUES

In 1974 the U.S. congress passed the Safe Drinking Water Act. This law requires the Environmental Protection Agency (EPA) to determine safe levels of chemicals in drinking water, which do or may cause health problems. The MCL for nitrate has been set at 10 ppm and 1 ppm for nitrite (3).

FATE AND TRANSPORT

Nitrate is a highly soluble anion that readily transports in groundwater, resulting in contamination of large subsurface areas. Many sites are affected by nitrate contamination. Nitrate is easily transported in oxygen-rich water with no transformation and little or no retardation. Nitrate is not removed by filtration and the compound is stable over a considerable range of conditions. Large numbers of activities contribute to the problem: farming, fertilization, animal feedlots, dairy; manufacturing of explosives and chemicals; nuclear industry, large amounts of nitric acid, dissolved metals and actinides; mining industry.

Use of agricultural fertilizers is the major source of contamination. Nitrate contamination depends on factors such as the amount of excess nitrate not used by plants, the soil type, and the underlying geology. Areas with soils that are sandy, gravelly, or shallow over porous limestone bedrock and areas with karsts topography (cave areas) have the greatest risk of nitrate contamination of groundwater sources.

The primary inorganic nitrates that may contaminate drinking water are KNO_3 and NH_4, both of which are widely used as fertilizers. Nitrates are highly soluble in water and do not bind to soils. They have a high potential to migrate to groundwater. Because they do not evaporate, nitrates are likely to remain in H_2O until consumed by plants or other organisms (3).

Nitrate is often the dominant source of nitrogen in the soil since it generally occurs in high concentrations and is free to move to the roots by mass flow and diffusion. In addition to KNO_3 and NH_4, other nitrate-containing fertilizers including $NaNO_3$ and $Ca(NO_3)$ are quite soluble and thus very mobile in soil solution. They are quickly available to crops because of their mobility. They are susceptible to leaching under conditions of high rainfall. Nitrate supplied in commercial fertilizer is subject to leaching. The NO_3^- form of nitrogen is completely mobile and within limits moves largely with soil water. Under conditions of excessive precipitation or irrigation, it is leached out of the vadose zone.

Immobility of nitrate occurs when large quantities of low nitrogen crop residues begin decomposing in the soil. The high amounts of carbohydrate in such residues cause the population of microflora to build up quickly. As new cells are formed, nitrogen is used to build up protoplasm. Almost invariably this leads to a decrease in levels of nitrates. Biodegradation of nitrates occurs through processes such as denitrification (5).

A study by the United States Geological Survey for point and nonpoint sources in major U.S. watersheds indicated that agricultural nitrate accounted for over 80% of the nitrogen input into the environment: (53%) fertilizers, (27%) animal manure, (14%) atmospheric, and (6%) point sources (6).

GROUNDWATER INVESTIGATION

Nitrate is highly soluble in water and poorly retained in the soil; therefore, it can move through the soil and into groundwater sources. The likelihood and seriousness of leaching is of concern as the public cost of groundwater contamination is high. Studies have shown that more public supply wells have been impacted by nitrate contamination than all other contaminants combined. Frequent sampling for nitrate contamination should be conducted.

REMEDIATION

Several approaches for actively treating nitrate contamination have been proposed. The duration, success, and cost of treatment are dependent on the method used.

Phytoremediation using shrubs and specific types of plants to remediate a nitrate-contaminated aquifer is a passive but cost effective method to remove contaminants. However, it is a slow process and could take decades to clean up nitrate contamination.

Active pump and treat remediation is also used successfully in depleting nitrate contaminant. Nitrate reduction by denitrification where nitrate is sequentially reduced to nitrite, nitric oxide, and nitrogen gas is also effective.

Nitrate can be removed in anaerobic groundwater systems, such as may occur in natural or contaminated environments with elevated concentrations of dissolved organic matter, by bacterial action through the process of denitrification (7). It is the major microbial process that destroys nitrate by reducing it into nitrogen gas (N_2):

$$\underset{}{\overset{(1)}{NO_3^-}} \rightarrow \underset{}{\overset{(2)}{NO_2^-}} \rightarrow \underset{}{\overset{(3)}{[NO]}} \rightarrow \underset{}{\overset{(4)}{N_2O}} \rightarrow N_2$$

Oxidation state:

$$+5 \qquad +3 \qquad +2 \qquad +1 \qquad 0$$

where (1) is nitrate reductase, (2) is nitrite reductase, (3) is nitric oxide reductase, and (4) is nitrous oxide reductase.

Bacteria use nitrate as a terminal electron acceptor when oxygen is not available. Denitrification has developed over millions of years and can occur readily in an oxygen-depleted environment (anaerobic) with abundant carbon and electron acceptors.

Electron acceptors include oxygen (O_2), nitrate (NO_3^-), nitrite (NO_2^-), manganese [Mn(IV)], ferric iron [Fe(III)], sulfate (SO_4^{2-}), and carbon dioxide (CO_2) (2). Usually by the time the sulfate and carbon dioxide are used as the electron acceptor or oxidant, the nitrate is already completely reduced to nitrogen gas (N_2). More information on denitrification can be found in References 2 and 8. The half-cell reaction for denitrification produces -16.9 kcal/mole $\cdot\, e^-$ of usable energy, also called the Gibbs free energy of reaction (9):

$$5e^- + 6H^+ + NO_3^- \rightarrow 0.5N_2 + 3H_2O$$

An injection of a carbon source into wells, well points, probe rods, trenches, or other delivery systems can move a nitrate-contaminated groundwater plume into the denitrification process, which will produce nitrogen gas as the end product. Laboratory bench testing is recommended prior to pilot scale field testing to optimize the site-specific geochemistry. Adjustments of pH or additions of nutrients may be required to optimize nitrate reduction rates.

Short-term solutions to high nitrate concentrations include bottled water and blending nitrate-impacted water with clean water to deliver water that is within the safe range for human consumption. Nitrate can be removed from drinking water by several physical/chemical methods, including distillation, reverse osmosis, electrodialysis or electrodialysis reversal, and ion exchange (4).

Distillation involves heating the water to boiling and collecting and condensing the steam generated as the water boils. Merely boiling water will increase rather than decrease the nitrate concentration. In the reverse osmosis process, pressure is applied to water to force it through a semipermeable membrane. As the water passes through the membrane, dissolved salts, including nitrate, are removed. Electrodialysis uses a driving force of direct current (DC) power to transfer ionic species (e.g., nitrate, sodium) from the feed water through cation and anion transfer membranes to a concentrated stream, creating a more dilute stream as the product water. Electrodialysis reversal is a variation on the electrodialysis process, in that it uses electrode polarity reversal to automatically clean membrane surfaces. Nitrate removal by ion exchange operates on the same principle as a household water softener. In a standard water softener, calcium and magnesium ions are exchanged for sodium ions. For nitrate removal, special anion exchange resins are used that exchange chloride ions for nitrate and sulfate ions in the water as it passes through the resin (4).

CONCLUSION

Nitrate is highly soluble and is subject to leaching. Therefore, it will migrate readily to groundwater sources. High levels of rainfall or frequent irrigating make groundwater sources more susceptible to nitrate contamination from agricultural fertilizers. Enhanced natural attenuation using a carbon source (such as propane gas, molasses, corn syrup, or lactic acid) can lead to denitrification of nitrates, producing nitrogen gas as the end product.

BIBLIOGRAPHY

1. Ilvento, X. and Tarabo, X. (1997).
2. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*, Lewis Publishers/CRC Press, Boca Raton, FL, p. 419.
3. United States Environmental Protection Agency (USEPA) (2004). Consumer factsheet on nitrates/nitrites, updated November 1, 2004. Available: http://www.epa.gov/safewater/contaminants/dw_contamfs/nitrates.html.
4. Ulrick, J. (2004). Preprint of Groundwater Resources Association of California Nitrate Overview Paper, Sacramento, CA.
5. Tisdale, S.L. and Nelson, W.L. (2004). *Soil Fertility and Fertilizers: An Introduction to Nutrient Management*, Prentice-Hall, Engelwood Cliffs, NJ, p. 634.

6. Pucket, L.J., *Nonpoint and Point Sources of Nitrogen in Major Watersheds of the United States*, U.S. Geological Survey National Water Quality Assessment Program, WRI94-4001, 1994.
7. Hem, J.D. (1992). *Study and Interpretation of the Chemical Characteristics of Natural Water*, 3rd Edn. U.S. Geological Survey Water Supply Paper 2254.
8. National Resource Council (NRC) (2000). *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington, DC.
9. Wiedemeier, T.H., Rifai, H.S., Newell, C.J., and Wilson, J.T. (1999). *Natural Attenuation of Fuels and Solvents in the Subsurface*, 1st Edn. John Wiley & Sons, New York.

GROUNDWATER AND PERCHLORATE: CHEMICAL BEHAVIOR AND TREATMENT

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Large-scale perchlorate production began in the 1940s. Perchlorate leakage has been ongoing in some cases for decades. The majority of perchlorate spills are related to the use of explosive propellant as a solid rocket fuel for missiles and for the NASA space shuttle. It has only been since the late 1990s, when laboratory methods improved detection of perchlorate in the groundwater, that the full impact of the groundwater contamination became evident. A variety of point of use treatments for perchlorate are available, at varying efficiencies and costs. Of the various *in situ* technologies, anaerobic bioremediation is the most promising for widespread subsurface perchlorate treatment.

INTRODUCTION

The environmental impact/toxicity of perchlorate is an active area of research, critical to the protection of groundwater resources. Perchlorate (ClO_4^-) is the soluble anion associated with the solid salts of ammonium, magnesium, potassium, and sodium perchlorate. Perchlorate is used in the United States to make rocket fuel, fireworks, road flares, and similar products. It remains one of the key ingredients in numerous national defense weapons systems. The occurrence of perchlorate in public drinking water supplies over the years may be inextricably linked with inadequate maintenance, storage, and disposal practices followed in the past. Consequently, varying quantities of the compound leached into the soil and groundwater, especially at or near sites that developed or manufactured aerospace materials or armaments for U.S. national defense programs.

Contamination of numerous sites is highest in California, where cities like Rialto, already affected by drought and increasing population, are continuing to lose water capacity to perchlorate contamination and its spreading plume. Perchlorate is an unregulated contaminant in the United States, meaning it does not have a set maximum concentration level (MCL). A good overview of perchlorate issues is summarized by Motzer (1).

Perchlorate

Perchlorate has the following uses:

- As a solid propellant in rockets, missiles, and fireworks (primarily ammonium perchlorate)
- In road flares
- As a component of airbag inflators
- In munitions for smokeless powder
- In nuclear reactors and electronic tubes
- As additive in lubricating oils
- In tanning and finishing leather
- As a mordant for fabrics and dyes
- In electroplating, aluminum refining, and rubber manufacture
- In the production of paints and enamels
- As a component of certain imported Chilean fertilizers

About 90% of the 20 million pounds of perchlorate produced each year goes into solid rocket fuel for Air Force missiles and the NASA space shuttle (2). Although the vast majority of locations where perchlorate has been detected in the groundwater are influenced by anthropogenic activity, perchlorate has been found to occur naturally in Chilean caliche. Perchlorate is reported to be present in some caliche formations in Chile that are used to produce nitrate fertilizers (3).

Ammonium Perchlorate (ClH_4NO_4)

Ammonium perchlorate is used as an energetics booster or oxidant in solid propellant for rockets and missiles. It is therefore a national technical asset integral to the nation's strategic defense system and space exploration. Ammonium perchlorate is also used in certain fireworks, the manufacture of matches, as a component of airbag inflators, and in analytical chemistry to preserve ionic strength. Large-scale production of ammonium perchlorate began in the United States in the mid-1940s. Ammonium perchlorate has a limited shelf life and must be periodically replaced in munitions and rockets or in inventory. This has led to the disposal of large volumes of the compound since the 1940s in Nevada, California, Utah, and other states.

Potassium Perchlorate ($KClO_4$)

Potassium perchlorate until recently was used to treat hyperthyroidism resulting from Graves' disease and is still used diagnostically to test thyroid hormone production in some clinical settings (medicinal use). In addition, potassium perchlorate is used in protective breathing equipment on Air National Guard (ANG) aircraft for use in the event of depressurization, and in naval emergency escape breathing devices (4).

Sodium Perchlorate ($NaClO4:H_2O$)

Sodium perchlorate is mainly used in the manufacture of perchloric acid, also used in the gun-powder industry.

HISTORY OF OCCURRENCE

Several hundred drinking water wells were sampled by the California Department of Health Services (CDHS) for perchlorate beginning February 1997. Perchlorate was first detected in drinking water wells (up to 260 μg/L) near the Aerojet site in Sacramento County. Groundwater treated to remove volatile organic chemicals (such as trichloroethylene) was reinjected into the groundwater. Perchlorate, also in the contaminated shallow groundwater, has been present in the reinjected water at concentrations up to 8000 μg/L (5).

Characteristics of Perchlorate

Perchlorate is a highly soluble inorganic anion (2.09 kg/L for $NaClO_4^-$) that adsorbs poorly to mineral surfaces and activated carbon and is not retarded during groundwater transport.

Persistence of Perchlorate in Groundwater

Perchlorate is very stable/inert in groundwater. It does not biodegrade unless there is an absence of available, dissolved oxygen (oxygen acts as an alternate electron acceptor). Groundwater has naturally occurring dissolved oxygen, which microbes will use first before turning to other sources, so natural biodegradation of perchlorate is unlikely.

Plumes may be nearly 8 miles (which is large). Perchlorate may disperse in the aquifer as it flows downgradient in the subsurface, to the extent that it may not be detectable using available analytical methods.

Taste and Odor

There is no perceptible odor or taste that perchlorate imparts to water.

Fate and Transport

Fate and transport of the chemical essentially depend on its physical characteristics and natural attenuation. Perchlorate is highly soluble in groundwater. Volatilization is not expected to be one of the predominant pathways of transport. Perchlorate and concentrated solutions of perchlorate are denser than water (ammonium perchlorate at 1.95 g/mL), which allows it to sink. Perchlorate is kinetically stable and adsorbs poorly to mineral surfaces and activated carbon and is not retarded during groundwater transport.

HEALTH RISKS

At present, there is a large amount of information available on the health effects from exposure to perchlorate; however, there is still widespread debate on the potential toxicity of perchlorate, the ecological receptors, and the long-term effects on humans. Health studies using data from patients who were given perchlorate to treat thyroid conditions indicate that high doses can affect metabolism, growth, and development of the body. Long-term exposure to high levels of perchlorate taken as medication has been linked to a potentially serious blood disorder. However, it is impossible for the levels of perchlorate in drinking water to cause such conditions. Perchlorate slows the uptake of iodide into the thyroid. Because iodide is an essential component of thyroid hormones, at high doses perchlorate can affect how the thyroid functions. In adults, the thyroid helps to regulate metabolism; in children, the thyroid also plays a role in proper development (6).

A clinical study using human volunteers was performed to determine whether levels of perchlorate similar to the low levels that are currently being found in the groundwater are safe for people. This human study was performed in the same way that pharmaceutical studies look at the effect that soon-to-be-approved medicines have on people. At the low levels used in the study, no health effects were observed (7). In Chile, an epidemiological study was performed on pregnant women who drank water that contained naturally occurring perchlorate, at levels at least 10 times higher than what we've detected in our drinking water. There were no health effects observed (8).

The maximum contaminant level (MCL) has not been established by the U.S. Environmental Protection Agency and review and evaluation are ongoing. California has more perchlorate sites than any other state or country. Until the MCL is in place, the California Department of Health Services (CDHS) will continue to use a 6-μg/L perchlorate level as a notification level or public health goal with which to protect water consumers (5).

Perchlorate is easily absorbed into the bloodstream after ingestion but leaves the body very quickly. Infants and small children may be more sensitive to perchlorate than adults. The U.S. Environmental Protection Agency (EPA) is focusing on those most sensitive in its ongoing evaluation. Perchlorate does not appear to cause cancer at low levels that are currently being measured in drinking water. Perchlorate does not cause Graves' disease. Perchlorate does not cause changes in thyroid hormones at the levels that are currently being measured in drinking water (6).

GROUNDWATER INVESTIGATION

Widespread perchlorate contamination of groundwater only became known when a new ion chromatography (IC) method lowered the anion's detection limit in water from 400 parts per billion (ppb) to 100 ppb. After more refinement in the spring of 1997, a method was developed (EPA Method 314 using IC-MS or LC-MS-MS) that could quantify perchlorate concentrations to a limit of 4 ppb (9,10).

REMEDIATION

Treatment of perchlorate contamination in water is essentially complex. The perchlorate anion does not

respond to typical water treatment techniques due to its fundamental physical and chemical nature. Chemical oxidation, granular activated carbon, and air sparging technologies have been evaluated as being relatively ineffective for perchlorate treatment. Tailored granular activated carbon impregnated with special amine coatings are being used with success for point of use applications. Fluidized bed bioreactors are being used at the Kerr McGhee, Henderson, Nevada Site. At that site, perchlorate influent is approximately 180 ppm; after 45 min of contact time, the effluent is less than 4 ppb (A. Eaton, personal communication, 2004).

The ideal treatment technology for a given perchlorate occurrence may depend on a number of factors, including perchlorate concentration, the presence and concentration of cocontaminants, pH, alkalinity, presence of natural organic matter (NOM), amount of total dissolved solids (TDS), presence of metals, and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc.). The presence of indigenous perchlorate-reducing microbes and substances inhibitory to microbial activity will also influence perchlorate treatment technology effectiveness. For *in situ* treatment of perchlorate contamination, variables related to the site hydrogeological setting, such as depth to and distribution of contaminants, soil permeability, and groundwater flow velocity, are also important.

PHYSICAL REMOVAL TECHNOLOGIES

Ion Exchange

This is a process with two similar applications of the same technology:

- Water softening removes ions from the water and replaces them with sodium (Na^+) and chloride (Cl^-) ions. This technique is employed at Aerojet, Sacramento, California.
- Deionization removes ions and replaces them with hydrogen (H^+) and hydroxyl (OH^-) ions, which combine to form water.

Ion exchange treatment has been successful in reducing perchlorate concentrations in water from 75 ppb to less than detectable levels at the San Gabriel Valley Superfund sites. Resulting brines from the ion exchange process can be problematic because the perchlorate is concentrated and not destroyed. Ion exchange is the preferred large-scale treatment method used by utilities for aboveground treatment of perchlorate.

Single Pass Adsorption Resins

This technology uses nonregenerative single-pass adsorption resins, which are tailored for perchlorate. This technology is currently being used by municipalities for large-scale water treatment.

Membrane Techniques

- *Reverse Osmosis and Nanofiltration*. This technology uses semipermeable membranes, allowing the water to pass through it, while retaining perchlorate. RO and NF can be costly due to the energy use and perchlorate disposal. They are typically used on small-scale systems.
- *Electrodialysis*. This is an electrically driven membrane separation process that separates ions from water. The process is based on the property of ion exchange membranes to selectively reject anions or cations.

In Situ Biological Treatment

In situ anaerobic biological remediation of perchlorate-contaminated waters is promising. The anaerobic conversion of chlorine in perchlorate to chloride requires the overall transfer of eight electrons (11):

$$\text{perchlorate}(ClO_4^-) \longrightarrow \text{chlorate}(ClO_3^-) \longrightarrow$$
$$\text{chlorite}\ (ClO_2^-) \longrightarrow \text{oxygen}\ (O_2) + \text{chloride}\ (Cl^-)$$

The perchlorate and chlorate are used as electron acceptors (11). An *in situ* treatment zone or wall could be emplaced with a biodegradable carbon source, such as propane (gas infusion), molasses, corn syrup, or lactic acid.

CONCLUSION

Perchlorate plumes have been developing for decades. New technologies are being developed for aboveground and *in situ* treatment for perchlorate.

BIBLIOGRAPHY

1. Motzer, W.E. (2001). Perchlorate: problems, detection, and solutions. *Environ. Forensics* **2**(4): 301–311.
2. United States Environmental Protection Agency (U.S. EPA) (1998). *Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization*. U.S. EPA, Washington, DC.
3. Urbansky, E.T., Collette, T.W., Robarge, W.P., Hall, W.L., Skillen, J.M., and Kane, P.F. (2004). United States Environmental Protection Agency (U.S. EPA), Survey of fertilizers and related materials for perchlorate; EPA/600/R-01/047; NRMRL/WSWRD. Available: http://www.epa.gov/ORD/NRMRL/Pubs/600R01047.htm; updated February 19, 2004.
4. California Environmental Protection Agency (CEPA) (2002). *Public Heath Goal for Perchlorate in Drinking Water*, Pesticide and Environmental Toxicology Section, Office of Environmental Health Hazard Assessment, December, draft, p. 100.
5. California Department of Health Services (CDHS) (2004). Perchlorate in California drinking water: overview and links. Available: http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/perchlindex.htm.
6. United States Environmental Protection Agency (U.S. EPA) (2004). Perchlorate. Available: http://www.epa.gov/safewater/ccl/perchlorate/perchlorate.html; updated August 5, 2004.
7. Greer, M.A., Goodman, G., Pleus, R.C., and Greer, S.E. (2002). Health effects assessment for environmental perchlorate contamination: the dose response for inhibition of

thyroidal radioiodine uptake in humans. *Environ. Health Perspect.* **110**(9): 927–937.

8. Crump, C. et al. (2000). Does perchlorate in drinking water affect thyroid function in newborns or school-age children? *J. Occup. Environ. Med.* **42**(6): 603–612.
9. Horst, J. (2004). *Technology Information Sheet: Emerging Contaminants: Perchlorate, ARCADIS*, Jan., p. 2.
10. Eaton, A. and Via, S. (2004). Verifying the reliability of EPA method 314 to measure perchlorate at sub ppb levels vs. new EPA method options, Abstracts, The Eleventh Symposium in GRA's Series on Groundwater Contaminants: ClO_4^-; 2004—Perchlorate in California's Groundwater, Groundwater Resources Association Meeting, Glendale, CA, August 4.
11. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL, p. 419.

GROUNDWATER AND VINYL CHLORIDE: CHEMICAL BEHAVIOR AND TREATMENT

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Vinyl chloride is a colorless, flammable gas at normal temperatures with a mild, sweet odor. It exists in liquid form if it is kept under high pressure or at low temperatures (less than −13.4 °C). Vinyl chloride is also known as chloroethene, chloroethylene, and ethylene monochloride (1). All vinyl chloride is manufactured or results from the breakdown of other manufactured substances, such as trichloroethane (TCA), tetrachloroethylene (PCE), and trichloroethylene (TCE). Vinyl chloride was first produced commercially in the 1920s and is now one of the highest volume chemicals produced in the United States (2). Of the vinyl chloride produced, 96–98% is used to make poly(vinyl chloride) (PVC) with the remaining 2–4% being utilized in the manufacture of specific chlorinated hydrocarbons such as 1,1,1-TCA, 1,1,2-TCA, and vinylidene chloride (3). PVC is used to make a variety of plastic products including pipes, wire, cable coatings, and packaging materials. Other uses include furniture and automobile upholstery, wall coverings, housewares, and auto parts. Vinyl chloride has been used in the past as a refrigerant, an extraction solvent for heat-sensitive materials, and in the production of chloroacetaldehyde and methyl chloroform (4). Also, limited quantities of vinyl chloride were used as an aerosol propellant and as an ingredient in drug and cosmetic products (4). However, these practices were banned by the United States Environmental Protection Agency (U.S. EPA) in 1974.

CHARACTERISTICS

Vinyl chloride is a colorless, flammable gas with a faintly sweet odor. It is slightly soluble in water, soluble in ethanol, and very soluble in ether, carbon tetrachloride, and benzene. It is extremely flammable and is easily ignited by heat, sparks, or flames. Explosive mixtures will form with air, and it tends to self-polymerize explosively if peroxidation occurs. It reacts vigorously with oxidizers and, in the presence of moisture, corrodes iron and steel. Fires may release irritating and toxic gases including carbon dioxide, carbon monoxide, hydrogen chloride, and traces of phosgene (2). A good overview of chlorinated solvents and vinyl chloride is included in Reference 5.

PRODUCTION

Vinyl chloride was first produced commercially in the 1920s (2). In the Unites States, production of vinyl chloride steadily increased from approximately 6 to 9 billion pounds per year in the late 1970s through the 1980s to approximately 15 billion pounds per year in the mid-1990s (2). The projected demand for 2001 was 16.8 billion pounds (2). There are at least 11 current chemical suppliers of vinyl chloride in the United States. Imports reached a peak of 302 million pounds in 1989. In 2000, the United States imported more than 231 million pounds compared to 29 million pounds in 1994 and 164 million pounds in 1991 (1). Exports fluctuated from approximately 685 million pounds per year to 2.2 billion pounds per year from the late 1970s to the mid-1990s (1). In 2000, U.S. exports were approximately 1.03 billion pounds (2).

Commercial Production of Vinyl Chloride

Vinyl chloride is produced commercially by the chlorination of ethylene through one of two processes, direct chlorination or oxychlorination. Direct chlorination reacts ethylene with chlorine to produce 1,2-dichloroethane. Similarly, oxychlorination produces 1,2-dichloroethane, but this is accomplished by reacting ethylene with dry hydrogen chloride and oxygen:

$$HCl + H_2C{=}CH_2 + 0.5\ O_2 \longrightarrow Y\ H_2C{=}CHCl + H_2O$$

After both processes, the 1,2-dichloroethane is subjected to high pressures (2.5–3.0 MPa) and temperatures (550–550 °C) (1). This causes the 1,2-dichloroethane to undergo pyrolysis, or thermal cracking, which forms the vinyl chloride monomer and hydrogen chloride. The vinyl chloride monomer is then isolated. The technical-grade product is available in 99.9% purity (1).

Production of Vinyl Chloride in Groundwater

Vinyl chloride is produced in groundwater through the biodegradation of chlorinated solvents such as PCE and TCE. Biodegradation is a process in which naturally occurring microorganisms, such as yeast, fungi, and bacteria, break down target substances, such as fuels and chlorinated solvents (6). In the absence of oxygen, microorganisms often use chlorinated compounds to aid in respiration. This is done through an electron transfer process called dehalorespiration (7). In the case where the carbon in the contaminant is the food source, the contaminant is an electron donor. In the case where food is obtained from another source, the contaminant sometimes

aids this transfer by accepting electrons that are shed through respiration (6). The most common anaerobic process for degrading chlorinated compounds is an electron transfer process called reductive dechlorination. In this process, hydrogen atoms are sequentially substituted for a chlorine atom in the contaminant molecules. PCE is reductively chlorinated stepwise through TCE, DCE, vinyl chloride, and then to ethene (ethylene). However, vinyl chloride resists reductive dechlorination once it is formed. The major requirement for reductive dechlorination is the presence of other organic compounds, such as fuels, that can serve as the food source (7).

FATE AND TRANSPORT

Anthropogenic sources are responsible for all of the vinyl chloride found in the environment. Most of the vinyl chloride released to the environment is eventually transported to the atmosphere. Lesser amounts are transported to groundwater. Vinyl chloride has been detected in the ambient air near vinyl chloride and PVC manufacturing plants and hazardous waste sites. It has been found in tobacco smoke, perhaps as a result of the manufacturing process (8). When vinyl chloride is released to the ground, it is not adsorbed onto soil; it migrates readily to groundwater, where it degrades to carbon dioxide and the chloride ion. It may also remain unchanged for several months to years. Vinyl chloride has been reported in groundwater as a degradation product of chlorinated solvents TCE and PCE (9).

Effluents and emissions from vinyl chloride and PVC manufacturers are responsible for most of the vinyl chloride released to the environment. It has entered the environment at hazardous waste sites as a result of its improper disposal or leakage from storage containers or from spills. When released to the atmosphere, vinyl chloride is expected to be removed by reaction with photochemically generated hydroxyl radicals (half-life = 1–2 days). When vinyl chloride breaks down in air, it can form other harmful chemicals. Reaction products include hydrochloric acid, formaldehyde, formyl chloride, acetylene, chloroacetaldehyde, chloroacetylchloranil, and chloroethylene epoxide. In photochemical smog, the half-life of vinyl chloride is reduced to a few hours. When released to water, volatilization is expected to be the primary fate process. In waters containing photosensitizers, such as humic materials, sensitized photodegradation may also be important. When released to soil, vinyl chloride either volatilizes rapidly from soil surfaces or leaches readily through soil, ultimately entering groundwater (1).

DISPOSAL

The recommended method of disposal is total destruction by incineration. The temperature of the incinerator must be sufficient to ensure the complete combustion of the vinyl chloride in order to prevent the formation of phosgene. The recommended temperature range for incineration is 450–1600 °C, with residence times of seconds for gases and liquids, and hours for solids (1). If in solution, the vinyl chloride product may need to be adsorbed onto a combustible material prior to incineration. Recommended materials include vermiculite, sawdust, or a sand–soda ash mixture (90/10) covered with wood and paper (1). The vinyl chloride can also be dissolved in a flammable solvent prior to incineration. An acid scrubber should be used in conjunction with the incinerator in order to remove any hydrogen chloride that is produced by the combustion process (1). Alternatively, chemical destruction may be used, especially with small quantities. From 1 to 2 days is generally sufficient for complete destruction. Aqueous by-product solutions from the production of vinyl chloride are usually steam-stripped to remove volatile organic compounds, neutralized, and then treated in an activated sludge system to remove nonvolatile organic compounds remaining in the wastewater (1).

EXPOSURE

Historically, exposure to vinyl chloride has been in the industrial workplace, in particular, from inhalation of factory air. As industry has made efforts to better protect workers from vinyl chloride exposure, attention has also been drawn to other avenues of exposure, such as environmental and commercial (10).

Since vinyl chloride commonly exists in a gaseous state, one is most likely to be exposed to it by breathing it in. Vinyl chloride is not normally found in urban, suburban, or rural air in amounts that are detectable by the usual methods of analysis. However, vinyl chloride has been found in the air near plastics industries, hazardous waste sites, and landfills. The amount of vinyl chloride in the air near these places ranges from trace amounts to 0.041 mg/L of air, but may exceed 1 mg/L. Levels as high as 44 mg/L have been found at some landfills. One can also be exposed to vinyl chloride in the air through tobacco smoke from cigarettes or cigars (10). Workers who produce or use vinyl chloride and PVC are at a high risk of exposure by breathing vapors in the workplace air, or if the chemical comes into contact with their skin or eyes (4)

Exposure to vinyl chloride may also occur by drinking water from contaminated wells, but how often this occurs is not known. Most drinking water supplies do not contain vinyl chloride. In a 1982 survey, vinyl chloride was found in less than 1% of the 945 groundwater supplies tested in the United States. The concentrations found in groundwater were up to 0.008 mg/L, with a detection limit of 0.001 mg/L. Other studies have reported groundwater vinyl chloride concentrations at or below 0.38 mg/L (8). High concentrations up to 200,000 μg/L were detected in well water in the vicinity of a PVC plant in Finland ten years after leakages (9).

At one time, the flow of water through PVC pipes added very low amounts of vinyl chloride to water. For example, in one study of newly installed pipes, the drinking water had 0.001 mg/L of vinyl chloride. No current information on the amount of vinyl chloride released from PVC pipes into water is available (8).

Owing to its high volatility, vinyl chloride has rarely been detected in surface waters; the concentrations

measured generally do not exceeding 10 μg/L, with a maximum of 570 μg/L from contaminated sites (9). A recent example is the finding of vinyl chloride up to 56 μg/L together with other volatile organic compounds in heavily polluted shallow rivers in Osaka, Japan (11).

Once set, poly(vinyl chloride) by itself is a hard, brittle, and inflexible material. To induce the flexibility needed for products such as food wraps, plasticizers are added. Poly(vinyl chloride) food wrappings, however, pose a potential problem as monomers and oligomers of vinyl chloride as well as some plasticizers can migrate into food from the wrappings (10). The U.S. government now regulates the amount of vinyl chloride in food packaging materials. A model of food systems shows that when levels less than 1 mg/L of vinyl chloride monomer are used in PVC packaging, "essentially zero" vinyl chloride enters food by contact with these products (8).

Estimated Total Exposure and Relative Contribution from Drinking Water

If an ambient air concentration of 0.1–2.0 $\mu g/m^3$ and a daily inhalation of 20 m^3 of air are assumed, daily intake by the inhalation route would amount to 2–40 μg. For those living and working in industrial areas, in particular, near vinyl chloride/PVC polymerization plants or near waste sites, this could be at least a factor of ten or more higher (i.e., daily intake 20–400 μg).

At a concentration of 1–2 μg/L in drinking water, daily intake would be about 2–4 μg. Daily intake from food has been estimated to be about 0.02–0.025 μg (9). It appears that inhalation is the most important route of vinyl chloride intake, although drinking water may contribute a substantial portion of daily intake where PVC piping with a high residual content of vinyl chloride monomer is used in the distribution network, in particular, in hot countries or where drinking water is from wells near sites contaminated with chlorinated hydrocarbons. Boiling drinking water reduces the risk of contamination of water with vinyl chloride (9).

HEALTH EFFECTS

A wide variety of deleterious health effects have been attributed to vinyl chloride exposure. However, prior to the 1974 discovery at the B. F. Goodrich plant in Kentucky, where the factory's doctor linked vinyl chloride exposure to angiosarcoma, most toxicologists believed that vinyl chloride did not pose a serious health risk. In fact, prior to 1974, the "safe" exposure level was set at 200 mg/L, rather than the 5 mg/L and under levels, which are standard for most jurisdictions today. The discovery in 1974 set in motion a series of events that led government, industry, labor, and science to the realization of the hazards of vinyl chloride exposure. Subsequently, industry, labor, and government all supported research into the biological consequences of vinyl chloride exposure (10).

Short-Term Exposure

Breathing high levels of vinyl chloride leads to feelings of dizziness and sleepiness. These effects occur within 5 min at about 10,000 mg/L of vinyl chloride. One can easily smell vinyl chloride at this concentration and one can rapidly recover from these effects by breathing fresh air (8). Limited exposure to vinyl chloride may also induce a feeling of dullness, nausea, and headache; irritate the eyes, mucous membranes, and respiratory tract; and have neurotoxic and dermatological effects. Escaping compressed gas or liquid can cause frostbite or irritation of the skin and eyes (1). It is difficult to clearly define the duration of a short-term or limited exposure, and its effect will almost surely differ from person to person (10).

Long-Term Exposure

There are many possible consequences of long-term exposure to vinyl chloride. These include various forms of liver disease such as liver sarcoma and liver carcinoma, as well as diseases in other tissues such as lung cancer, digestive system cancers, cardiovascular disease, genetic defects, and even melanoma. In the case of angiosarcoma, which appears to be the signature disease of long-term vinyl chloride exposure, the average length of exposure to vinyl chloride necessary to trigger angiosarcoma development has been estimated at 18 years, though a recent study has documented workers with as little as 3.5 and 4 years of exposure contracting angiosarcoma (10). Another condition attributed to prolonged vinyl chloride exposure is a cold-induced pallor of the extremities, referred to as Raynaud's syndrome. A potentially serious side effect of chronic exposure to vinyl chloride, even at low doses, is associated with the body's defense mechanisms. More medical information is contained in the ATSDR Medical Management Guidelines report (12).

Many of the health effects listed above are specific to workers in VC and PVC factories. These include sclero dermiform lesions, acroosteolysis, Raynaud's syndrome, and liver function abnormalities (10). Some men who work with vinyl chloride have complained of a lack of sex drive. Results of studies in animals show that long-term exposure may damage the sperm and testes. Some women who work with vinyl chloride have had irregular menstrual periods. Some have developed high blood pressure during pregnancy. Studies of women who live near vinyl chloride manufacturing plants could not prove that vinyl chloride causes birth defects. Studies using pregnant animals show that breathing vinyl chloride may harm their unborn offspring. Animal studies also show that vinyl chloride may cause increased numbers of miscarriages early in pregnancy. It may also cause decreased weight and delayed skeletal development in fetuses. The same very high levels of vinyl chloride that caused these fetal effects also caused adverse effects in the pregnant animals (8).

Mutation and Cancer

Vinyl chloride has been shown to be mutagenic in almost all assay systems in which it has been tested. Phylogenetically, vinyl chloride has been shown to be mutagenic in all life forms tested including bacteria, yeast, insects, plants, mammalian cells in culture, human cells, and whole animals. In fact, vinyl chloride is currently

used as the positive control substance in many studies. Vinyl chloride is known to induce almost a full spectrum of mutations including several types of point mutations and chromosome aberrations. Studies have indicated that certain chromosomes elicit a greater sensitivity to vinyl chloride than most of the chromosomes, suggesting some degree of specificity in the action of vinyl chloride (10).

Results from several studies suggest that breathing air or drinking water containing low levels of vinyl chloride may increase the risk of getting cancer. The monomer of vinyl chloride is a potent human carcinogen while only a weak to moderate animal carcinogen. Unlike many carcinogens, the carcinogenic metabolite(s) of vinyl chloride is considered a complete carcinogen; that is, it does not need a cocarcinogen to produce cancer. In rodents, the mechanism by which vinyl chloride and its metabolites transform normal cells into the neoplastic state appears to initially follow the pathway involved in the development of genotoxic effects (10). The primary cancer produced by vinyl chloride is its signature disease, angiosarcoma. Sarcomas of the liver are extremely rare and have been strongly linked to vinyl chloride exposure. Evidence also exists, however, that links vinyl chloride to hepatocellular carcinoma, cancers of the digestive system, lung cancer, brain cancer, and melanoma. Many cohort and epidemiology studies have attempted to correlate exposure to vinyl chloride with the abovementioned cancers. In almost all cases, the clearest correlation is with angiosarcoma. Studies indicate that induction of angiosarcoma generally requires a fairly extensive exposure (~18 years) to vinyl chloride. Based on at least one calculation, the latency period, the time from the initial exposure to the onset of the disease, for angiosarcoma is approximately 22.6 years. From this calculation, it has been estimated that by the year 2010 there will be another 500 cancer-related mortalities in North America and approximately 2000 more in Europe due to previous vinyl chloride exposure (10).

DETECTION OF VINYL CHLORIDE

Biological Samples

The analytical method used to analyze for the presence of vinyl chloride in biological samples is separation by gas chromatography (GC) combined with detection by mass spectrometry (MS), flame ionization detector (FID), or electron capture detector (ECD). Vinyl chloride and/or its metabolite, thiodiglycolic acid, have been detected in breath, urine, blood, and tissues. Breath samples can be concentrated by cryogenic trapping. The two methods most commonly used to prepare liquid and solid samples are concentration by a purge-and-trap technique or headspace analysis. Concentration not only increases the sensitivity but also, in certain instances, may decrease the sample separation time prior to quantization (1).

Vinyl chloride can be determined in exhaled air by concentration with a multistage cryogenic trapping system followed by thermal desorption using GC/FID, GC/ECD, and GC/MS (1). Sensitivity is in the low-ppb range. One limitation of this method is its reduced ability to detect vinyl chloride when air concentrations in the workplace are below 50 mg/L (1).

Environmental Samples

Analysis of environmental samples is similar to that of biological samples. The most common methods used to detect vinyl chloride in environmental samples are GC/MS, GC/ECD, and GC/FID. Concentration of samples is usually done by sorption on solid sorbent for air and by the purge-and-trap method for liquid and solid matrices. Alternatively, headspace above liquid and solid samples may be analyzed without preconcentration (1).

Air. The primary method of analyzing vinyl chloride in air is GC combined with MS, ECD, or FID. Air samples are usually pumped through a sample collection column with Tenax-GC, coconut activated charcoal, or spherocarb (a carbon molecular sieve material) as the most common adsorbents. It has been noted that Tenax-GC displays poor retention for vinyl chloride when the compound is present in the very low ppb range (1).

Vinyl chloride is thermally desorbed from the collection column and concentrated on a cryogenic trapping column located on the gas chromatograph. Vapors are heat released from the trapping column directly to the gas chromatograph (1). Grab samples of air can also be obtained and preconcentrated on a cryogenic trapping column. With careful technique, precision is adequate, ranging from 5% to 20% (1).

Water. Vinyl chloride can be detected in drinking water, groundwater, wastewater, and leachate from solid waste. Analysis of vinyl chloride is done by purge-and-trap or headspace GC. The primary analytical method is separation by GC combined with MS, ECD, FID, Hall's electrolytic conductivity detector (HECD), or another type of halogen-specific detector (HSD). In most methods, vinyl chloride is liberated from the liquid matrix by purging with an inert gas and concentrated by trapping on a suitable solid sorbent. Vinyl chloride is thermally desorbed and back flushed onto the column of the gas chromatograph with an inert gas. Detection of vinyl chloride is generally achieved using HECD, HSD, or MS (1). Accuracy is greater than 98% and precision ranges from 11% to 25% for GC/HECD and GC/MS (1).

REGULATIONS

In September 1974, eight months after a correlation between angiosarcoma and vinyl chloride exposure was observed, the U.S. EPA established a national emissions standard for vinyl chloride which came into effect two years later when published as part of the U.S. Clean Air Act (October 1976) (10).

The U.S. EPA requires that the amount of vinyl chloride in drinking water not exceed 0.002 mg/L. It is also required that spills or accidental releases into the environment of 1 lb or more of vinyl chloride be reported to the EPA (1). The Occupational Safety and Health Administration (OSHA) set the maximum allowable level

of vinyl chloride in workroom air during an 8-h workday in a 40-h workweek at 1 mg/L (1).

The EPA has set emission standards for vinyl chloride and PVC plants. The amount of vinyl chloride allowed to be emitted varies depending on the type of production and discharge system used. To limit intake of vinyl chloride via foods to levels considered safe, the Food and Drug Administration (FDA) regulates the vinyl chloride content of various plastics. These include plastics that carry liquids and plastics that come into contact with food. The limits for vinyl chloride content vary depending on the nature of the plastics and its use (4). However, the FDA has set the allowable level for vinyl chloride at 0.002 mg/L in bottled water (2).

GROUNDWATER REMEDIATION

A variety of technologies can be used for VC removal and destruction. Selected technologies are described below.

In Situ Biological Treatment

In situ bioremediation techniques are destruction techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favorable environment for the microorganisms. Generally, this means providing some combination of oxygen (electron acceptor), nutrients, and moisture, controlling the temperature and pH for aerobic conditions, providing a carbon source as a food source and nutrients and moisture, and controlling the temperature and pH for anaerobic conditions.

Contaminants are usually destroyed and little to no residual treatment is required. Some compounds break down and the breakdown products are more toxic than the original product: for example, PCE and TCE, which break down to form the more toxic vinyl chloride. For *in situ* applications, the vinyl chloride may be mobilized in groundwater if no control techniques are used.

Enhanced Biodegradation. The rate of bioremediation of organic contaminants by microbes is enhanced by increasing the concentration of electron acceptors and nutrients in groundwater, surface water, and leachate. Oxygen is the main electron acceptor for aerobic bioremediation. Nitrate, manganese (4+), iron (3+), sulfate, and ultimately carbon dioxide serve as an alternative electron acceptor under anaerobic and reducing conditions.

Although vinyl chloride can be released into the environment as a liquid product, vinyl chloride is also a degradation by-product of the anaerobic reductive dechlorination process that starts with tetrachloroethylene (PCE) (4 chlorine atoms) and proceeds to trichloroethylene (TCE) (3 chlorine atoms) and moving through *cis*-1,2-dichloroethene (*cis*-1,2-DCE) (2 chlorine atoms) before creating vinyl chloride (VC) (1 chlorine atom) by primarily biological reactions. Other pathways to VC include limited biological reactions from 1,1-dichloroethene (1,1-DCE) and *trans*-1,2-dichroloethene (*trans*-1,2-DCE) (13). For chlorinated solvents, the carbon source for anaerobic degradation is a food source and the contaminant is the anaerobic electron acceptor.

Once at VC, the aerobic breakdown of VC into ethene and later into ethane is best done using oxygen as the electron acceptor under aerobic conditions. Oxygen enhancement for VC breakdown can be achieved by a variety of methods: air sparging, pure oxygen gas infusion using mass transfer tools in monitoring wells, and injection of peroxide compounds [hydrogen peroxide (H_2O_2), calcium peroxide (CaO_2), and, to a lesser extent, magnesium peroxide (MgO_2)]. Even ozone (O_3) can be used as an oxygen source. Vinyl chloride has been observed to degrade four times faster under aerobic conditions than under anaerobic conditions (14).

In Situ Physical/Chemical Treatment

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy (i.e., chemically convert) or separate the contamination. Available *in situ* physical/chemical treatment technologies include chemical oxidation, air sparging, bioslurping, directional wells, dual phase extraction, thermal treatment, hydrofracturing, in-well air stripping, passive/reactive treatment walls, and soil vapor extraction (SVE).

Chemical Oxidation. The chemical oxidants most commonly employed to date include rapidly reacting hydrogen peroxide, Fenton's reagent, and ozone. Slower oxidizers include potassium permanganate and sodium persulfate. These oxidants have been able to cause the complete chemical destruction of many toxic organic chemicals including vinyl chloride. In general, the oxidants have been capable of achieving high treatment efficiencies (>90%) for chlorinated solvents. Field applications have clearly affirmed that matching the oxidant and *in situ* delivery system to the contaminants of concern and the site conditions is the key to successful implementation and achieving performance goals. Bench testing is recommended prior to performing pilot studies in the field. Oxidant delivery systems often employ vertical or horizontal injection wells and sparge points, probe rods, or lances under pressures from 40 psi up to 5000 psi. Reaction temperatures, pH, DO, and other field variables are used to help monitor progress of the subsurface reactions.

Passive Reactive Treatment Walls. Passive reactive treatment walls are barriers that allow the passage of water while causing the degradation or removal of contaminants. A permeable reaction barrier (PRB) is installed across the flow path of a contaminant plume, allowing the water portion of the plume to passively move through the wall. These barriers allow the passage of water while prohibiting the movement of contaminants by employing such agents as zero-valent metals, chelators (ligands selected for their specificity for a given metal), sorbents, and microbes. The contaminants will either be degraded or retained in a concentrated form by the barrier material. The wall could provide permanent containment for relatively benign residues or provide a decreased volume of the more toxic contaminants for subsequent treatment. An iron treatment wall consists of iron granules or other iron-bearing minerals for the

treatment of chlorinated contaminants such as TCE, DCE, and vinyl chloride. As the iron is oxidized, a chlorine atom is removed from the compound by one or more reductive dechlorination mechanisms, using electrons supplied by the oxidation of iron. The iron granules are dissolved by the process, but the metal disappears so slowly that the remediation barriers can be expected to remain effective for many years, possibly even decades.

Soil Vapor Extraction. Soil vapor extraction (SVE) is an *in situ* unsaturated (vadose) zone soil remediation technology in which a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semivolatile contaminants from the soil. The gas leaving the vadose zone may be treated to recover or destroy the contaminants, depending on local and state air discharge regulations.

For the soil surface, plastic sheeting or membranes are often placed over the soil surface to prevent short circuiting and to increase the radius of influence of the wells. Groundwater depression pumps may be used to reduce groundwater upwelling induced by the vacuum or to increase the depth of the vadose zone. Air injection is effective for facilitating extraction of deep contamination, contamination in low permeability soils, and contamination in the saturated zone. The duration of operation and maintenance for *in situ* SVE is typically medium to long term. Dual phase extraction is a variation of the SVE–groundwater extraction approach that can be used successfully with VC.

Ex Situ Physical/Chemical Treatment

Once the VC is extracted using SVE or groundwater extraction, the contaminant must be treated and destroyed on the surface.

Advanced Oxidation Processes. Advanced oxidation processes including ultraviolet (UV) radiation, ozone, and/or hydrogen peroxide are used to destroy organic contaminants as water flows into a treatment tank. UV oxidation is a destruction process that oxidizes organic and explosive constituents in wastewater by the addition of strong oxidizers and irradiation with UV light. Oxidation of target contaminants is caused by direct reaction with the oxidizers, UV photolysis, and through the synergistic action of UV light, in combination with ozone and/or hydrogen peroxide. If complete mineralization is achieved, the final products of oxidation are carbon dioxide, water, and occasionally salts. Easily oxidized organic compounds such as those with double bonds (e.g., vinyl chloride) are rapidly destroyed in UV/oxidation processes.

The main advantage of UV oxidation is that it is a destruction process, as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase. UV oxidation processes can be configured in batch or continuous flow modes, depending on the residence treatment time required. The UV oxidation process is generally done with low pressure UV lamps operating at 65 W of electricity for ozone systems and lamps operating at 15–60 kW for hydrogen peroxide systems (15).

Air Stripping. Air stripping is a full-scale technology in which volatile organics are partitioned from groundwater by greatly increasing the surface area of the contaminated water exposed to air. Henry's law constant is used to determine whether air stripping will be effective and organic compounds with constants greater than 0.01 atm·m^3/mol are considered amenable to stripping. Vinyl chloride has a constant of 1.2 atm·m^3/mol. Types of aeration methods include packed towers, diffused aeration, tray aeration, and spray aeration. The typical packed tower air stripper includes a spray nozzle at the top of the tower to distribute contaminated water over the packing in the column, a fan to force air countercurrent to the water flow, and a sump at the bottom of the tower to collect decontaminated water. Packed tower air strippers are installed as permanent installations on concrete pads or as temporary units on a skid or a trailer. Aeration tanks strip volatile compounds by bubbling air into a tank through which contaminated water flows. A forced air blower and a distribution manifold are designed to ensure air–water contact without the need for any packing materials. The baffles and multiple units ensure adequate residence time for stripping to occur (15).

Containment

Containment technologies are often performed to prevent, or significantly reduce, the migration of contaminants in soils or groundwater. Containment is necessary whenever contaminated materials are to be buried or left in place at a site, such as at a landfill. Available containment technologies include physical/biological barriers.

Physical Barriers. Physical barriers (or slurry walls) are used to contain contaminated groundwater, divert contaminated groundwater from the drinking water intake, divert uncontaminated groundwater flow, and/or provide a barrier for the groundwater treatment system. Most slurry walls are constructed of a soil, bentonite, and water mixture. Unfortunately, most barriers do not provide complete containment unless active hydraulic control is maintained using a groundwater extraction system.

BIBLIOGRAPHY

1. ATSDR (1997). Agency for Toxic Substances and Disease Registry. *Toxological Profile for Vinyl Chloride*, U.S. Department of Health and Human Services, Public Health Service. Available: http://www.atsdr.cdc.gov/toxprofiles/tp20.pdf.
2. VC (2002). *Vinyl Chloride*, Tenth Report on Carcinogens. Available: http://ehp.niehs.nih.gov/roc/tenth/profiles/s186viny.pdf.
3. BMZ (1992). German Federal Ministry for Economic Cooperation and Development. *Environmental Handbook—Documentation on Monitoring and Evaluating Environmental Impacts*. Available: http://www.gtz.de/uup/publica/English/vol369.htm.
4. Val Iyioke, I. (2003). *Vinyl Chloride*. Available: http://www.iet.msu/Tox_for_Journ/Chemicals/Vinyl.htm.
5. Pankow, J.F. and Cherry, J.A. (1996). *Dense Chlorinated Solvents, and Other DNAPLs in Groundwater: History, Behavior, and Remediation*. Waterloo Press, Guelph, Ontario, Canada, p. 522.

6. NAOC (1998).
7. Doctorflood (2004). *Biodegradation Processes for Chlorinated Solvents*. Available: http://doctorflood.rice.edu/envi518/Handouts/Lisbon/04_chlor.ppt.
8. Eco-USA (2003). *Vinyl Chloride*. Available: http://www.eco-usa.net/toxics/vinylcl.shtml.
9. VC2 (2003). *Vinyl Chloride*. Available: http://www.who.int/docstore/water_sanitation_health/GDWQ/draftchemicals/vinylchloride2003.pdf.
10. Salamone, M.F. and Westlake, G. (1998). *Vinyl Chloride: An Annotated Bibliography with Emphasis on Genotoxicity and Carcinogenicity*, Ministry of the Environment, Ontario, Canada. Available: http://www.ene.gov.on.ca/envision/techdocs/3698e.pdf.
11. Yamamoto, K., Fukushima, M., Kakutani, N., and Tsurho, K. (2001). Contamination of vinyl chloride in shallow urban rivers in Osaka, Japan. *Water Res.* **35**: 561–566.
12. ATSDR (2004). Agency for Toxic Substances and Disease Registry. Medical management guidelines (MMGs) for vinyl chloride. Available: http://www.atsdr.cdc.gov/mmg.html.
13. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL, p. 419.
14. Brady, P.V. and Brady, W.D. (2000). Monitored natural attenuation. In: *McGraw-Hill Standard Encyclopaedia of Environmental Science, Health and Technology*, J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.1–14.11.
15. Chhetry, S., Liou, R., Lloyd, T., Peck, J., and Van Duren, J. (2002). *Remediation Technologies Screening Matrix and Reference Guide*, 4th Edn. Federal Remediation Technologies Roundtable. Available: http://www.frtr.gov/matrix2/top_page.html.

GROUNDWATER AND URANIUM: CHEMICAL BEHAVIOR AND TREATMENT

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The element uranium, symbol U, is a chemically reactive radioactive metallic element. It is the main fuel used in nuclear reactors. Uranium has atomic number 92, which places it in the actinide series of the periodic table. The German chemist Martin Heinrich Klaproth discovered uranium in 1789 in pitchblende. He named it after the planet Uranus. Uranium was first isolated in the metallic state in 1841and the radioactive properties were first demonstrated in 1896 by the French physicist Antoine Henri Becquerel (1).

Uranium melts at about 1132 °C and boils at about 3818 °C. It has a specific gravity of 19.05 at 25 °C and the atomic weight of the element is 238.03. Uranium has three crystalline forms, of which the one that forms at about 770 °C is malleable and ductile. Uranium is soluble in hydrochloric and nitric acids, and it is insoluble in alkalis. It displaces hydrogen from mineral acids and from the salt solutions of such metals as mercury, silver, copper, tin, platinum, and gold. When finally divided, it burns readily in air at 150–175 °C. At 1000 °C, uranium combines with nitrogen to form a yellow nitride (1).

FATE AND TRANSPORT

Uranium has multiple oxidation states of three, four, five, and six. The hexapositive compounds include uranyl trioxide, UO_3, and uranyl chloride, UO_2Cl_2. Uranium tetrachloride, UCl_4, and uranium dioxide, UO_2, are examples of the tetrapositive, or uranous, compounds. Uranous compounds are usually unstable; they revert to the hexapositive form when exposed to excess air. Uranyl salts, such as uranyl chloride, may decompose in the presence of strong light and organic matter. *In situ* soil moisture pH greatly influences the formation of uranium surface complexes (2). The carbon dioxide (CO_2) partial pressure in soil gas is a dominant factor in controlling the pH of soil moisture.

Uranium never occurs naturally in the free state but is found as an oxide or complex salt in minerals such as pitchblende and carnotite. It has an average concentration in the crust of the earth of about 2 ppm (parts per million) and, among the elements, ranks about 48th in natural abundance in crustal rocks. Pure uranium consists of more than 99% of the isotope uranium-238, 0.72% of the fissile isotope uranium-235, and a trace of uranium-234, formed by radioactive decay of uranium-238. Among the artificially produced isotopes of uranium are uranium-233, uranium-237, and uranium-239. Isotopes ranging from mass number 222 to 242 are known (3).

Uranium has a generally low solubility and will not easily reach groundwater. It is also easily adsorbed to soil particles. Uranium oxide will precipitate from uranium-bearing groundwaters as they enter a reducing environment.

Uranium is unstable and, as it decays, it releases radiation and forms decay products. Uranium-238 decay products include uranium-234, radium-226 (both of which are solids), and radon-222, a gas. Radon is soluble but does not remain in water. It can be released by simple agitation. All the decay products are radioactive as well. The half-life for uranium-238 is about 4.5 billion years; for uranium-235 it is 710 million years, and for uranium-234 it is 250,000 years.

PROCESSING OF URANIUM

There are two major methods of producing uranium. In the classical procedure for extracting uranium, pitchblende is broken up and mixed with sulfuric and nitric acids. Uranium dissolves to form uranyl sulfate, UO_2SO_4; radium and other metals in the pitchblende ore are precipitated as sulfates. With the addition of sodium hydroxide, uranium is precipitated as sodium diuranate, $Na_2U_2O_7 \cdot 6H_2O$, known also as the yellow oxide of uranium. To obtain uranium from carnotite, the ore is finely ground and treated with a hot solution of caustic soda and potash to dissolve out uranium, radium, and vanadium. After the sandy matrix is washed away, the solution is treated with sulfuric acid and barium

chloride. A caustic alkali solution added to the remaining clear liquid precipitates the uranium and radium in concentrated form. These classical methods of extracting uranium from its ores have been replaced in current practice by such procedures as solvent extraction, ion exchange, and volatility methods. *In situ* leaching is another method that is used in the United States. The artificial isotope uranium-233 is produced from thorium, another actinide metal (1).

Uranium oxide precipitates from uranium-bearing groundwaters as they enter a reducing environment. It can be mobilized (redissolved) *in situ* by oxygenated leach solution.Uranium ores are widely distributed throughout the world. Deposits of pitchblende, the richest uranium ore, are found chiefly in Canada, the Democratic Republic of the Congo (DRC, formerly Zaire), and the United States. Most of the uranium mined in the United States is obtained from carnotite occurring in Colorado, Utah, New Mexico, Arizona, and Wyoming. A mineral called coffinite, discovered in 1955 in Colorado, is a high grade ore containing nearly 61% uranium. Coffinite deposits were found subsequently in Wyoming and Arizona and in several foreign countries.

USES OF URANIUM

After the discovery of nuclear fission, uranium became a strategic metal, and its uses were at first restricted mainly to the production of nuclear weapons. In 1954 the United States government relaxed controls to permit leasing of uranium enriched in the isotope uranium-235 to various private and foreign agencies for the development of nuclear power. Peacetime applications were discussed at the three International Conferences on the Peaceful Uses of Atomic Energy held in Geneva, Switzerland, in 1955, 1958, and 1964.

The potentiality of uranium as a vast source of industrial power became apparent with the launching in 1954 of the first nuclear-powered submarine, the USS *Nautilus*. By 1989, 112 nuclear power plants in the United States produced more than 101,000 megawatts electric, MW(E). In addition, there are 316 plants in 40 countries outside the United States, which produced more than 213,000 MW(E). The first such U.S. plant, which began operations at Shippingport, Pennsylvania, generates 60,000 kW and requires about 15 lb of uranium-235 per month. Conventional plants producing 60,000 kW consume about 40 million lb of coal per month. Problems of uranium scarcity, plant safety, and storage of radioactive uranium and plutonium waste products, however, have prevented the full realization of nuclear energy's potential.

Uranium-235 is used in nuclear weapons and nuclear reactors. Depleted uranium (natural uranium in which almost all of the uranium-235 has been removed) is used to make ammunition for the military, guidance devices and compasses, radiation shielding material, and X-ray targets. Uranium dioxide is used to extend the lives of incandescent lamps used for photography and motion pictures. Very small amounts of other uranium compounds are used in photography for toning, in the leather and wood industries for stains and dyes, and in the wool industry. Uranium has also been used in the past in ceramics as a coloring agent.

HEALTH EFFECTS AND TOXICITY

Natural uranium releases alpha particles and low levels of gamma rays. The alpha particles can travel only short distances and cannot penetrate human skin. Gamma radiation, however, can penetrate the body. In general, uranium outside the body is less harmful than inside the body.

Uranium can enter the body in several ways. It is inhaled or swallowed or enters through cuts in the skin. About 99% of the uranium ingested in food or water will leave a person's body in the feces; however, a small quantity may enter the bloodstream where it is eventually filtered by the kidney.

Although uranium is radioactive and can cause cancer, its primary toxic effect when consumed in water is that of a heavy metal. Heavy metals, like uranium, lead, cadmium, and arsenic, are deposited in the kidneys and can cause irreparable damage to the chief filtering mechanism of the body (4–6).

METHODS OF REMEDIATION

Several methods of remediation have been tried with sites contaminated with uranium. These include pump and treat systems for groundwater and removal of contaminated soils. In light of the high potential for negative health effects on workers, these methods are not favored. Three *in situ* remedial approaches that do not adversely affect worker health are phytoremediation, chemical precipitation, and bioremediation.

Phytoremediation

More recent methods include phytoremediation. Rhizofiltration technology uses the plant roots to uptake the contaminant. In 1996, a rhizofiltration study was performed using hydroponically grown plants in uranium-impacted groundwater. The original study was performed in a greenhouse under controlled conditions. Sunflower plants were found to have the best uptake of uranium in the laboratory studies. In the study, the uranium-impacted water was introduced into a recirculation loop with inlet concentrations of 80–350 ppb. After treatment, the outlet treatment water was reduced to less than 5 ppb, and most of the concentrations were below 0.5 ppb. The uranium contaminant was recovered from the sunflower plant roots, with no translocation of the uranium to the plant shoots. The roots were disposed of as radioactive waste (7). Additional uranium speciation and plant uptake studies are described in detail in References 8–10.

Chemical Precipitation

Long-term sequestration of uranium by *in situ* U(VI) phosphate mineral precipitation has been documented (11). In one case at Coles Hill, Virginia, uranium remains essentially immobile and mineralized during the oxidation and

chemical weathering of the uranium ore. The groundwater at the site is oxic, has a pH of 6, and falls within the uranyl phosphate stability field showing that the Coles Hill U(VI) phosphates may precipitate rapidly (weeks) relative to groundwater flow. In this location, the groundwater contains 15 μg/L or parts per billion (ppb) of dissolved uranium in the groundwater. These levels are well below the EPA maximum contaminant level (MCL) of 30 μg/L (4). In similar hydrologic conditions, phosphate-based remediation of uranium could be considered. Other uranium compounds may also provide long-term stabilization of uranium-impacted groundwater.

Bioremediation

Bioremediation has been used in uranium treatment. Microbial reduction of soluble U(VI) to insoluble U(IV) can immobilize uranium from contamianted groundwater. This remedial method may be added to soil washing for concentrating uranium from contaminated soils. Laboratory studies (12) have demonstrated that U(VI) is reduced concurrently with Fe(III) reduction and molecular studies have suggested that, in most instances, metal reduction can be attributed to the activity of the bacteria Geobacteraceae. Currently, field studies are under way to evaluate *in situ* bioremediation options for uranium.

BIBLIOGRAPHY

1. United States Environmental Protection Agency (U.S. EPA) (2004). Uranium, updated Sept. 21, 2004. Available: http://www.epa.gov/radiation/radionuclides/uranium.htm.
2. Langmuir, D. (1997). *Aqueous Geochemistry*, Simon & Schuster, Upper Saddle River, NJ.
3. Seborg, G.T. (2004). Uranium. *Microsoft® Encarta® Online Encyclopedia*. Available: http://encarta.msn.com/encyclopedia_761557628/Uranium.html.
4. United States Environmental Protection Agency (U.S. EPA) (2002). Radionuclides in drinking water, updated November. Available: http://www.epa.gov/safewater/standard/pp/radnucpp.html.
5. United States Environmental Protection Agency (U.S. EPA) (2004). Use of uranium drinking water standards under 40 CFR 141 and 40 CFR 192 as remediation goals for groundwater at CERCLA sites. Available: www.epa.gov/swerffrr/documents/uranium_drinking_water_standards.htm.
6. World Health Organization (WHO) (2003). Fact sheet no. 257 on depleted uranium; revised January. Available: http://www.who.int/mediacentre/factsheets/fs257/en/.
7. Lehr, J. (2000). Phytoremediation: a Promising path to the elimination of heavy metals and radionuclides in groundwater and soil. In: *McGraw-Hill Standard Encylopedia of Environmental Science, Health and Technology*, J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.26–14.29.
8. Ebbs, S.D., Norvell, W.A., and Kochian, L.V. (1998). The effect of acidification and chelating agents on the solubilization of uranium from contaminated soil. *J. Environ. Qual.* **27**: 1486–1494.
9. Ebbs S.D., Brady, D.J., and Kochian, L.V. (1998). Role of uranium speciation in the uptake and translocation of uranium by plants. *J. Exp. Bot.* **49**: 1183–1190.
10. Ebbs, S., Brady, D., Norvell, W., and Kochian, L. (2001). Uranium speciation, plant uptake, and phytoremediation. *Pract. Period. Hazard. Toxic Radioactive Waste Manage.* **5**: 130–135.
11. Jerden, J.L. Jr. and Sinha, A.K. (2002). Long-term stabilization of uranium by U(VI) phosphate mineralization: a model for uranium remediation, Geological Society of America (GSA) 2002 Denver Annual Meeting, October 27–30, Paper No. 138-8.
12. Holmes, D.E., Finneran, K.T., O'Neil, R.A., and Loverly, D.R. (2002). Enrichment of members of the family Geobacteracea associated with stimulation of dissimilatory metal reduction in uranium-contaminated aquifer sediments. *Appl. Environ. Microbiol.* May: 2300–2306.

GROUNDWATER AND MERCURY: CHEMICAL BEHAVIOR AND TREATMENT

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INTRODUCTION

Mercury is rarely found as a pure metal. The chief ore of mercury is cinnabar, also called vermilion, a bright red mineral composed of mercury sulfide. Metallic mercury is recovered by heating cinnabar ore in air and condensing the mercury vapor. It was originally found primarily in Spain and Italy. Mercury's chemical symbol comes from the Greek word *hydrargyrum*, which means "liquid silver." Mercury has an atomic number of 80, atomic weight of 200.59, and a density of 13.5336 g/cm^3. It is the only metal element that is a liquid at room temperature. Mercury is not an active element, combining with other elements only with some difficulty. It is therefore a *noble* metal, like gold, silver, and the platinum group, which are all highly resistant to chemical reactions and oxidation. Mercury accumulates most efficiently in the aquatic foodweb and is highly toxic to humans (1).

There are three forms of mercury in the environment: elemental, inorganic, and organic mercury. All forms of mercury are toxic. Elemental mercury occurs naturally in three valence states: elemental (Hg^0), monovalent mercurous (Hg^{1+}), and the divalent mercuric (Hg^{2+}). Elemental mercury is the most stable form and is only slightly water soluble. Both mercuric and mercurous mercury are thermally unstable and readily decompose to elemental mercury. Vapors of elemental mercury can occur at room temperature, presenting a hazard if spills occur.

Inorganic mercury compounds contain ionic mercury usually in a salt formation (e.g., mercuric chloride).

Organic mercury compounds can be chemically synthesized or biologically converted from mercury compounds by bacteria (e.g., methylmercury). Some organic mercury compounds are water soluble and capable of transport in the aquatic food chain through the process of bioaccumulation.

Although mercury does not combine easily with other elements to form compounds, it will, however, dissolve other metals to form a solution with two or more metals. These alloys are called amalgams. Dentists have used silver–mercury amalgams, consisting of silver powder dissolved in mercury, to fill teeth. Mercury is used in mining applications to recover gold from gold ore. In this application, the mercury containing dissolved gold is heated and vaporized to leave behind the gold.

HISTORY AND USES

Spain has mercury mines that have been operating continuously for over 2000 years. Mercury was well known to the ancient Chinese. Samples of the metal have been found in Egyptian tombs dating back to 1500 B.C. Mercury was an important chemical for medieval alchemists and was suspected of being an element from which all matter is made. When a solid, mercury was thought to be gold. It was also called "quicksilver" because it is liquid and silver-white in appearance. Mercury is not usually found free in nature and is primarily obtained from the mineral cinnabar (HgS). Spain and Italy produce about half of the world's supply of mercury. Mercury has been used in mining for hundreds of years in the separation of valuable metals, such as gold, from placer deposits (1).

Mercury has been used to produce chlorine and caustic soda; in wiring devices and switches; for electric lights; for measuring and control instruments (such as blood pressure gauges, barometers, and thermometers); and in other industrial applications.

HEALTH RISKS

All forms of mercury are highly toxic to humans and animals. Its toxicity was recognized in the nineteenth century when hat makers, who used a mercury compound in making hats, began to exhibit damage to their nervous systems. This is the origin of the phrase "mad as a hatter." Workers in mercury-battery factories, mercury processing plants, power plant workers, and dentists are in occupations associated with mercury exposure to mercury liquid or dust. The U.S. EPA has performed a detailed assessment of exposure using various computer models (2).

Mercury concentrations in air are usually low and of little direct concern for exposure to humans (3). From the standpoint of public health, when mercury enters the water, it is the most serious problem because of the manner in which mercury accumulates in the living tissue of animals. Mercury combines chemically with enzymes in the body, causing them to lose the ability to act as catalysts for vital body functions (1).

When mercury is deposited into waterways, bacteria and algae in the water convert inorganic mercury into organic methylmercury (CH_3Hg). Fish that eat these bacteria and algae accumulate the mercury in their tissues, and the larger fish up the food chain that feed on fish with mercury in their tissues accumulate even higher levels of mercury (biomagnification) (4).

Elemental Mercury

The major health effect from elemental mercury results from inhalation of mercury vapor. Acute (short-term) inhalation exposure to high levels of elemental mercury in humans results in central nervous system effects such as hallucinations and delirium. Gastrointestinal and respiratory effects have also been noted. Studies are inconclusive regarding elemental mercury and cancer.

The central nervous system is the major organ affected by chronic (long-term) exposure to elemental mercury. Effects noted include increased excitability, irritability, insomnia, severe salivation, loss of teeth, and tremors. Chronic exposure to elemental mercury also affects the kidneys (2).

Inorganic Mercury Compounds

The major risk from inorganic mercury occurs through ingestion. Acute oral exposure to inorganic mercury compounds has been known to produce a metallic taste in the mouth, nausea, vomiting, and severe abdominal pain. The primary effect from chronic exposure to inorganic mercury is kidney damage.

Organic Mercury Compounds

The major risk posed by organic mercury occurs through ingestion. The most important organic mercury compound in terms of human exposure is methylmercury. Acute exposure to high levels of methylmercury can result in damage to the central nervous system, including blindness, deafness, intellectual deterioration, and death. No human studies are available on the carcinogenic effects of methylmercury.

Chronic methylmercury exposure occurs primarily through diet, with fish and fish products as dominant sources. The primary effect from chronic exposure to methylmercury is damage to the central nervous system, which produces malaise, numbness and tingling, blurred vision, deafness, speech difficulties, and constriction of the visual field. Infants born to women who ingest high levels of methylmercury may exhibit blindness, mental retardation, lack of coordination, and cerebral palsy. The U.S Environmental Protection Agency (EPA) currently advises pregnant women not to eat shark, swordfish, king mackerel, tilefish, and tuna.

What is known about the health effects of mercury has come from several accidental exposures, including two high dose episodes that occurred in Japan and Iraq. From 1953 to 1960, manufacturing plants in Japan discharged methylmercury into the local waterways. In 1956, the population living near Minamata Bay in southwestern Japan suffered severe neurotoxic effects from ingesting fish from the bay that had accumulated high levels of mercury because a chemical manufacturing plant had dumped tons of mercury into the water. Levels of mercury in Minamata Bay were found to be as high as 550 ppm (aquatic biota impact level for mercury is 0.000025 ppm or 0.025 μg/L). In the 1970s, over 6000 people were hospitalized in Iraq after eating imported wheat seeds that had been treated with a methylmercury fungicide. Several hundred people

died, although because the incident occurred in a rural area the exact magnitude of the accident is not known (2).

FATE AND TRANSPORT

When liquid mercury spills, it forms drops that can accumulate in the smallest of spaces and then emits vapors into the air. Once in surface water, mercury enters a complex cycle in which one form can be converted to another. Mercury can easily be adsorbed onto small particles of matter. Mercury attached to particles can settle on the sediments, where it can diffuse into the water column, be resuspended, be buried by other sediments, or be methylated. Methylmercury can enter the food chain, or it can be released back into the atmosphere by volatilization (3).

The concentration of dissolved organic carbon (DOC) and pH have a strong effect on the ultimate fate of mercury in the ecosystem. Studies have shown that for the same species of fish taken from the same region, increasing the acidity of the water (decreasing pH) and/or the DOC content generally results in higher mercury levels in fish, an indicator of greater net methylation. Higher acidity and DOC levels enhance the mobility of mercury in the environment, thus making it more likely to enter the food chain. More information is given in Reference 2.

Mercury and methylmercury exposure to sunlight (specifically ultraviolet light) has an overall detoxifying effect. Sunlight can break down methylmercury to Hg(II) or Hg(0), which can leave the aquatic environment and enter the atmosphere as a gas. Since mercury is an element, it is not biodegradable. Mercury is converted among its various forms through a range of abiotic and biogeochemical transformations and during atmospheric transportation. Although its form and availability to living organisms may change over time, mercury persists in the environment.

Nearly 8 million pounds of mercury were produced in the United States in 1986. From 1987 to 1993, according to the EPA's Toxic Chemical Release Inventory, releases of mercury to land and water totaled nearly 68,000 lb, primarily from chemical and allied industries (3).

REMEDIATION

Although mercury is a globally dispersed contaminant, it is not a problem everywhere. Pollution prevention controls and equipment to contain airborne mercury and mercury spills would greatly limit future mercury releases into the environment. Aside from grossly polluted environments, mercury is normally a problem only where the rate of natural formation of methylmercury from inorganic mercury is greater than the reverse reaction. Environments that are known to favor the production of methylmercury include certain types of wetlands, dilute low pH lakes in the northeast and north central United States, parts of the Florida Everglades, newly flooded reservoirs, and coastal wetlands, particularly along the Gulf of Mexico, Atlantic Ocean, and San Francisco Bay. The highest concentration of mercury in freshwater sediments in the world is found in a section of Berry's Creek in New Jersey, near the Meadowlands Sports Complex. Several defunct industrial plants, including one mercury plant, are parts of some Superfund environmental cleanup sites (4).

In highly polluted areas where mercury has accumulated through industrial or mining activities, natural processes may bury, dilute, or erode the mercury deposits, resulting in declines in concentration. In many relatively pristine areas, however, mercury concentrations have actually increased because atmospheric deposition has increased.

For instance, concentrations of mercury in feathers of fish-eating seabirds from the northeastern Atlantic Ocean have steadily increased for more than a century. In North American sediment cores, sediments deposited since industrialization have mercury concentrations about 3–5 times those found in older sediments (2). Some sites may have become methylmercury hot spots inadvertently through human activities. Although scientists from the United States Geological Survey (USGS) and elsewhere are beginning to unravel the complex interactions between mercury and the environment, a lack of information on the sources, behavior, and effects of mercury in the environment has impeded identification of effective management responses to the nation's growing mercury problem.

Mercury contamination of shallow soil is commonly remediated by excavation and importation of clean backfill, as in the example of the mercury contamination remediation at gas pipeline sites in Kansas (5). Off-site treatment or transportation to a licensed disposal facility may be part of the remedial action.

Bioremediation is not an option for mercury, as the metal is also toxic to most microbial colonies (6). The following treatment methods have been approved by the U.S. EPA for removing mercury from drinking water: coagulation/filtration, granular activated carbon, lime softening, and reverse osmosis (3).

Remediation of mercury has been treated using capping and containment strategies wherein the mercury is surrounded by low permeability (bentonite) or nonpermeable material (steel shoring, plastic sheeting) to prevent the migration of the mercury. Other techniques include *in situ* vitrification.

Mercury is one of the most difficult wastes to stabilize. Aboveground stabilization techniques employing cement, kiln dust, fly ash, or other materials have been used to treat mercury-contaminated soils (7). Sulfide chemistry has also been used to chemically precipitate mercury into mercury sulfide. Calcium polysulfide (CaS_5) has been used in an aboveground soil washing treatment of mercury-impacted soil and refractory bricks at the Red Devil Mine in Alaska. The project converted toxic mercury and lead compounds into insoluble mercury sulfide and lead sulfide precipitates (B. Graves, personal communication). Mercury with zinc was encapsulated using an alkali-activated slag matrix. The physical encapsulation and chemical fixation mechanisms were responsible for the

immobilization of the mercury ions in the alkali-activated slag matrix (8).

SPECIFIC REGULATORY GUIDELINES

The United States Environmental Protection Agency (U.S. EPA) has established a Maximum Contaminant Level of Goal for mercury in drinking water at 2 μg/L or parts per billion (ppb) (3). This is the lowest level that water systems can reasonably attain, given current treatment technologies and health information.

Efforts by manufacturers of mercury-containing products, by government programs, and by solid waste management facilities have significantly reduced mercury entering the environment from products that contain it. For example, Hennepin County programs to keep mercury out of the waste stream, together with pollution control equipment on the county's waste-to-energy plant, have brought mercury emission levels down from 67% of the amount allowed under the Minnesota Pollution Control Agency permit, to under 6% of the permitted amount (9).

The EPA has issued several major studies on mercury to the U.S. Congress, including the *Mercury Study Report to Congress* in 1997 and *Utility Hazardous Air Pollutant Report to Congress* in 1998 (2,4). The agency has also taken steps to reduce human sources of mercury, including issuing regulations for the medical waste combustion, municipal waste combustion, and chloralkali production. The EPA has proposed regulations for industrial boilers, another large source of mercury. On December 15, 2003, the EPA announced a plan to significantly reduce mercury emissions from coal power plants through a cap and trade program, a market-based approach that worked successfully to reduce acidic precipitation from sulfur dioxide. The proposal would require utilities to cut emissions by 70% over the next 15 years. The EPA has also proposed a second option that is a traditional "command and control" regulation. This alternative would require utilities to install what is known as "maximum achievable control technologies" (MACT), as required under the Clean Air Act, to reduce mercury emissions by 29% over the next three years. It is not clear which of these two approaches will become the final regulation.

CONCLUSIONS

Mercury is highly toxic to humans. Significant reduction of mercury in the environment can be attained through better pollution prevention programs and control of both mercury vapors and liquid spills. Mercury waste is difficult to remediate and several treatment methods have been developed.

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BIBLIOGRAPHY

1. Stewertka, A. (2002). *A Guide to the Elements*, 2nd Edn. Oxford University Press, New York, p. 247.
2. United States Environmental Protection Agency (U.S. EPA) (1997). *Mercury Study Report to Congress*, EPA-452/R-97-003. U.S. EPA, Washington, DC.
3. United States Environmental Protection Agency (U.S. EPA) (2004). *Consumer Fact Sheet on Mercury*, U.S. EPA, Washington, DC. Available: http://www.epa.gov/safewater/contaminants/dw_contamfs/mercury.html. Updated April 27, 2004.
4. United States Environmental Protection Agency (U.S. EPA) (2003). *Mercury Study Report to Congress. Whitepaper*, U.S. EPA, Washington, DC. Available: http://www.epa.gov/oar/merwhite.html. Updated August 19, 2003.
5. Kansas Department of Health and Environment (KDHE) (1994). Mercury contamination remediation at gas pipeline sites, October, p. 8.
6. Suthersan, S. (2002). *Natural and Enhanced Remediation Systems*. Lewis Publishers/CRC Press, Boca Raton, FL.
7. United States Environmental Protection Agency (U.S. EPA) (1998). *Technologies for Immobilizing High Mercury Subcategory Wastes*, EPA Contract No. 68-W4-0005, WA No. R11032, July 17. Submitted to TechLaw, Inc., Chantilly, VA, p. 15.
8. Qian, G., Sun, D.D., and Tay, J.H. (2003). Immobilization of mercury and zinc in an alkali-activated slag matrix. *J. Hazard. Mater.* **101**(1): 65–77.
9. Minnesota Office of Environmental Assistance (MOEA) (2001). Reducing mercury in the environment; May. Available: http://www.moea.state.mn.us/berc/mercury.cfm.

GROUNDWATER AND LEAD: CHEMICAL BEHAVIOR AND TREATMENT

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Lead (Pb) occurs naturally in the earth's crust and is reported as being the most abundant among the heavy metals, with the average Pb content of the crust ranging from 13 to 16 parts per million (1). Lead has a crustal abundance of 1.4×10^1 mg/kg, with an estimated oceanic abundance of 3×10^{-5} mg/L (2). Lead makes up 0.013% of the earth's crust. There are more than 200 minerals of Pb. Natural mobilization of Pb into the environment occurs mainly from the erosion of Pb-containing rocks and via gaseous emissions during volcanic activity. Lead is mined and refined easily. On a worldwide basis, most lead is concentrated by roasting galena, also called lead sulfide (PbS), in hot air. Nearly one-third of the consumption in the United States is obtained by recycling efforts (2).

INTRODUCTION

The impact of Pb on the environment has been long and persistent. Approximately 5000 years ago Pb mining

waste began the first time a curious human picked at an outcropping of lead, pulled away the dirt and rock, and discarded the unwanted material. The Romans were the first of the ancient people to use Pb on a large scale and they used Pb more than any other people until recent time. In fact, there were laws prohibiting the production of excess amounts, according to *Pliny the Elder's Natural History* (3). The name lead comes from the Anglo-Saxon word for lead. The symbol, Pb comes from the latin word for lead, *plumbus*. Plumbers were lead workers using lead pipes and lead solder.

Lead is a cumulative poison and the ancient Romans were exposed to significant levels of lead in their water system. The blood levels of Pb in the post-Roman Italian population are as high as the Roman population, which is indicative that Pb was obtained in food and drink; this may be the result of continued use of Pb water pipes and cisterns or a result of the use of pewter, poor Pb glazes, and Pb salts (e.g., Pb acetate, "sugar of lead", which was used as a sweetener). Poor wine was improved in the Middle Ages by the addition of Pb even though it was known to be a dangerous practice and outlawed and sometimes punishable by death. There are many records of Pb epidemics, which persist well into the eighteenth century (4).

New centuries brought new uses for Pb, some of which helped change the course of history. In the mid-1400s, Johannes Gutenberg created the printing press by casting letters of molten Pb and tin. Later, Pb made possible electronic circuitry, computer screens, and televisions.

As the uses of lead increased, driven by the growing number of social benefits it provided, there was more lead mining and mining waste. Until a few decades ago, there was little concern about the environmental impact of mining waste. Limited engineering solutions and lack of public concern about the issue meant that, over the years, mining companies have developed their own methods of handling and disposing of these materials. In fact, before engineers spent time deciding how to keep piles of tailings from washing or blowing away and before society understood the need for such controls, tailings were simply left in piles. As the early Pb mines were exhausted of ore and closed, the tailing piles were left behind. In some cases the piles have slumped into streams; in other cases, wind has blown away portions of the piles. In recent years, society's concern about the impact of tailings on the environment and human health has grown. That, along with engineering advancements that help stabilize tailing piles, has led to changes.

PROPERTIES

Lead is a bluish-white metal of bright luster, soft, highly malleable, ductile, and a poor conductor of electricity. Lead is a soft, malleable, and corrosion-resistant metal, belonging to group IV of the periodic table. Lead has an atomic weight of 207.19, a melting point of 327.5 °C, a boiling point of 1744 °C, and specific gravity of 11.342 g/cm^3. Lead is a solid at room temperature. The oxidation states of Pb are II and IV and there are four stable isotopes (204, 206, 207, 208) and two radioactive isotopes (210, 212). A variety of lead oxide compounds exist in nature.

USE

In ancient times the need for silver propelled Pb production. This was coupled with its properties—that is, its low melting point, ductility, malleability, and durability contributed to its use as a construction material. Currently, the construction and automobile industries are the primary users of Pb. It is estimated that 60% of Pb is consumed in the auto industry for solder in the building of cars, buses, trucks, vehicular batteries, and as gasoline additive. The use of Pb as gasoline additive has been declining since the mid-1970s as a result of legislation in many countries, responding to environmental concern about the release of Pb from auto exhausts.

Other important uses of Pb are in the manufacture of cable sheathings, pigments, pipe, foil and tube, and various alloys. Secondary use of Pb includes ammunition and type metal, varnishes, the production of inorganic compounds, protective coating, glassware, ceramics, TV tubes, shield against radioactivity, galvanizing, Pb plating, weights, and ballasts. Lead carbonate ($PbCO_3$), also called cerussite, is a white pigment used in early paints, especially in interior white paints. These paints have caused significant lead-based-paint (LBP) poisoning, especially of infants and children who might chew on the sweet-tasting lead paint chips. Currently, titanium oxide (TiO_2) has replaced the toxic lead in paints. Other lead compounds used in paints include lead sulfate or anglesite ($PbSO_4$) and lead chromate or crocoite ($PbCrO_4$). Other lead compounds include lead nitrate [$Pb(NO_3)_2$] used in fireworks and lead silicate ($PbSiO_3$) used in glass making and in the production of paints and rubber (2).

Lead arsenate [$Pb(AsO_4)_2$] was used as an insecticide and has been banned as an ingredient in pesticides (5). The high density of lead makes it useful to shield against X-ray and gamma-ray radiation in X-ray machines and other scientific instruments. It is used to absorb vibrations, as well as in the manufacture of ammunition. Most lead currently is used in lead-acid storage batteries, the type found in vehicles. Lead has been used in crystal and glass as well as solder (with tin).

The elevated levels are due:

- to the continued use of lead (Pb) pipes in drinking water transport
- chips and dust from leaded paint
- emissions from various industrial combustion processes
- deterioration of leaded paint
- historical fall-out from leaded gasoline (6).

HEALTH RISKS

The health risks associated with Pb include poisoning, with the most common symptoms being insomnia, delirium, hallucinations, tremor, colic, nausea, and vomiting. (Persons at risk would include those handling

tetraethyl lead or leaded gasoline.) Symptoms of lead poisoning also include neuropathy, encephalopathy (both adult and children), renal failure, intoxication, and death. Lead anemia is seldom severe unless concomitant with iron deficiency. More importantly, low level Pb exposure can have profound, adverse physiological and cognitive effects that can have long-lasting impacts. In children this could lead to permanent damage to the central nervous system, lower performance I.Q., and impairment of fine motor function. Children are more susceptible due to their greater rates of absorption (an area that needs further examination). Lead poisoning in adults is manifested by a decrease in reaction time, lower memory capacity, weakness in fingers, wrists, or ankles, anemia, insomnia, weight loss, anorexia, malnutrition, nausea, abdominal pain, constipation, and vomiting. Lead in men may increase blood pressure and high levels may damage the male reproductive system (6,7).

Pb is incorporated in the hair, nails, and sweat, but losses from the body by these routes are trivial. Blood Pb levels tend to be higher in city dwellers than in rural dwellers, while within cities those living in areas with the greatest traffic density tend to have the highest blood levels (8). The relative contribution which the various environmental sources of Pb make to the blood Pb concentration is not known with certainty and more study needs to be done in this regard. Currently, the EPA guideline for Pb blood level is 10 Mg/dL.

FATE AND TRANSPORT

Lead released to land, surface water, and groundwater is usually elemental lead, lead oxides, lead hydroxides, and lead–metal oxyanion complexes (9).

Pb naturally is present in small quantities in practically all environmental matrices, which includes air, water, soil, and plants. The distribution of Pb is greatly exacerbated as a result of emission from the combustion of Pb-containing fuel. It must be pointed out that Pb toxicity is inversely proportional to pH in soil. Pb in water originates from a variety of sources: atmosphere, lithosphere, and, for drinking water, the possibility from plumbing fixtures as well as from mines that may percolate into underlying aquifers. In the 1970s Pb from anti-knock additives resulted in approximately 180,000 tons/yr in the United States alone. Lead is the most common metal contaminant found at U.S. Superfund sites (460 sites) (10).

Pb is rarely found in source water, but Pb mining and smelting operations may be sources of significant contamination. Eighty-eight percent of the Pb mined in the United States comes from seven mines in the New Lead Belt in southeastern Missouri. From 1987 to 1993, according to the Toxics Release Inventory, Pb compound releases to land and water totaled nearly 144 million pounds. These releases were primarily from Pb and copper smelting industries. The largest releases occurred in Missouri, Arizona, and Montana. The largest direct releases to water occurred in Ohio. Pb in the form of very small particles may be airborne and disseminated over long distances. Metal-rich mine tailings, metal smelting, electroplating, gas exhausts, energy and fuel production, downwash from power lines, intensive agriculture, and sludge dumping are the human activities that introduce the largest quantities of Pb into soils. When released to land, Pb binds to soils and does not migrate to groundwater. A total of 71,529 tons of lead were released to the land in the United States over a seven-year period. In water, it binds to sediments. A total of 485 tons were released to water in the United States over a seven-year period. The worst industries for releasing lead to water are the steelworks, lead smelting, and refining and iron foundries. The worst industries for releasing lead to land are the lead smelting and refining, copper smelting, and steelworks. Lead does not accumulate in fish but does in some shellfish, such as mussels (11).

Lead (Pb^{2+}) and lead–hydroxy complexes are the most stable forms of lead (9). Lead forms low solubility compounds by complexation with inorganic ions (Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids) (12). Lead carbonate solids form above pH 6. Lead sulfide forms with high sulfide concentrations under reducing conditions. Most lead released into the environment is retained in the shallow soil. The main processes affecting the fate of lead in soil generally limits the amount of lead entering the groundwater. The processes include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter in the soil (13). The amount of lead dissolved in groundwater and surface water is heavily pH dependent and to a lesser degree related to the concentration of dissolved salts and types of mineral surfaces present. In surface and groundwater, lead usually occurs as a precipitate (rather than in solution), as $PbCO_3$, PB_2O, $PB(OH)_2$, and $PbSO_4$, as sorbed ions or surface coatings on minerals, or as suspended organic matter (13).

The major pathways of exposure to lead are:

- the inhalation of lead-containing car exhausts or industrial emission
- the ingestion of lead-based paint
- the ingestion of contaminated soil or dust from hand-to-mouth activities of those living in lead-polluted environments
- the inhalation of leaded dust carried on clothing or by the wind

The specific pathways of exposure to lead for children are:

- swallowing lead paint chips
- eating contaminated food
- putting hands, toys, or objects contaminated with lead dust or soil in their mouths

GUIDELINES AND STANDARDS

In 1974, the U.S. Congress passed the Safe Drinking Water Act. This law requires the EPA to determine safe levels of chemicals in drinking water, which do or may cause health problems. These nonenforceable levels, based solely on

possible health risks and exposure, are called Maximum Contaminant Level Goals (MCLG).

The MCLG for lead has been set at zero because the EPA believes this level of protection would not cause any of the potential health problems. Since lead contamination generally occurs from corrosion of household lead pipes, it cannot be directly detected or removed by the water system. Instead, the EPA is requiring water systems to control the corrosiveness of their water if the level of lead at home taps exceeds an Action Level.

The Action Level for lead has been set at 15 parts per billion (ppb) because the EPA believes, given present technology and resources, this is the lowest level to which water systems can reasonably be required to control this contaminant should it occur in drinking water at their customers' home taps.

These drinking water standards, and the regulations for ensuring these standards are met, are called National Primary Drinking Water Regulations. All U.S. public water supplies must abide by these regulations.

REMEDIATION

Various remedial methods exist for the treatment of Pb contamination such as excavation, phytoremediation, soil containment, soil washing and flushing, deep tilling, and geochemical fixation. Other remedial approaches include isolation by capping and subsurface barriers including slurry walls. Immobilization includes solidification/stabilization using cement-based binders and stabilizers, organic binders, and vitrification. Permeable treatment walls, *in situ* soil flushing, and electrokinetic extraction are also gaining popularity in the treatment of heavy metals (13). Phytoremediation, soil washing, and geochemical fixation are described below.

Phytoremediation

Phytoremediation is a relatively new technology that has been gaining commercial acceptance as research on the field scale has confirmed greenhouse and pilot scale success. While it has been used mainly in open, industrial settings, phytoremediation has been used in several urban, residential applications for Pb reduction. For example, in Massachusetts phytoremediation significantly reduced high soil lead levels in both an open lot that was revitalized into a community garden and in an urban residential backyard. In the case of the community garden, several plantings of Indian mustard lowered the Pb levels that initially exceeded 1000 ppm to concentrations less than half that amount. While phytoremediation in a full-scale residential application presents a few more challenges than that in an industrial site or an isolated lot, it can be successfully implemented over time through the use of a comprehensive monitoring and planting regime. This method is inexpensive and is particularly suited for developing countries.

Soil Washing

Soil washing is a remediation system that leaches and recovers Pb and other metals from contaminated soil, dust, sludge, or sediment. Soil washing also uses physical and mechanical sorting methods to separate the various fractions of the sediment by size. The Pb compounds are often tightly bound by fine soil constituents such as clay, manganese and iron oxides, and humus. A pretreatment, physical separation stage may involve dry screening to remove gross oversized material. The soil can be separated into oversized (gravel), sand, and fine (silt, clay, and humus) fractions. Soil, including the oversized fraction, is first washed. Most Pb contamination is typically associated with fines fraction, and this fraction is subjected to countercurrent leaching to dissolve the adsorbed Pb and other heavy metal species. The sand fraction may also contain significant Pb, especially if the contamination is due to particulate Pb, such as that found in battery recycling, ammunition burning, and scrap yard activities. In this case, the sand fraction is pretreated to remove dense metallic or magnetic materials before subjecting the sand fraction to countercurrent leaching. Sand and fines can be treated in separate parallel streams.

After dissolution of the Pb and other heavy metal contaminants, the metal ions are recovered from the aqueous leachate by a metal recovery process such as reduction, liquid ion exchange, resin ion exchange, or precipitation. The metal recovery technique depends on the metals to be recovered and the leachate employed. In most cases, a reduction process is used so that the metals are recovered in a compact form suitable for recycling. After the metals are recovered, the leachate can be reused within the soil washing system for continued leaching.

Geochemical Fixation

An *in situ* technology for Pb treatment is geochemical fixation using a chemical reductant such as calcium polysulfide, ferrous sulfate, or sodium metabisulfite. As an example, calcium polysulfide generally produces hydrogen sulfide, thiosulfate, and colloidal sulfur when placed in groundwater. The soluble Pb^{2+} in the groundwater is precipitated as an insoluble lead sulfide by thiosulfate breakdown products and the hydrogen sulfide. Lead sulfide is less soluble than lead hydroxide. The reductants tend to be injected or poured into wells, trenches, or delivery points. Some chemical reductants can remain active in the groundwater for months to years.

BIBLIOGRAPHY

1. Swaine, D.J. (1978). Lead in the environment. *J. Proc. R. Soc. New South Wales Australia*, **111**: 41–47.
2. Jefferson Lab (JLAB) (2004). It's elemental: lead. Available: http://education.jlab.org/itsselemental/ele082.html.
3. Healy, J.F. (1991). *Pliny the Elder's Natural History: A Selection*, translated by J.F. Healy, Penguin Books, London.
4. Waldron, H.A. (1980). Lead. *London School Hyg. Trop. Med.*, 155–191.
5. Adriano, D.C. (1986). *Trace Elements in the Terrestrial Environment*, Springer, New York, pp. 219–256.
6. ATSDR (1997). Agency for Toxic Substances and Disease Registry. *Toxological Profile for Vinyl Chloride,* U.S. Department of Health and Human Services, Public Health Service. Available: http://www.atsdr.cdc.gov/toxprofiles/tp20.pdf.

7. ATSDR (2004). Agency for Toxic Substances and Disease Registry. Medical management guidelines (MMGs) for vinyl chloride. Available: http://www.atsdr.cdc.gov/mmg.html.
8. World Health Organization (1977). *Inorganic Lead* (EHC 165, 1995) Health Criteria 3: *Lead*, WHO, Geneva, Switzerland.
9. Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C., Tixier, J.S. Jr., Brauning, S.E., Gavaskar, A.R., and Royer, M.D. (1995). *Remedial Options for Metals-Contaminated Sites*, Lewis Publishers/CRC Press, Boca Raton, FL.
10. United States Environmental Protection Agency (U.S. EPA) (1996). Recent developments for *in situ* treatment of metals-contaminated soils, Office of Solid Waste and Emergency Response, Draft.
11. United States Environmental Protection Agency (U.S. EPA) (1994). Available: http:www.epa.gov/Superfund/accomp/sarc/1994/chap_.pdf.
12. Bodek, I., Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H. (1988). *Environmental Inorganic Chemistry; Properties, Processes and Estimation Methods*. Pergamon Press, Elmsford, NY.
13. Evanko, C.R. and Dzombak, D.A. (2000). Remediation of metals-contaminated soil and groundwater. In: *McGraw-Hill Standard Handbook of Environmental Science, Health and Technology*. J. Lehr (Ed.). McGraw-Hill, New York, pp. 14.100–14.134.

LAMINAR FLOW

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INTRODUCTION

The prime objective of this text is to describe the elementary concepts involved in laminar fluid flows. In general, any flow is characterized by the continuous deformation of fluid particles and a corresponding internal state of stress. It has been experimentally established that, under laminar situations, the rate of deformation is directly proportional to local viscous stress. Laminar flows thus fall under the category of viscous flows. The principle laws that govern the motion of fluids are also discussed. We shall take geometrically simple configurations and provide a more specific introduction of laminar fluid dynamics. The outlines given in this article provide basic concepts of laminar flows. For more detailed analysis, the reader should consult specialized texts within this topic. Some of these texts are listed in the references given at the end of this article.

VISCOSITY AND OSTWALD'S EXPERIMENT

Viscosity is a measure of how easily the fluid deforms or flows under an applied stress. Alternatively, viscosity is a measure of the fluid's internal resistance to deformation or internal friction between the fluid layers. Experimentally, under conditions of laminar flow, the force required to move a plate at constant speed against the resistance of a fluid is proportional to the area of the plate and to the velocity gradient perpendicular to the plate. The constant of proportionality is called the viscosity. Consider a simple fluid flow between the two plates shown in Fig. 1.

If the force per unit area of the top plate is measured as F, we can write that as

$$\frac{F}{A} = \mu \frac{v}{d} \tag{1}$$

with d as the separation between the plates, which essentially defines the absolute or dynamic viscosity, μ, which has the units of kg/ms. The ratio of dynamic viscosity to density of the fluid is known as kinematic viscosity and has the units of m^2/s. Experimentally, the viscosity can be measured using specially designed viscometers, whose operation is based on simple flow between one plate fixed and another moving with constant velocity v. If the gap d between the plates is small compared with the length of the plates, the flow with reasonable accuracy can be assumed to be one-dimensional. For such flows, the velocity is constant in the direction of flow but varies in the normal direction. For example, in Fig. 1, the velocity in x-direction is a function of y coordinate, i.e., $v = v(y)$. Equation (1) also represents that the viscous stresses are directly proportional to the velocity gradient, i.e.,

$$\textit{Viscous stresses} = \mu(\textit{Rate of deformation})$$

These stresses developing in the viscous transfer can be divided into normal and shear stresses. For example, τ_{xx} is the normal stress, whereas τ_{yx} is the shear stress resulting from the viscous forces. At each point in a continuous medium, whether it is solid or fluid, we need six components, each of them representing a component of force per unit area, to define the local stress completely. The local stresses acting in the x-y plane have been shown in Fig. 2.

Equation (1) can be cast in a more generalized form as given by Eq. (2). The shear stress exerted in the x-direction on a fluid surface of constant y by the fluid in the region of lesser y is designated as τ_{yx}, and the x-component of the fluid velocity vector is designated as v_x

$$\tau_{yx} = -\mu \frac{du}{dy} \tag{2}$$

This law is commonly known as Newton's law of viscosity. It states that the shear force per unit area is

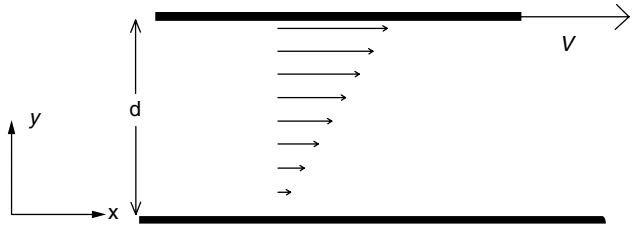


Figure 1. Viscous drag between two plates; the bottom plate is held fixed.

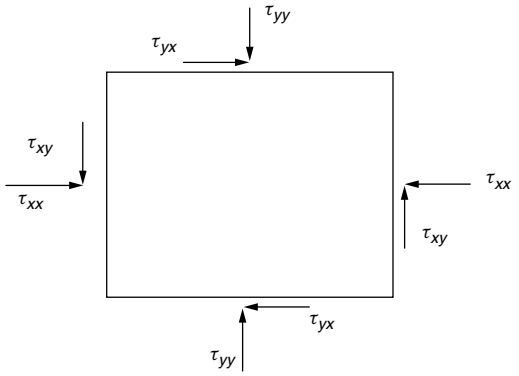


Figure 2. Local stresses acting in a *x*-*y* plane on a cubic element.

proportional to the negative of the local velocity gradient. In an arbitrary three-dimensional laminar flow, this relation can be generalized as

$$\begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} = \mu \begin{bmatrix} \left(2\dfrac{\partial u}{\partial x}\right) & \left(\dfrac{\partial u}{\partial y}+\dfrac{\partial v}{\partial x}\right) & \left(\dfrac{\partial u}{\partial z}+\dfrac{\partial w}{\partial x}\right) \\ \left(\dfrac{\partial u}{\partial y}+\dfrac{\partial v}{\partial x}\right) & \left(2\dfrac{\partial v}{\partial y}\right) & \left(\dfrac{\partial w}{\partial y}+\dfrac{\partial v}{\partial z}\right) \\ \left(\dfrac{\partial u}{\partial z}+\dfrac{\partial w}{\partial x}\right) & \left(\dfrac{\partial w}{\partial y}+\dfrac{\partial v}{\partial z}\right) & \left(2\dfrac{\partial w}{\partial z}\right) \end{bmatrix} \quad (3)$$

For detailed derivations and discussion of viscous stresses, one should refer to References 1 and 2.

Flows in which fluid viscosity is important can be of two types, namely laminar and turbulent. The basic difference between these flows was demonstrated by Osborne Reynolds in 1883. A thin stream of dye was introduced into the flow of water through the tube. At low flow rates, the dye stream was observed to follow a well-defined straight path, indicating that the fluid moves in parallel layers (*laminas*) with no macroscopic mixing across the layers, which is known as *laminar flow*. As the flow rate was increased beyond certain critical values, the dye streak broke up into an irregular motion and spread throughout the cross section of the tube, indicating the macroscopic mixing motions perpendicular to the direction of flow. Such a chaotic fluid motion is known as *turbulent flow*.

REYNOLDS NUMBER

The Reynolds Number (Re) is a quantity that engineers use to estimate if a fluid flow is laminar or turbulent. Consider the flow of an incompressible fluid through a circular pipe as shown in Fig. 3.

The variables associated with this pipe-flow configuration are the dimensions of the pipe, the rate of flow, and the physical properties of the fluid.

d = Internal diameter of the pipe

ρ = Density of the fluid and in an incompressible flow

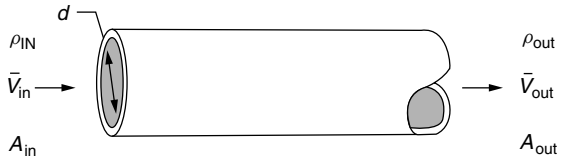


Figure 3. Flow through a pipe.

$\rho_{in} = \rho_{out}$ because it is constant

$\overline{v}$ = Average velocity

Q = Volumetric flow rate

A = Cross-sectional area and is constant, i.e., $(A_{in} = A_{out})$

We can then represent the Reynolds Number as a dimensionless entity as

$$\mathrm{Re} = \frac{\rho \overline{v} d}{\mu} = \frac{\rho\left(\dfrac{Q}{A}\right)d}{\mu} = \textbf{Unitless Number} \quad (3)$$

The Reynolds Number also indicates the relative significance of the inertial forces compared with the viscous forces. Laminar flow occurs at low Reynolds Numbers, where viscous forces are dominant, and is characterized by smooth, constant fluid motion, whereas turbulent flow occurs at high Reynolds Numbers and is dominated by inertial forces, producing random eddies, vortices, and other flow fluctuations. Different ranges of Reynolds Numbers determine the nature of different flow regimes, as shown in Fig. 4.

In laminar flow, the particles in the fluid follow streamlines (see Fig. 4), and the motion of particles in the fluid is predictable. If the flow rate is very large, or if objects obstruct the flow, the fluid starts to swirl in an erratic motion. No longer can one predict the exact path a particle on the fluid will follow. This region of constantly changing flow lines (see Fig. 4) is said to consist of turbulent flow.

RANGE 1: laminar flow (see Fig. 4)

Generally, a fluid flow is laminar from $\mathrm{Re} = 0$ to some critical value $\mathrm{Re} = 2100$, at which transition flow begins.

RANGE 2: transition flow (see Fig. 4)

Flows in this range may fluctuate between laminar and turbulent flow. The fluid flow is on the verge of becoming turbulent. In this zone, $2100 < \mathrm{Re} < 4000$.

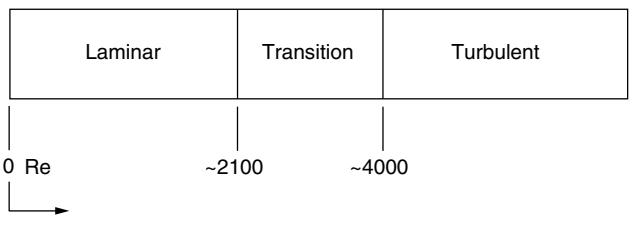


Figure 4. Different flow regimes and Reynolds Number in pipe flow.

RANGE 3: turbulent flow (see Fig. 4)

The fluid flow has become unstable. In turbulent flow, increased mixing exists that results in viscous losses, which are generally much higher than in those in laminar flow. In this zone, the values of Reynolds Number is greater than 4000.

It should be noted that the critical Reynolds Number depends on the flow type and the definition of the Reynolds Number, which varies for different geometries.

CONSERVATION LAWS FOR FLUID FLOW SYSTEMS

The behavior or dynamics of any fluid flow system can be described by laws of conservation of mass, momentum, and energy. In order to yield the detailed descriptions of variables of interest within the flow system, the control volume must be of infinitesimal dimensions that can shrink to zero, yielding a point volume. This approach reduces the quantities to point variables. The application of the conservation principles to this infinitesimal system produces microscopic or differential conservation equations. The governing momentum, energy, and mass balance differential equations for a given flow system can be derived using the shell balance concepts or directly from equations of change, which have been discussed in detail in References 2 and 3. Shell balance concepts are generally valid for simple flow systems, whereas equations of change can describe the flow behavior in complex flow real-life situations.

The governing differential equations for any flow system can be expressed in Lagrangian and Eulerian coordinate systems. In the Lagrangian approach, the fluid is assumed to be composed of particles, and the motion of individual particles is tracked. However, in the Eulerian approach, the attention is instead focused on a fixed coordinate system that defines space. We consider a prime variable of interest in fluid dynamics, that is, velocity. In the Lagrangian approach, this parameter is a function of time, whereas in Eulerian systems, it is a function of both time and spatial coordinates. Therefore, the acceleration of a particle that at time t occupies a fixed location can be calculated either by using the material or substantial derivatives as

$$a = \frac{DV}{Dt} \tag{4}$$

or by chain rule of differentiation as

$$a = \frac{\partial v}{\partial t} + \frac{\partial v}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial v}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial v}{\partial z}\frac{\partial z}{\partial t} \tag{5}$$

Equations (4) and (5) are the same; Eq. (4) represents the Lagrangian approach, whereas Eq. (5) is representative of an Eulerian system.

$$\underset{\text{Lagrangian Approach}}{\frac{DV}{Dt}} = \underbrace{\frac{\partial v}{\partial t} + \frac{\partial v}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial v}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial v}{\partial z}\frac{\partial z}{\partial t}}_{\text{Eulerian Approach}} \tag{6}$$

For advanced discussions about Lagrangian and Eulerian coordinate systems, the readers are advised to refer to References 2, 4, and 5.

EQUATIONS OF CHANGE IN LAMINAR FLOW SYSTEMS

The governing differential equations corresponding to mass and momentum conservation are solved to obtain field variables of interest in fluid dynamics (i.e., velocities and pressures), which are also known as the continuity equation and equations of change, which describe the laminar flow of a pure isothermal fluid.

EQUATION OF CONTINUITY

Equation of continuity is derived by applying the law of conservation of mass to a small 3-D volume element (see Fig. 5) within a flowing fluid. In vector notation, this equation can be represented as

$$\frac{\partial \rho}{\partial \mathbf{t}} = -(\nabla . \rho v) \tag{7}$$

Here, $(\nabla . \rho v)$ is called the "divergence" of $\rho\mathbf{v}$. This vector $\rho\mathbf{v}$ is the mass flux and is the net rate of mass efflux per unit volume. Equation (7) states that the rate of increase of the density within a small volume element fixed in space is equal to the net rate of mass influx to the element divided by its volume. A very special form of the equation of continuity is Equation (8), which is applicable for fluids of constant density, that is, incompressible fluids.

$$(\nabla . \mathbf{v}) = 0 \tag{8}$$

EQUATION OF MOTION

The equation of motion is developed by implementing the shell momentum balance concept on a 3-D volume element, as shown in Fig. 5.

It should be noted that momentum is a vector quantity, and hence the equation of motion will have components in each of the three coordinate directions x, y, and z, respectively. For detailed derivation of equation of motion, readers should refer to References 2 and 5. Adding the three components of equation of motion, the equation of

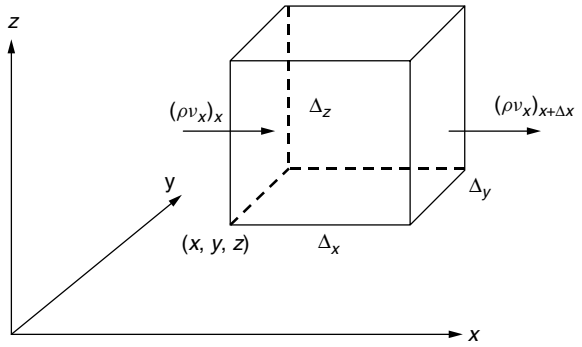


Figure 5. Region of volume in $\Delta x \Delta y \Delta z$ through which the fluid is flowing.

motion can be represented in vector notation as

$$\frac{\partial}{\partial t}\rho\mathbf{v} = [\nabla.\rho\mathbf{vv}] - [\nabla p] - [\nabla\cdot\boldsymbol{\tau}] + \rho\mathbf{g} \tag{9}$$

$\frac{\partial}{\partial t}\rho\mathbf{v}$	$[\nabla.\rho\mathbf{vv}]$	$-$	$[\nabla p]$	$-[\nabla\cdot\boldsymbol{\tau}]$	$+$	$\rho\mathbf{g}$
Rate of increase of momentum per unit volume	Rate of momentum gain by convection per unit volume		Pressure force on element per unit volume	Rate of momentum gain by viscous transfer per unit volume		Gravitational force on element per unit volume

$\boldsymbol{\tau}$ is known as "stress tensor" and has nine components, $[\nabla.\rho vv]$ represents the rate of loss of momentum per unit volume by fluid flow, and $(\nabla.\rho v)$ represents the rate of loss of mass per unit volume. In order to use Equation (9) to determine velocity distribution, appropriate expressions for various stresses in terms of velocity gradients and fluid properties are substituted, which yields the equations of motion for a Newtonian fluid with varying density and viscosity.

For constant ρ and μ, the equation of motion can be written as

$$\rho\left(\frac{\partial v}{\partial t} + v.\nabla v\right) = -\nabla p + \mu\nabla^2 v + \rho\mathbf{g} \tag{10}$$

Equation (10) is the well-known Navier–Stokes equation, first developed by Navier in France in 1822.

The equations of motion together with equation of continuity, equation of state $p = p(\rho)$, viscosity models for different fluids [see References 4 and 6], and the initial and the boundary conditions [see References 1, 3, 4, and 7], complete the problem specification for any laminar flow problem in hand. These equations, when solved mathematically, determine completely the density, pressure, and velocity components in an isothermal laminar flow situation.

Equation (10) can be written in nondimensional form as

$$\left(\frac{\partial v'}{\partial t} + v'.\nabla v'\right) = -\nabla p' + \frac{1}{\mathrm{Re}}\nabla^2 v' + \mathbf{g} \tag{11}$$

where the primed quantities are dimensionless. The ratio of second term to the fourth term in Equation (11) is of order *Re*, which indicates the physical representation of Reynolds Number as

$$\mathrm{Re} = \frac{\text{inertia forces}}{\text{viscous forces}} \tag{12}$$

Detailed derivation of nondimensional form of Navier–Stokes and Stokes equations can be found in References 2 and 8.

Concept of Dynamic Pressure

If the body of fluid is at rest, the pressure is hydrostatic and

$$\rho\mathbf{g} - \nabla p = 0 \tag{13}$$

Subtracting Eq. (13) from Eq. (10), we get

$$\rho\left(\frac{\partial v}{\partial t} + v\cdot\nabla v\right) = -\nabla p_\mathrm{d} + \mu\nabla^2 v \tag{14}$$

where $p_\mathrm{d} = p_\mathrm{s} - p$ is the pressure change because of dynamic effects. However, no accepted terminology exists for p_d, but we shall call it dynamic pressure. Other common terms are modified pressure (9) and excess pressure (10). For a fluid of uniform density, introduction of p_d eliminates gravity from the differential equations in Eq. (10). However, the process may not eliminate gravity from the problem. Gravity reappears in the problem if the boundary conditions are given in terms of total pressure p. Examples are surface gravity waves where the total pressure is fixed at the free surface. Without a free surface, however, gravity has no dynamic role, and its only effect is to add a hydrostatic contribution to the pressure field.

Equations (7)–(14) have been presented in rectangular coordinate systems. However, in real complex flow situations, depending on the geometrical configurations of the flow system, other coordinate systems such as spherical and cylindrical can be used. Hence, in these cases, Equations (7)–(14) can be cast in alternative coordinate systems using coordinate transforms. Detailed literature and methodology for performing coordinate transformations can be found in References 2 and 5.

STEADY-STATE FLOW BETWEEN PARALLEL PLATES

A laminar flow within two parallel plates is considered in Fig. 6.

The term fully developed in the figure signifies that we are considering regions beyond the developing stage near the entrance, where the velocity profile changes in the direction of flow because of the development of boundary layers from the two walls. The discussion of boundary layer theory is beyond the scope of the present text, and we shall only consider the flows under fully developed situations, i.e., far away from the entrance. For advanced discussions on boundary layer theory, readers may consult References 2 and 11.

Consider the fully developed stage of a two-dimensional flow between two infinite parallel plates, as shown in Fig. 7.

The flow is driven by an externally imposed pressure gradient, and the motion of the upper plate is maintained

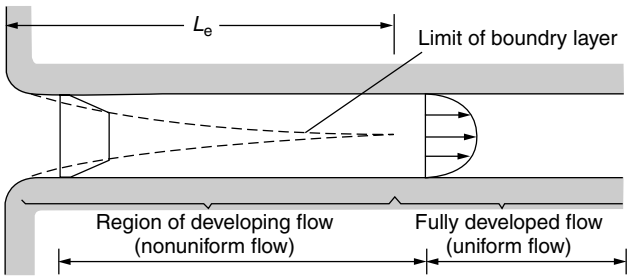


Figure 6. Developing and fully developed flows in a channel. Flow is fully developed after the boundary layers merge.

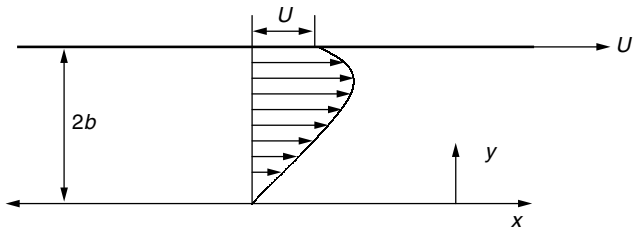


Figure 7. Steady-state flow between two parallel plates.

at velocity U. The x coordinate axis is parallel to the direction of flow. Two-dimensionality of the flow requires that $\frac{\partial}{\partial z} = 0$. Flow characteristics are also invariant in the x-direction, so that continuity requires $\frac{\partial v}{\partial z} = 0$. As $v = 0$ at $y = 0$, it follows that $v = 0$ everywhere, which implies that the flow is parallel to the walls. The momentum balance equations in x and y directions can be written as

$$0 = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \mu\frac{d^2u}{dy^2} \tag{15}$$

$$0 = -\frac{1}{\rho}\frac{\partial p}{\partial y} \tag{16}$$

The y-momentum in Eq. (16) shows that p is not a function of y. In the x-momentum in Eq. (15), the first term can only be a function of x, whereas the second term can only be a function of y. The only way this can be established is that both the terms are constants. The pressure gradient is hence a constant, implying that the pressure varies linearly across the channel. Integrating Eq. (15) twice, we get

$$0 = \frac{y^2}{2}\frac{dp}{dx} + \mu u + Ay + B \tag{17}$$

where p is a function of x only. The constants of integration are determined by using the conditions imposed on lower and upper plates. For the lower boundary, $u = 0$ at $y = 0$ requires that $B = 0$. The upper boundary condition $u = u$ at $y = 2b$, requires that $A = b\frac{dp}{dx} - \mu\frac{u}{2b}$.

The velocity profile from Eq. (17) then becomes

$$u = \frac{yU}{2b} - \frac{y}{\mu}\frac{dp}{dx}\left(b - \frac{y}{2}\right) \tag{18}$$

The volumetric flow rate per unit width of the channel can be calculated using

$$Q = \int_{\mathrm{O}}^{2\mathrm{b}} u dy = Ub\left[1 - \frac{2b^2}{3\,\mu U}\frac{dp}{dx}\right] \tag{19}$$

The average velocity can further be written as

$$\overline{V} = \frac{Q}{2b} = \frac{u}{2}\left[1 - \frac{2b^2}{3\,\mu U}\frac{dp}{dx}\right] \tag{20}$$

Two special cases of interest have been discussed in the subsequent section,

1. *Plane Couette Flow*. The flow driven by the motion of the upper plate, without the imposition of any external pressure gradient, is called a plane Couette flow.

Equation (18) then reduces to a linear profile represented by Eq. (21) and can be seen in Fig. 8.

$$u = \frac{yU}{2b} \tag{21}$$

The magnitude of shear stress is given by

$$\tau_{\mathrm{yx}} = \mu\frac{dU}{dy} = \frac{\mu u}{2\mathrm{b}} \tag{22}$$

which is uniform across the channel.

2. *Plane Poiseuille Flow*. The flow driven by an externally imposed pressure gradient through two stationary flat walls is called a plane Poiseuille flow. In this case, Eq. (18) reduces to Eq. (23), which represents a parabolic profile, as seen in Fig. 9.

$$u = -\frac{y}{\mu}\frac{dp}{dx}\left(b - \frac{y}{2}\right) \tag{23}$$

The magnitude of shear stress is given by

$$\tau_{\mathrm{yx}} = \mu\frac{du}{dy} = (b - y)\frac{dp}{dx} \tag{24}$$

which shows that the stress distribution is linear with a magnitude of $b(dp/dx)$ at the walls (as seen in Fig. 9).

It should be noted that the constant pressure gradient and the linearity of the shear stress distribution are general results for a fully developed flow and even hold in a turbulent flow situation.

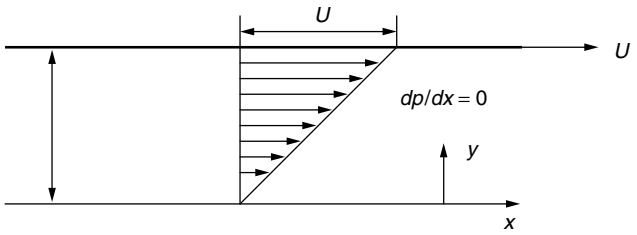


Figure 8. Plane Couette flow between two parallel plates.

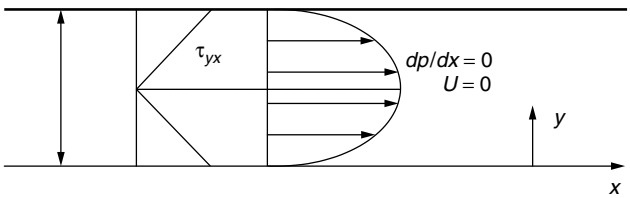


Figure 9. Plane Poiseuille flow between two parallel plates.

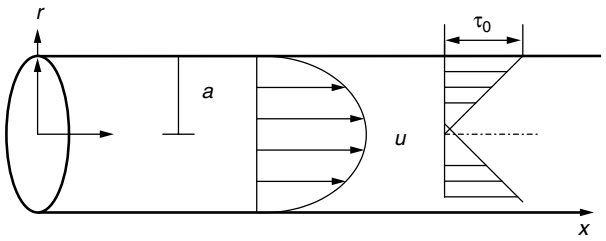


Figure 10. Laminar flow through a circular pipe.

STEADY-STATE FLOW IN A PIPE

Consider the fully developed laminar motion of a fluid through a circular pipe of radius a as shown in Fig. 10.

This type of flow is commonly known as circular Poiseuille flow. In this case, cylindrical coordinates (r, θ, x) have been used, with the x-axis coinciding with the axis of the pipe. The only nonzero component of velocity is the axial velocity u(r), and none of the variables depend on θ. The equations of motion are written in cylindrical coordinates [for detailed derivation, please refer to (2)]. The radial equation of motion gives,

$$0 = \frac{\partial p}{\partial r} \tag{25}$$

showing that p is a function of x only. The x-momentum equations gives

$$0 = \frac{dp}{dx} + \frac{\mu}{r}\frac{d}{dr}\left(r\frac{du}{dr}\right) \tag{26}$$

As the first term can only be a function of x and the second term can only be a function of r, it follows that both terms should be constants. The pressure, therefore, falls linearly along the length of the pipe. Integrating twice, we get

$$0 = \frac{r^2}{4\mu}\frac{dp}{dx} + A\ln r + B \tag{27}$$

As u must be bounded at $r = 0$, we must have $A = 0$. The wall condition, $u = 0$ at $r = a$, gives $B = -\left(\frac{a^2}{4\mu}\right)\left(\frac{dp}{dx}\right)$. The velocity profile is hence parabolic and can be represented as in Eq. (28),

$$u = \frac{r^3 - a^2}{4\mu}\frac{dp}{dx} \tag{28}$$

The shear stress at any point can be expressed using Eq. (29),

$$\tau_{xr} = \mu\frac{du}{dr} = \frac{r}{2}\frac{dp}{dx} \tag{29}$$

The shear stress distribution is linear with a maximum value of $\frac{a}{2}\frac{dp}{dx}$ at the walls.

The volumetric flow rate is given by

$$Q = \int_0^a u 2\pi r dr = -\frac{\pi a^4}{8\mu}\frac{dp}{dx} \tag{30}$$

Equation (30) is also commonly known as the Hagen–Poiseuille law. It gives the relationship between the volumetric flow rate and the forces causing the flow, that is, the forces associated with the pressure gradient and the viscosity.

The average velocity over the circular cross section can be written as

$$\overline{v} = \frac{Q}{\pi a^2} = \frac{a^2}{8\mu}\frac{dp}{dx} \tag{31}$$

CREEPING FLOW PAST A SPHERE

When the motion of fluid is "very slow" (Re $\ll 1$), the flow is said to be creeping or Stokes flow. Examples of such flows are the motion of settling of particles near the ocean bottom and the fall of moisture drops in the atmosphere. In creeping motions, viscous forces are dominant and, hence, the nonlinear inertia term present in Eq. (10) is neglected. We then have

$$\rho\frac{\partial v}{\partial t} = -\nabla p + \mu\nabla^2 v + \rho g \tag{32}$$

Equation (32) is the well-known **Stokes** equation, which is used to model creeping flows. The solution of creeping flow around a sphere was first given by Stokes in 1851. The detailed solution of velocity and pressure distributions around a sphere is quite advanced for the present text. Interested readers can refer to (2), (8), and (11) for detailed derivations. The positive pressure difference in front and negative in the rear of the sphere creates pressure drag on the sphere. Consider a fluid flowing with velocity U past a sphere of radius r. The total drag force on a sphere is obtained by calculating the total viscous stress and the normal stress and then multiplying it with the surface area of the sphere, which is found out to be

$$D = 6\pi\mu r U \tag{33}$$

One-third of the total drag comprises pressure drag, whereas two-thirds is the viscous or skin drag. It can be seen from Eq. (33) that the resistance in a creeping flow is proportional to the velocity, and is commonly known as Stokes Law.

Drag coefficient can be defined as the drag force nondimensionalized by $\rho u^2/2$ and the projected area of the sphere, which is πr^2, and stated as follows:

$$C_D = \frac{d}{\frac{1}{2}\rho u^2 \pi r^2} = \frac{24}{\mathrm{Re}} \tag{34}$$

where $\mathrm{Re} = 2rU\rho/\mu$

Most of the problems in fluid dynamics fall under two broad categories, namely flow in channels and flow around submerged objects. Relatively simple geometrical configurations were presented in prior sections. However, real-life examples of flows in channels include pumping oil in pipes, flow of water in channels, extrusion of plastics through dyes, and fluid flows in filters. Examples of flow around submerged objects are the flow of air around an airfoil, an airplane wing, motion of fluid around particles undergoing sedimentation, etc. Flow in channels are

mainly concerned with establishing a relationship between the volumetric flow rate and the pressure gradient. However, in flow past submerged objects, one is more interested in determining the relationship between the velocity of the fluid approaching the object and the drag force. As in many flow systems velocity and pressure profiles cannot be determined, the concept of friction factors/drag coefficient is found to be very useful. In other words, standard correlations are used to estimate the flow in geometrically complex systems. For an in-depth analysis, one can refer to Reference 2.

REMARKS

For understanding the physics and making generalizations in laminar flow situations, analytical solutions to simple flow configurations have been presented in the main text. With an advanced knowledge in mathematics, the readers should find it easy to solve any analytically tractable problem in laminar flow situation. Another area of utmost importance these days is Computational Fluid Dynamics, in which the equations of change are solved numerically using computers. Some of the commonly used numerical techniques for fluid flows include finite difference, finite element, and the finite volume methods. It is expected that the current text shall encourage the reader to learn numerical methods in a separate study.

BIBLIOGRAPHY

1. Alexandraou, A. (2001). *Principles of Fluid Mechanics*. Prentice-Hall, Englewood Cliffs, NJ.
2. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (1994). *Transport Phenomena*. John Wiley & Sons, New York.
3. Hanspal, N.S., Das, D.B., and Nassehi, V. (2004). Viscous flow. *Encyclopedia of Water*. John Wiley & Sons, New York.
4. Nassehi, V. (2002). *Practical Aspects of Finite Element Modelling of Polymer Processing*. John Wiley & Sons, New York.
5. Aris, R. (1997). *Vectors, Tensors and the Basic Equations of Fluid Mechanics*. Dover, New York.
6. Bird, R.B., Armstrong, R.C., and Hassager, O. (1997). *Dynamics of Polymeric Liquids: Fluid Mechanics*. John Wiley & Sons, New York.
7. Papanastasiou, T.C., Georgiou, G.C., and Alexandrou, A.N. (2000). *Viscous Fluid Flow*. CRC Press, New York.
8. Tritton, D.J. (1987). *Physical Fluid Dynamics*. Oxford Science Publications, Clarendon Press, Oxford, UK.
9. Batchelor, G.K. (1967). *An Introduction to Fluid Dynamics*. Cambridge University Press, London, UK.
10. Lighthill, M.J. (1986). *An Informal Introduction to Fluid Mechanics*. Clarendon Press, Oxford, UK.
11. White, F.M. (1991). *Viscous Fluid Flow*. McGraw-Hill, New York.

APPENDIX 1

NOMENCLATURE

A	Area
C_d	Drag coefficient
d	Diameter of the pipe
D	Drag force
F	Force
$\mathbf{g}$	Gravity force vector
p	Pressure
Q	Volumetric flow rate
r	Radius of the sphere
Re	Reynolds number
$\mathbf{v}$	Velocity vector
$\overline{v}$	Average velocity
t	Time variable
u	Velocity in x direction
v	Velocity in y direction
w	Velocity in z direction

Greek Symbols

μ	Viscosity of the fluid
τ	Stress
ρ	Density of the fluid

Subscripts

x	Stands for x component
y	Stands for y component
z	Stands for z component

FINITE ELEMENT MODELING OF COUPLED FREE AND POROUS FLOW

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INTRODUCTION

The article discusses the finite element modeling (FEM) of groundwater flow in coupled free and porous domains in natural hydroenvironmental conditions. In general, free flow regime can be viewed as if the flow were in a layer of fluid or a pipe, which needs only the fluid dynamic characterization of the domain, e.g., Reynolds Number. On the other hand, porous flow regime indicates that fluid flow takes place through a porous medium, which needs the characterization for both the fluid dynamics and the medium, e.g., permeability, porosity, pore size distribution, etc. Coupled free and porous flow is observed in many hydroenvironmental conditions. As an example, conjunctive surface and subsurface flow may be cited. The flow on the surface is characterized as free flow. Some of the water from the surface seeps into the underground soil, which is a porous medium. The flow in the underground soil may be called as the subsurface or porous flow. As well as the expected media heterogeneity, e.g., presence of layers, laminations, etc., the subsurface also contains nonporous

sections, e.g., conduits, fissures, buried structures that are often damaged, macropores, vugular inclusions and fractures, etc. The hydrodynamics of groundwater flow in the nonporous (e.g., vugs) and porous sections are fundamentally governed by the Navier–Stokes and Darcy equations, respectively (1–3), although simplified forms of Navier–Stokes equations are often used in practice for the nonporous domains. The overall flow behavior in the coupled nonporous and porous region can be modeled with an approach that combines Navier–Stokes and Darcy equations with suitable interfacial, boundary, and initial conditions. However, the complexity of the subsurface regions is such that it is usually not possible to predict the coupled flow behavior with confidence using the traditional analytical methods or experiments. FEM is a powerful method that can be used to validate results from experiments and/or analytical method. In other cases, where such results are not available, FEM modeling can be used independently to predict the flow field in the subsurface. The versatility of FEM lies in its ability to cope with complex and irregular geometries of the flow domain found in subsurface regimes.

In this article, the finite element method will be discussed in the context of solving coupled free and porous flow governed by Navier–Stokes and Darcy equations, respectively. Boundary conditions that may be used for simulating coupled flow problems are also discussed very briefly.

COUPLED FREE AND POROUS FLOW MODEL

The flow in the free flow regime can be mathematically expressed by the well-known Navier–Stokes equations in vector form as

$$\rho\frac{\partial\vec{v}}{\partial t}+\rho\vec{v}\cdot\nabla\vec{v}=-\nabla p\vec{\vec{\delta}}+\nabla\cdot\vec{\vec{\tau}}+\rho\vec{g} \tag{1}$$

where ρ is the density of the incompressible fluid; $\vec{v}$, p, $\vec{\vec{\tau}}$, and $\vec{g}$ represent velocity, pressure, extra stress, and body force, respectively; and $\vec{\vec{\delta}}$ is the Kronecker delta tensor. Equation (1) expresses the conservation of momentum of free flow for an incompressible viscous fluid. The first term on the left-hand side represents the rate of change of momentum, whereas the second term represents the convective flow. On the right-hand side, the first term represents the hydrostatic pressure gradient; the second term is the deviatoric stress, whereas the last term contributes to the momentum because of the gravitational force.

The porosity of soil in the subsurface is generally low (<0.5). In such a case, the inertia forces seem to be dominated by the viscous forces, although this cannot be generalized because of its heterogeneous nature. Nevertheless, the flow in the subsurface can be mathematically expressed by the Darcy equation as

$$\rho\frac{\partial\vec{v}}{\partial t}=-\nabla p-\frac{\eta}{\vec{\vec{K}}}\cdot\vec{v} \tag{2}$$

where $\vec{\vec{K}}$ represents the permeability tensor.

According to Newton's first law, the total mass of fluid flowing in the flow regions must be equal to the amount of fluid leaving the domain without any accumulation or consumption. This mass conservation can be represented by the continuity equation for a fluid of constant density as

$$\nabla\cdot\vec{v}=0 \tag{3}$$

The governing equations for the groundwater flow system are either solved analytically or numerically. Analytical models contain an analytical solution of the field equations, continuously in space or time. In numerical models, a discrete solution is obtained in both space- and time-domains by using numerical approximations of the governing partial differential equations. In general, a wide variety of numerical techniques are used in groundwater flow modeling. The most commonly used methods are the finite difference, finite element, finite volume, and analytical element methods. However, we will limit this text to discuss the use of finite element method for reasons explained earlier.

PRINCIPLES OF FINITE ELEMENT MODELING

The finite element method (FEM) is based on the principles of variational calculus. In this method, the overall geometrical domain is divided into a number of small discrete regions, termed as finite elements, with each element associated with a fixed number of nodal points. The variables within each element can be approximated by their values at each elemental node multiplied by an appropriate shape function associated with that node. This approximation is substituted in the mathematical statement of a problem, and the residual statement is weighted over the entire elemental domain. The solution is achieved by minimizing the errors introduced by the approximation.

TYPES OF FINITE ELEMENTS

Various finite element families are available, mainly based on the geometrical shapes of the elements, such as triangular or rectangular in 2-D cases or brick or prismatic elements for 3-D situations. In the context of 2-D modeling, we briefly discuss triangular and rectangular elements. Typical triangular elements are shown in Fig. 1(a) and (b).

To define the variations of the dependent variable over the elemental domain, nodal geometrical functions associated with each node, commonly known as shape functions, need to be derived. For a two-dimensional

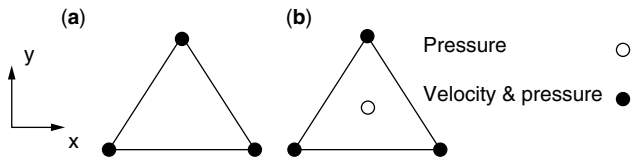


Figure 1. Triangular finite elements.

element, the approximation for the dependent variable in terms of the nodal shape functions can be written as

$$f(x,y) = \tilde{f}(x,y) = \sum_{i=1}^{p} N_i(\overline{x},\overline{y}) f_i \tag{4}$$

where the overbar indicates the values at each node of the element.

Multidimensional elements should also satisfy the following conditions:

$$\sum_{i=1}^{p} N_i(\overline{x},\overline{y}) = 1$$
$$N_i(\overline{x}_j,\overline{y}_j) = 1, \quad i = j$$
$$N_i(\overline{x}_j,\overline{y}_j) = 0, \quad i \neq j$$

In case of a three-noded element, shown in Fig. 1(a), the shape functions are

$$\left.\begin{aligned} N_i &= \frac{1}{2A}[a_i + b_i x + c_i y] \\ N_j &= \frac{1}{2A}[a_j + b_j x + c_j y] \\ N_k &= \frac{1}{2A}[a_k + b_k x + c_k y] \end{aligned}\right\} \tag{5}$$

where

$$\begin{vmatrix} 1 & X_i & Y_i \\ 1 & X_j & Y_j \\ 1 & X_k & Y_k \end{vmatrix} = 2A$$

$$\begin{aligned} a_i &= X_j Y_k - X_k Y_j, \quad b_i = Y_j - Y_k \quad \text{and} \quad c_i = X_k - X_j \\ a_j &= X_k Y_i - X_i Y_k, \quad b_j = Y_k - Y_i \quad \text{and} \quad c_j = X_i - X_k \\ a_k &= X_i Y_j - X_j Y_i, \quad b_k = Y_i - Y_j \quad \text{and} \quad c_k = X_j - X_i \end{aligned}$$

where (X_i, Y_i), (X_j, Y_j), and (X_k, Y_k) are the coordinates corresponding to the nodes i, j, and k, respectively. For detailed derivations, the readers can refer to Nassehi (4) and Segerlind (5). A four-noded rectangular finite element is shown in Fig. 2. The shape functions for this element can be written as

$$\left.\begin{aligned} N_i &= \frac{1}{4}\left(1 - \frac{q}{b}\right)\left(1 - \frac{r}{a}\right) \\ N_j &= \frac{1}{4}\left(1 + \frac{q}{b}\right)\left(1 - \frac{r}{a}\right) \\ N_k &= \frac{1}{4}\left(1 + \frac{q}{b}\right)\left(1 + \frac{r}{a}\right) \\ N_k &= \frac{1}{4}\left(1 - \frac{q}{b}\right)\left(1 + \frac{r}{a}\right) \end{aligned}\right\} \tag{6}$$

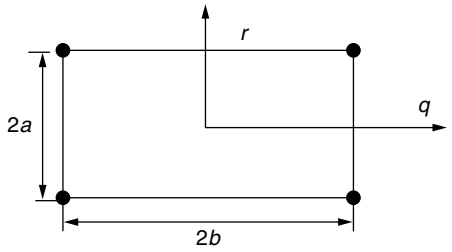


Figure 2. A linear rectangular finite element.

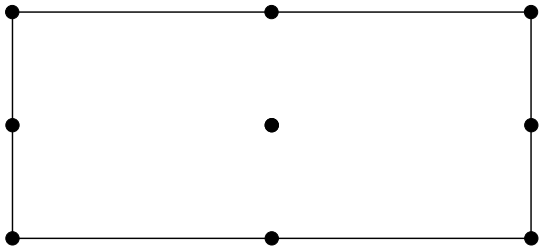


Figure 3. A biquadratic rectangular finite element.

The second member of this group is the nine-noded biquadratic rectangular element with equal order interpolation functions for velocity and pressure, as shown in Fig. 3.

Higher order elements of this family can also be readily generated using the tensor products of the higher order one-dimensional interpolation functions. In addition to all these classes of finite elements, some nonstandard elements exist, such as the Taylor–Hood elements specially designed for the solution of incompressible flow problems. In the Taylor–Hood elements, interpolation of pressure is always based on a lower order polynomial than the velocity interpolation functions.

PARAMETRIC MAPPING

Finite element method can deal with irregular or curved geometries in a straightforward and systematic way using parametric mapping (6). A regular element, known as the master element, is chosen and a local finite element approximation based on this master elemental shape function is selected. The Master element is mapped into the global coordinates to generate required curved irregular element. Two independent elements can be used in the finite element analysis, one for approximating geometry and the other for interpolation of field variable. When a typical element in global coordinate system is transformed to a master element, it is requisite to transform the global coordinate system to local coordinate system of the master element. Depending on the relationship between the degree of approximation used for coordinate transformation and for the field variable, three different types of mapping schemes can be employed.

1. *Subparametric Transformation*: Shape functions used for geometry are of lower order than that used for dependent variable.
2. *Isoparametric Transformation*: Shape functions used for mapping geometry are of the same order as for the dependent field variable.
3. *Superparametric Transformation*: Shape functions for mapping geometry are of higher order than that used for the field variable.

FINITE ELEMENT SCHEMES FOR INCOMPRESSIBLE FLOW PROBLEMS

Application of the weighted residual method to the solution of incompressible flow equations of continuity

and momentum conservation is commonly based on two different schemes.

U-V-P Scheme

The name U-V-P implies U as the component of velocity in x-direction, V as a component of velocity in y-direction, and P as pressure with all these variables calculated simultaneously in the solution scheme. Zienkiewiez and Taylor (6) classified the U-V-P scheme to general category of mixed finite element methods. In this technique, both velocity and pressure are termed as primitive variables and are discretised as unknowns. In the U-V-P method, the weighted residual statements for the groundwater flow model can be formulated as

Free Flow Zone

$$\int_\Omega N_P \nabla \cdot \overline{v} d\Omega = 0$$

$$\int_\Omega \rho N_V \left(\frac{\partial \overline{v}}{\partial t} + \overline{v}^0 \nabla \overline{v} \right) d\Omega = \int_\Omega N_V \left(-\nabla \overline{p} \delta + \nabla \cdot \overline{\tau} + \rho g \right) d\Omega \tag{7}$$

Porous Flow Zone

$$\left.\begin{aligned} &\textstyle\int_\Omega N_P \nabla \cdot \overline{v} d\Omega = 0 \\ &\textstyle\int_\Omega \rho N_V \left(\frac{\partial \overline{v}}{\partial t} \right) d\Omega = \int_\Omega N_V \left(-\nabla \overline{p} + \frac{\eta}{K} \cdot \overline{v} \right) d\Omega \end{aligned}\right\} \tag{8}$$

where an over bar indicates interpolated variables over an element. N_v and N_P are the appropriate basis functions or weight functions.

The interpolating functions for the field variables are substituted in the formulations, and the equations are then integrated, which yields a final set of finite element working equations (7).

Penalty Scheme

The penalty method is a standard technique to reduce the number of variables in the flow calculation (4). In the penalty method, the pressure is expressed in terms of the incompressibility condition (4)

$$p = -\lambda(\nabla \cdot v) \tag{9}$$

This relation is then substituted in the momentum balance equation, after which the weighted residual finite element method is applied. λ is the penalty parameter that generally has a very large value. Elimination of pressure as a field variable leads to a compact set of working equations reducing the computational cost. The only problem with the penalty scheme lies in the selection of appropriate value of the penalty parameter to avoid ill conditioning of the solution matrices.

MODELING SCHEMES BASED ON U-V-P FORMULATION

In the modeling of incompressible flows, the Ladyzhenskaya–Babuska–Brezzi (LBB) stability condition must be satisfied (8), which poses a severe restriction on the type of approximating functions that can be used in finite element formulations. Different finite element models based on various strategies have been developed that satisfy the LBB condition. They range from the use of elements generating unequal order interpolation functions (6) for the field unknowns to a perturbed form of continuity equation (9) representing slightly compressible fluids.

Taylor–Hood Scheme

In order to satisfy the LBB condition, unequal order interpolation functions for velocities and pressure can be used. In this scheme, the incompressibility constraint can be used without any modifications (i.e., Eq. (3) remains as $\nabla \cdot \vec{v} = 0$). In addition to the requirement of LBB criterion, it is also known that because of the incompatibility of the operators in the Navier–Stokes and Darcy equations, the approximating function spaces used for the numerical solution of these equations need to be different. In essence, the Darcy equation should be treated as an elliptic Poisson equation, where the degrees of freedom should be kept as low as possible. This scheme is developed using C^0 continuous Taylor–Hood elements (10). This element is a member of the bubble element family (11), and it is expected that all other members of this family will generate stable solutions for incompressible flows with a variety of time-stepping schemes. A typical Taylor–Hood element can be seen in Fig. 4.

Perturbed Continuity Scheme

The perturbed continuity method (12) depends on the inclusion of the term $\frac{1}{\rho c^2}\frac{\partial p}{\partial t}$ in the continuity equation (i.e., Eq. 3), where ρ is the fluid density and c is the velocity of sound in the fluid. Therefore, this results in the incorporation of the temporal derivative of pressure in the continuity equation, which in physical terms amounts to considering the fluid to be slightly compressible (9). To use the time-dependent continuity equation, transient terms, such as $\frac{\partial \vec{v}}{\partial t}$, should also be added into the Navier–Stokes and the Darcy equations, which inherently forces the use of a time-stepping scheme in the numerical solution of the coupled flows. The perturbed continuity scheme allows the use of equal order interpolation functions for velocity and pressure. Steady-state conditions can be obtained iteratively using different time-stepping schemes.

TEMPORAL DISCRETIZATION

The finite element solution of time-dependent flow problems produces a system of linear first-order differential

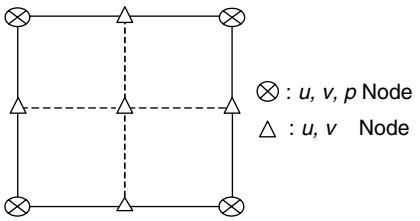


Figure 4. Taylor–Hood element.

equations in the time-domain. The method for solving time-dependent partial differential equations is the Partial Discretization Method. In this method, the space-time domain is not discretized as a whole, but the time derivatives are treated separately.

θ Time-Stepping Method

In this method, the time derivatives are kept unchanged, and the spatial discretization is carried out to form a weighted residual statement, which yields a system of ordinary differential equations in time. Consider a partial differential equation

$$\frac{\partial \phi(x,t)}{\partial t} + f[\phi(x,t)] - c = 0 \tag{10}$$

where f is a linear differential operator with respect to x.

At any time level θ, the temporal derivative is approximated by a forward difference as

$$\left.\frac{\partial \phi}{\partial t}\right|_{\theta} = \frac{\phi|_{n+\theta\Delta t} - \phi|_n}{\theta \Delta t} = \frac{\phi|_{n+1} - \phi|_n}{\Delta t} \tag{11}$$

In general, this differential system can be shown in matrix form as

$$[M]_\theta \left\{\phi^{\bullet}\right\}_\theta + [K]_\theta \{\phi\}_\theta = \{F_\theta\} \tag{12}$$

where $0 \le \theta \le 1$.

The terms, except the differential term, in the equation are approximated using a linear interpolation as

$$[K]_\theta \{\phi\}_\theta = (1-\theta)[K]_n \{\phi\}_n + \theta [K]_{n+1} \{\phi\}_{n+1} \tag{13}$$

$$\{F\}_\theta = (1-\theta)\{F\}_n + \theta \{F\}_{n+1} \tag{14}$$

Substitution of these equations and carrying out algebraic manipulation gives

$$([M]_\theta + \theta \Delta t [K]_{n+1})\{\phi\}_{n+1} = ([M]_\theta - (1-\theta)\Delta t [K]_n)\{\phi\}_n + ((1-\theta)\{F\}_n + \theta \{F\}_{n+1})\Delta t \tag{15}$$

On the basis of this equation, a global set is derived and solved to obtain unknowns at time level $n+1$ using the known value at time level n.

Taylor–Galerkin Method

The Taylor–Galerkin time-stepping technique is elaborated in detail in the work by Donea (13). Consider the same differential equation. Taylor series expansion of variable ϕ within the time steps n and $n+1$ gives

$$\phi^{n+1} = \phi^n + \Delta t \left.\frac{\partial \phi}{\partial t}\right|^n + \frac{1}{2}(\Delta t)^2 \left.\frac{\partial^2 \phi}{\partial t^2}\right|^n + \ldots . \tag{16}$$

The temporal derivatives in Eq. (15) can be substituted from the parent differential Eq. (9) evaluated at that time level. Hence, we have

$$\left.\frac{\partial \phi(x,t)}{\partial t}\right|_n = -f[\phi(x,t)]|_n + c \tag{17}$$

Similarly, the second-order derivative at time step n can be replaced as

$$\left.\frac{\partial^2 \phi(x,t)}{\partial t^2}\right|_n = \frac{\partial}{\partial t}\{-f[\phi(x,t)]|_n + c\} \tag{18}$$

All the temporal derivatives in the Taylor series expansion can be substituted principally from the original differential equation. Taylor series expansion of the field variable is truncated, keeping only first few terms. Accuracy of the scheme is solely dependent on the highest order of derivative remaining in the expansion after truncation.

MATHEMATICAL MODELS FOR COUPLED FLOWS

The main challenge is to construct a sound mathematical formulation for the coupled free and porous flow dynamics (14). The selection of appropriate approximating function spaces for the numerical solution of these equations, which guarantee unified stability of both the free flow and porous flow models, is not straightforward (15). In order to circumvent this problem, most of the solution algorithms are based on two approaches.

The first approach employs the Brinkman's equation to describe the flow on a free/porous interface (16). The Brinkman's equation includes the Laplacian of the velocity field and, hence, is of the same order as the Stokes equation. Therefore, its use across a free/porous interface ensures continuity of velocity and pressure fields. The Brinkman's equation is only applicable to media of high permeability (17). In addition, the Brinkman's equation is constructed using a parameter called "effective viscosity." The second approach is based on the imposition of a slip-wall boundary condition at the free/porous interface, as suggested by Beavers and Joseph (18). Using this approach, the interfacial boundary condition is modified to match the free and porous flow conditions by an auxiliary relationship. This approach is empirical and deduced from a simple one-dimensional situation, and its extension to multidimensional cases is not well understood. The value of the slip coefficient depends on many physical parameters such as the geometrical features of the interface.

Discacciati et al. (19) developed a model for coupling of Navier–Stokes and Shallow Water equations for surface flows and Darcy equations for groundwater flows. They applied the boundary conditions similar to that of the Beavers and Joseph (18) at the free/porous interface. They developed an iterative method for the solution, which requires the solution of one problem in the fluid part and one in the porous medium.

Recently, Burman and Hansbo (15) proposed a unified approach for the solution of the coupled Stokes/Darcy problem using an edge stabilization technique in conjunction with the use of mixed P_1/P_0 finite elements. The edge stabilization, as named by these authors, involves the splitting of the viscous stress term into its normal and tangential components at the free/porous interface. The normal stress component is then equated to the pressure differential across the free/porous interface.

NODAL REPLACEMENT SCHEME FOR COUPLED FLOWS

In addition to the schemes described in the previous section, Nassehi et al. (7) have developed a nodal replacement technique based on finite element method, which can be used for modeling coupling the free and the porous flow dynamics in two-dimensional situations.

The scheme is based on the imposition of Darcy equation as a boundary condition for the Navier–Stokes equations at the free/porous interface (and vice-versa at the porous/free interface). The field variable velocities and pressures are forced to be continuous in both the free and porous regions across the interface. In the stiffness matrix corresponding to the elements in the free flow regime, which are also present on the free/porous interface, the Navier–Stokes terms corresponding to the interfacial nodes are replaced by the appropriate form of the discretised Darcy components and vice-versa. This procedure is illustrated in Fig. 5.

BOUNDARY CONDITIONS FOR COUPLED FLOW DOMAINS

For the solution of free flow equations, no-slip-wall boundary conditions (20) are generally specified on the impermeable walls of the domain. A velocity boundary condition is given at the inlet of the flow domain, whereas at the exit, stress-free boundary conditions (21) are used.

For the solution of porous flow equations, a partial slip boundary condition (4) may be specified, and at the flow exit, a pressure datum can be imposed. In the coupled flow situation, the Darcy equation is imposed as the boundary condition for the Navier–Stokes equation at the free/porous interface.

COMMERCIAL GROUNDWATER FLOW MODELS

There are many commercially available groundwater flow models based on a numerical method, which have been developed in the past. They are widely used in industries and academia for carrying out a variety of numerical studies. For example, FEMWATER is commonly used for 3-D modeling of flow and transport in groundwater systems. Salient features of some of the other frequently used groundwater flow tools have been presented in Table 1.

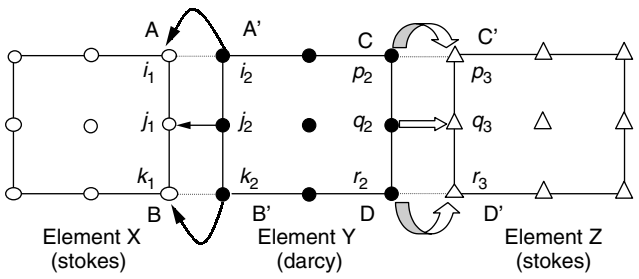


Figure 5. Schematic representation for linking of Navier–Stokes and Darcy regimes.

Table 1. Commercial Finite Element Groundwater Models

S No.	Model	Application
1	**3DFEMFAT**	3-D finite-element model of flow and transport through saturated-unsaturated media.
2	**AQUA3D**	3-D groundwater flow and contaminant transport model.
3	**ChemFlux**	Finite element mass transport model.
4	**FEFLOW**	Finite element subsurface flow system. FEFLOW is a finite-element package for simulating 3-D and 2-D fluid density coupled flow, contaminant mass (salinity), and heat transport in the subsurface.
5	**FLONET/TRANS**	2-D cross-sectional groundwater flow and contaminant transport modeling.
6	**GMS**	Groundwater Modeling Environment for MODFLOW, MODPATH, MT3D, RT3D, FEMWATER, SEAM3D, SEEP2D, PEST, UTCHEM, and UCODE.
7	**MicroFEM**	Finite-element program for multiple-aquifer steady-state and transient groundwater flow modeling.
8	**MODPATH**	3-D particle tracking program for MODFLOW.
9	**MOFAT**	Multiphase (water, oil, gas) flow and multicomponent transport model.
10	**SUTRA**	2-D saturated/unsaturated transport model.
11	**VAM2D**	2-D Variably-Saturated Groundwater Analysis Model.
12	**WinTran**	Groundwater Flow and Finite-Element Contaminant Transport Model.
13	**FEMWATER**	3-D Finite Element Model for Coupled Groundwater Flow and Contaminant Transport.

BENEFITS OF FINITE ELEMENT MODELING FOR MODELING COUPLED FLOW

The finite element method is generally found to be more robust and reliable toward obtaining stable and convergent solution, which is because it involves the minimization of errors introduced because of variable approximation. The Galerkin weighted residual finite element method is very flexible and can cope with irregular, complex, and curved geometries of the problem domain, which is the normal case in the free surface and subsurface flows. The previously developed mathematical models for the coupled free/porous problems are based

on concepts like the use of the Brinkman's equation or the specification of slip-wall boundary condition at the interface. Although both of these methodologies appear to be simple, they seem to be compromising their accuracy and lacking flexibility with suitability only for specific problem domains. The novel nodal replacement technique available in FEM is a simple mathematical concept that links the physics behind the free flow and porous flow phenomena without any simplified assumptions and can be easily extended to three-dimensional flow regimes. The linking of the free and the porous flow regimes is achieved without imposition of any artificial boundary conditions at the free/porous interface. It can be concluded that the FEM schemes are highly robust and reliable for the combined flow without any mathematical problems developing from stability requirements, numerical incompatibility, or time-stepping schemes.

SUMMARY

The coupled free and porous flow phenomenon has been discussed in the context of natural hydroenvironmental conditions. Mathematical statements of free and porous flow models have been represented elaborating physical significance of each flow regime. Various finite element families have been listed and classified mainly according to the geometric shapes of the elements. Finite element formulations for the incompressible flow problems based on two common methods, namely the U-V-P and penalty schemes, have been derived. In the context of unsteady-state studies, time-stepping schemes like θ-method and Taylor–Galerkin methods have been explained for the temporal discretization of the governing equations. The currently available mathematical models for the coupled flow problems have been discussed regarding their conceptual details and related assumptions. A recently developed nodal replacement scheme for the coupled flow situation has been analyzed with the help of a pictorial representation and required boundary conditions.

Nomenclature

v	Fluid velocity
$\vec{v}$	Velocity vector
p	Fluid pressure
$\vec{g}$	Gravitational acceleration vector
$\vec{\vec{K}}$	Permeability tensor
A	Area of the finite element
N	Shape functions
c	Speed of sound in fluid

Subscripts

x	In x-direction
y	in y-direction
v	For velocity
p	For pressure

Greek Symbols

ρ	Fluid Density
η	Fluid viscosity
θ	Time-stepping parameter
Ω	Elemental domain
λ	Penalty parameter
∇	Gradient
$\vec{\vec{\delta}}$	Kronecker delta tensor
$\vec{\vec{\tau}}$	Extra stress tensor

BIBLIOGRAPHY

1. Zimmerman, R.W. and Yeo, In-W. (2000). Fluid flow in fractures: from the Navier–Stokes equations to the cubic law, In: *Dynamics of Fluids in Fractured Rock*. B. Faybishenko, P.A. Witherspoon, and S.M. Benson (Eds.). Geophysical Monograph Series, American Geophysical Union, Washington, DC, pp. 213–224.
2. Das, D.B. and Nassehi, V. (2003). *Water Resour. Res.* **39**(3): 1072.
3. Abrogast, T., Brunson, D.S., Bryant, S.L., and Jennings, Jr., J.W. (2004). A preliminary computational investigation of a macro-model for vuggy porous. *Proceedings of the Computational Methods in Water Resources 2004 International Conference*, Chapel Hill, NC, June 13–17.
4. Nassehi, V. (2002). *Practical Aspects of Finite Element Modelling of Polymer Processing*. Wiley, Oxford, UK.
5. Segerlind, L.J. (1984). *Applied Finite Element Analysis*, 2nd Edn. Wiley, New York.
6. Zienkiewicz, O.C. and Taylor, R.L. (2002). *The Finite Element Method*, Vol. 3, 5th Edn. Butterworth-Heinemann, Oxford, UK.
7. Nassehi, V., Hanspal, N.S., Waghode, A.N., and Wakeman, R.J. (2004). Finite element simulation of flow through pleated cartridge filters. *Chemical Engineering Science*.
8. Reddy, J.N. (1993). *An Introduction To Finite Element Method*, 2nd Ed. McGraw-Hill, London, UK.
9. Zienkiewicz, O.C. and Wu, J. (1991). *Int. J. Numeric. Methods Engineer*. **32**: 1189–1203.
10. Taylor, C. and Hood, P. (1973). *Computers and Fluids*. **1**: 73–101.
11. Fortin, M. and Fortin, A. (1985). *Newer Elements for Incompressible Flow: Finite Element Methods*. Vol. 6, Wiley, New York.
12. Hanspal, N.S., Waghode, A.N., Nassehi, V., and Wakeman, R.J. (2004). Numerical analysis of coupled Stokes/Darcy flows in industrial filtrations. *Transport Porous Media*.
13. Donea, J. (1984). *A Taylor-Gallerkin Method for Convective Transport Problem. Int. J. Numeric. Methods Eng*. **20**: 101–119.
14. Layton, W.J., Schieweck, F., and Yotov, I. (1993). *SIAM J. Numeric Anal.* **40**(6): 2195–2218.
15. Burman, E. and Hansbo, P. (2002). *A Unified Stabilized Method for Stokes' and Darcys' Equations*. Chalmers Finite Element Center, Chalmers University of Technology, Göteborg, Sweden.
16. Brinkman, H.C. (1947). *Appl. Scientif. Res.* **A1**: 27–34.
17. Kim, S. and Russell, W.B. (1985). *J. Fluid Mechan.* **154**: 269–286.
18. Beavers, G.S. and Joseph, D.D. (1967). *J. Fluid Mechan.* **30**(1): 197–207.
19. Discacciati, M., Miglio, E., and Quarteroni, A. (2002). *Appl. Numeric. Mathemat.* **43**: 57–74.
20. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (2000). *Transport. Phenomena*. Wiley, New York.
21. Papanastasiou et al. (1992).

UNCONFINED GROUNDWATER

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INTRODUCTION

An unconfined aquifer is a geologic formation with subterranean water that is not confined by relatively impermeable layers. Part of the precipitation and irrigation water as well as water from recharge basins, reservoirs, and ponds moving downward from the soil layer will reach the saturated groundwater zone. The top of this zone is the water table, which separates the fully saturated zone from a partially saturated zone. The latter zone is simply referred to as the unsaturated zone, but it is also known as the zone of aeration or vadose zone. Generally, the water in the unsaturated zone is under less than atmospheric pressure. The unsaturated zone includes the capillary fringe, directly above the water table, which is near saturation but still under negative pressure relative to the atmospheric pressure.

Often, groundwater flow discharges into or receives water from surface water bodies such as river channels or lakes. An effluent or gaining stream is supplied by groundwater, which is usually the case in humid climates. An influent or losing stream supplies water to the groundwater and is a characteristic of arid climates. In addition to the flow to streams from the saturated zone, there exists throughflow, which is the sporadic horizontal water flow above the water table. Such a flow normally takes place when parts of the soil are completely saturated. Flow rates are usually low, with maximum flow likely occurring on steep slopes and in pervious sediments.

The presence of a low conductivity zone or an impermeable layer (called perching bed) can lead to the formation of a perched water table above the aquifer's main water table. Springs are often formed when a perched water table intersects the ground surface. Perched groundwater can be permanent if recharge is frequent enough to maintain a saturated zone above the perching bed. Intermittent cases occur when recharge is not large or frequent enough to prevent the perched water from disappearing at times due to drainage through the perching bed or over its edges.

Water input to an unconfined aquifer mainly includes recharge due to rainfall and return irrigation, direct injection, and leakage from surface water bodies. Major outflow can include pumping of groundwater, plant usage, evaporation from the soil surface, and leakage onto surface water bodies. Water table elevation will change according to the relative magnitude of groundwater replenishment versus depletion.

When compared to confined aquifers, unconfined aquifers are more susceptible to contamination by dissolved chemicals, such as agricultural chemicals, and nonaqueous phase liquids (NAPLs), such as hydrocarbon products, due to the absence of a confining layer. Light nonaqueous phase liquids (LNAPLs), such as gasoline, can form a floating lens on top of the water table. The lens moves in the direction of groundwater flow. A dissolved phase plume can form in the saturated zone that also moves in the direction of water flow. A plume of dense NAPLs (DNAPLs) can penetrate down through the unsaturated and saturated zones and move by gravity in a direction that is independent of groundwater flow. A dissolved phase plume due to DNAPLs can also exist.

WATER FLOW

Mathematical Formulation

A description of processes involved in saturated/unsaturated flow in unconfined aquifers is covered by Bear (1) and more recently by El-Beshry (2) and Charbeneau (3). Flow in parts of the unconfined aquifer is characterized by the existence of water and air. Various mathematical approaches for flow in unconfined aquifers are described by Brutsaert and El-Kadi (4). The approaches cover various degrees of complexities. The engineering approach includes a two-equation system for the flow of water and air. If the air phase is considered as continuous and at atmospheric pressure, a single equation that describes water flow will result. The equation will include the effects of unsaturation and solid-matrix and water compressibility. If compressibility effects are ignored, the equation will reduce to the well-known Richards equation (5), which can be written in the following form:

$$\nabla \cdot (K \nabla h) = \frac{\partial \theta}{\partial t} \tag{1}$$

where K is the hydraulic conductivity, h is the hydraulic head, θ is the water content, and t is time. The hydraulic head is related to pressure head ψ by $h = \psi + z$, in which z is the elevation above an arbitrary datum. Equation 1 is also applicable to the saturated zone, where K equals its saturated value and θ equals porosity. Following solution of Equation 1, the water table would be identified as the surface where the pressure head value equals zero.

Needed for a complete formulation are the relationships $K(\psi)$ and $\theta(\psi)$. Popular forms of these relationships are provided by van Genuchten (6):

$$S_e = [1 + |\alpha\psi|^n]^{-m} \tag{2}$$

in which S_e is defined as

$$S_e = \frac{(\theta - \theta_r)}{(\theta_s - \theta_r)} \tag{3}$$

In Equations 2 and 3, θ_s and θ_r are saturated and residual water content, respectively, and α, n, and m are parameters with n and m related by

$$m = 1 - 1/n \tag{4}$$

The hydraulic conductivity function is given by van Genuchten (6) as

$$K = K_s S_e^{0.5}[1 - (1 - S_e^{1/m})^m]^2 \tag{5}$$

where K_s is the saturated hydraulic conductivity.

Solutions for Equation 1 are complicated by its nonlinearity due to the dependence of the conductivity and saturation on hydraulic head. Analytical solutions

are available for simplified conditions, such as those for infiltration and discharges from sources in the unsaturated zone (6,7).

Numerical solutions are suitable for general problems involving more realistic flow conditions and spatially varied parameters, such as hydraulic conductivity. Examples of numerical models include VS2D (8,9), HYDRUS (10; http://www.pc-progress.cz/Fr_Hydrus.htm), and FEMWATER (11). VS2D is in the public domain and can be downloaded from the U.S. Geological Survey web site: http://www.usgs.gov/software/vs2di.html. FEMWATER is included in the commercial package GMS (http://www.ems-icom), which serves as the data pre- and postprocessor for the model. The original version of the model is in the public domain (http://www.epa.gov/ceampubl/gwater/femwater/). FEMWATER is a three-dimensional model, in contrast to HYDRUS and VS2D, which are two-dimensional models.

Care is required in choosing the size of the mesh or grid for numerical models. Small sizes, on the order of centimeters, are needed in some cases for achieving good numerical accuracies, mostly due to the nonlinear nature of Equation 1 (12). Such a restriction puts a severe limitation on the use of numerical models for large-scale three-dimensional aquifers with thick unsaturated zones.

Solutions for Equation 1 also require specification of initial and boundary conditions. The initial condition may include location of the water table and the relevant distribution of pressure head. Boundary conditions may include specified head or water flux rates. Wells are usually treated as sources (injection) or sinks (pumping).

In some applications, flow in the unsaturated zone can be overlooked and only the flow in the saturated zone is considered. In this case, a number of mathematical formulations exist, which include the use of a specific yield parameter that assumes instantaneous flow from the unsaturated zone toward the water table (1). Saturated flow models, such as MODFLOW (13), can be used in this regard. The limitations have to be recognized, however, especially for aquifers with a thick unsaturated zone compared to the saturated thickness of the aquifer.

Infiltration Models

Infiltration is the process of water entry to the subsurface en route to the saturated zone. Infiltration quantification is an important part of estimating runoff needed for watershed assessment. Numerical models can simulate infiltration. However, their use is cumbersome for watershed assessment. Empirical and physically based models are useful in this regard. Such models are reviewed by Philip (14) and El-Kadi (15). Popular models include those developed by Green and Ampt (16), Kostiakov (17), Horton (18), and Philip (19). More recent models include those by Smith and Parlange (20), Parlange et al. (21), and Parlange and Haverkamp (22).

Models for Aquifer Test Analysis

Aquifer test analysis is a popular technique for estimating hydraulic parameters that control an aquifer's capacity to transmit and store water. Both analytical and numerical solutions can be used in the process through an automatized or manual fitting process. The nature of the flow in an unconfined aquifer causes failure of the classic Theis solution (23), which is based on restrictive assumptions relevant to the nature of confined aquifer flow. Most analytical models attempt to account for the water table condition and flow in the unsaturated zone by assigning a certain boundary condition at the water table. Theoretical developments and model assumptions can be found in Freeze and Cherry (24), Kruseman and de Ridder (25,26), Driscoll (27), Dominico and Schwartz (28), Walton (29), and Fetter (30).

Popular aquifer test models include those by Boulton (31), Boulton and Streltsova (32), Boulton and Pontin (33), Dagan (34), Neuman (35–37), Moench (38,39), and Moench et al. (40). The pioneering model of Boulton (31) approximates drainage from the zone above the water table by using an exponential relation containing an empirical parameter considered as a delay index. Moench (38) substituted Boulton's (41) convolution integral for Neuman's (35,36) boundary condition for the free surface. Additional improvements were introduced by Moench (39) and Moench et al. (40).

Available commercial pump-test packages include AquiferTest (42; http://www.waterloohydrogeologic.com). The package includes the solutions of Moench (43) and Neuman (37). The package also includes a solution with a correction term that allows the use of the Theis (23) and Cooper–Jacob (44) solutions for the analysis of pumping test data for an unconfined aquifer.

CONTAMINATION

Mathematical Formulation

As discussed earlier, contamination can be caused by dissolved chemicals or NAPLs. Subsurface solute transport and fate in the unsaturated/saturated zone are described by Charbeneau (3), including degradation due to biological, chemical, and photochemical processes, volatilization, immobilization, sorption, ion exchange, advection, diffusion, dispersion, residual saturation, and preferential flow. Further discussion of these processes is provided by Hughes (45).

For conservative dissolved chemicals, that is, in the absence of chemical and biological transformations, the governing equation can have the following form (3):

$$\nabla \cdot (\theta \boldsymbol{D} \cdot \nabla C) - \nabla (\boldsymbol{V} C) = \frac{\partial \theta C}{\partial t} \tag{6}$$

where C is the solute concentration, D is the dispersion coefficient, and V is the seepage velocity. The seepage velocity is estimated by dividing Darcy's flux by the effective porosity, which is defined as the porosity available for water flow. Darcy's flux is estimated by solving Equation 1. Mathematical formulation for nonconservative chemical transport is covered by Freeze and Cherry (24), Fetter (46), and Charbeneau (3). Equation 6 is applicable to the saturated zone, where θ equals the effective porosity, which is constant with respect to time but can be spatially varied.

Multiphase flow in cases of NAPL contamination requires the use of various phase equations that include water flow, liquid product flow, gas flow, and dissolved

phase transport and fate processes. Discussion of concepts involved, as well as practical aspects of addressing NAPL contamination, is covered by Bedient et al. (47) and Charbeneau (3).

A free interactive guide for the fate, transport, and remediation of LNAPLs is available for downloading from the website of the American Petroleum Institute: http://www.groundwater.api.org/lnaplguide/. The guide provides understanding of principles and some tools for evaluating the mobility, stability, and recoverability of LNAPLs. The guide is designed to provide an overall approach for evaluating the LNAPL at a site, assessing its potential risk, quantitatively defining mobility and recoverability, developing remedial strategies, and examining methods to enhance site-closure opportunities.

Saltwater Contamination

In addition to potential contamination by dissolved chemicals and NAPLs, saltwater can be a contamination threat for unconfined aquifers in coastal zones and islands. Classic textbooks, such as those by Bear (1), Todd (48), and Fetter (30), discuss the subject, including theoretical developments and practical aspects of the processes involved. Density effects, which can be justifiably overlooked in the cases for dissolved chemicals, dominate saltwater contamination situations.

For coastal aquifers, fresh groundwater discharges to the ocean and mixes with saltwater. The contact between saltwater and fresh water creates a zone of mixing that is characterized by brackish water with a salinity gradient. Such a transition can be sharp, with a thin mixing zone. However, under freshwater head fluctuations, excessive well pumping, and tidal fluctuations, the mixing zone can be quite large.

For unconfined aquifers, fresh groundwater moves upward to discharge near the shoreline, while cyclic water flow occurs in the salty water near the interface (49). Under ideal conditions that include a sharp interface and hydrostatic condition, the depth to the freshwater extent below sea level, Z, is expressed by the Ghyben–Herzberg equation (50,51):

$$Z = \frac{\rho_f}{\rho_s - \rho_f} H \tag{7}$$

where H is the elevation of the water table above sea level, ρ_f is the density of fresh water, and ρ_s is the density of saltwater. Such a relationship would provide a ratio of 1 to 40 for H to Z.

Equation 7 is also valid under conditions for mainly horizontal flow, which is usually valid away from the shoreline. Todd (48) and Fetter (30) provide other useful analytical expressions, such as that of the depth to the interface between fresh water and saltwater for an oceanic island with groundwater recharge. The U.S. Geological Survey has developed the numerical modes SHARP (52), which can be used in simulating freshwater and saltwater flow under the assumption of a sharp interface. The model is available from the URL site http://water.usgs.gov/software/sharp.html.

AQUIFER VARIABILITY

Variability of soil and aquifer material is common and may cause substantial difficulties in assessing water flow and contaminant transport and fate in unconfined systems. Jury et al. (53,54) summarized results from a number of unsaturated zone field studies regarding variability of hydraulic conductivity, porosity, and infiltration. Properties can be highly heterogeneous due to the nature of geological formations, including the existence of various geological units of contrasting features. Fractures due to structural or other factors can cause preferential flow and transport (55,56). Overlooking preferential flow may lead to unacceptable errors in estimating travel times and the risk of contamination (57).

Estimating parameters under variable conditions is difficult due to the costs involved in physically collecting data and the potential for affecting the integrity of the aquifer. Inverse methods involve the indirect estimation of parameters based on hydraulic head or solute concentration values. An example of available software is PEST (58), which can be used with various models in estimating their parameters. However, questions arise regarding model uniqueness.

Approaches to model systems under variable conditions include both deterministic approaches and stochastic approaches. For deterministic approaches, continuum models are adapted in which it is assumed that a representative control volume exists where aquifer or soil properties are defined. For example, a continuum model for flow in an unconfined aquifer would assume validity of the Richards equation but would use soil hydraulic properties that are modified to reflect a fracture-porous system (59). Examples of soil properties for this system are provided by Durner (60) and Mohanty et al. (61).

Other deterministic approaches include the use of discrete fracture models to account for water flow and solute transport in fractured rocks by taking into consideration the location and aperture of rock fractures (62). Charbeneau (63) and Germann (64) adopted a kinematic wave approach to account for water flow in fracture or macropore domains, which are also known as dual- or double-porosity domains. Two-domain models were developed by Duguid and Lee (65), Gerke and van Genuchten (66), Ray et al. (67), and Vogel et al. (68), while a three-domain model was developed by Gwo et al. (69). Such models simulate mobile water in soils or fractured porous media conceptualized to have two- or three-pore domains. These models are commonly referred to as dual- or multipermeability models, where advective movements of chemicals are considered in the matrix domain. Zyvoloski et al. (70, 71) developed a general purpose finite-element code for the simulation of water, heat, and multisolute species at the Yucca Mountain nuclear waste repository site.

Stochastic models assume that parameters are described as statistical variables derived from certain distributions and may include spatial correlation structures. The simplest approach involves the use of the Monte Carlo method, which is based on the repetitive solution of the governing equation with different sets of parameters derived from their statistical distributions, followed by a statistical analysis of results

to quantify uncertainties (72). Other stochastic methods include the spectral approach (73) and the similar-media approach (74). For solute transport in unsaturated media, available approaches include the models of Dagan and Bresler (75), Simmons (76), and Jury et al. (77).

A CASE STUDY

Extensive studies of an unconfined aquifer at a Cape Cod site in Massachusetts have been completed. The hydrogeology of the site is described in Moench et al. (40), Hess et al. (78), LeBlanc et al. (79), Garabedian et al. (80), and Rudolf et al. (81). The unconfined aquifer is composed of unconsolidated glacial outwash sediments, which overlie crystalline bedrock at a depth of about 100 m. Clean, medium-to-course-grained, high permeability deposits cover fine-grained, relatively low permeability material at about 50 m below the water table.

Moench et al. (40) analyzed data for an aquifer test conducted at the Cape Cod site. After the aquifer was pumped at a rate of $0.02\ m^3/s$ for 72 h, drawdown measurements were made in the pumped well and in 20 piezometers located at various distances from the pumped well and various depths below the land surface. The estimated hydraulic parameter values were consistent with estimates from prior studies (78). The results indicated that effects of heterogeneity at the site were small. The estimated parameter values were as follows: specific yield, 0.26; saturated thickness, 52 m; horizontal hydraulic conductivity, 11.68×10^{-4} m/s; vertical hydraulic conductivity, 7.11×10^{-4} m/s; and specific storage, $4.3 \times 10^{-3}\ m^{-1}$.

El-Kadi (82) used the same aquifer test data to examine the validity of the generalized Richards equation (GRE), which includes unsaturation and compressibility effects. The solution of the GRE closely matched the field-measured drawdowns, with some parameters close to their independently measured values, including conductivity and storage coefficient. However, the model was not fully validated due to the need for calibrated soil-hydraulic parameters that represent a finer soil than the coarse-grained highly permeable material characteristic of the site (83). Good accuracy was obtained using a physically based value for the storage coefficient when well-pore storage was considered. Saturated flow models did not provide results as accurate as those provided by the GRE model. Classifying the aquifer material as coarse can be misleading, considering that its effective soil properties are that of a finer-textured material. As such, unsaturated flow effects should not be overlooked.

Hess et al. (78) assessed the variability of hydraulic conductivity in the Cape Cod aquifer and used stochastic transport theories to estimate macrodispersivities. About 1500 estimates were obtained from borehole flowmeter tests and permeameter analyses of cores. The geometric mean for the flowmeter tests (0.11 cm/s) were larger than the mean for the permeameter tests (0.035 cm/s), possibly because of compaction of the cores. Geostatistical analyses estimated correlation scales that ranged from 2.9 to 8.0 m in the horizontal direction and from 0.18 to 0.38 m in the vertical direction. Estimates of asymptotic longitudinal dispersivity were in the range of 0.35–0.78 m.

McCobb and LeBlanc (84) studied a plume of contaminated groundwater that migrated from a former landfill on the Massachusetts Military Reservation to Red Brook Harbor, a small coastal embayment along the Cape Cod coast of Buzzards Bay. The primary contaminants were trichloroethene (TCE) and tetrachloroethene (PCE). The landfill was capped in December 1995, and a groundwater remediation system was established in 1999. The study identified the location of maximum concentrations of the contaminants. Fresh groundwater was present beneath the harbor at locations within 76 m of the shoreline. TCE was detected at several locations in fresh groundwater obtained from the sandy aquifer materials beneath the harbor.

LeBlanc et al. (79) analyzed data from a three-dimensional large-scale natural gradient experiment in the Cape Cod aquifer. Bromide (a conservative tracer) and lithium and molybdate (reactive tracers) injected in July 1985 were monitored for distances up to 280 m. The bromide cloud moved at a rate of 0.42 m/d, while the reactive chemicals moved at a reduced rate of about 50% of that for bromide. The dispersive characteristics of the aquifer were analyzed in the follow-up paper by Garabedian et al. (80). The asymptotic value for longitudinal dispersivity was 0.96 m, while the respective values for transverse-horizontal and transverse-vertical dispersivities were 1.5 cm and 1.55 mm, respectively.

BIBLIOGRAPHY

1. Bear, J. (1979). *Hydraulic of Groundwater*. McGraw-Hill, New York.
2. El-Beshry, M. (1999). Flow and transport in the unsaturated zone. In: *Groundwater Contamination, Transport and Remediation*, P.B. Bedient, H.S. Rifai, and C.J. Newell (Eds.), 2nd Edn. Prentice-Hall PTR, Upper Saddle River, NJ, pp. 289–334.
3. Charbeneau, R.J. (2000). *Groundwater Hydraulics and Pollutant Transport*. Prentice-Hall, Upper Saddle River, NJ.
4. Brutsaert, W. and El-Kadi, A.I. (1984). The relative importance of compressibility and partial saturation in unconfined groundwater flow. *Water Resour. Res.* **20**: 400–409.
5. Richards, L.A. (1931). Capillary conduction of liquids in porous mediums. *Physics* **1**: 318–333.
6. Broadbridge, P., and White, I. (1988). Constant rate rainfall infiltration: a versatile nonlinear model, I. Analytic solution. *Water Resour. Res.* **24**(1): 145–154.
6. van Genuchten, M.Th. (1978). *Calculating the unsaturated hydraulic conductivity with a new closed-form analytical model*. 78-WR-08, Water Resources Program, Department of Civil Engineering, Princeton University.
7. Warrick, A.W., Lomen, D.O., and Islas, A. (1990). An analytical solution to Richards' equation for a draining soil profile. *Water Resour. Res.* **26**(2): 253–258.
8. Healy, R.W. (1990). *Simulation of Solute Transport in Variably Saturated Porous Media with Supplemental Information on Modifications to the US Geological Survey's Computer Program VS2D*. Water-Resources Investigations Report 90–4025. U.S. Geological Survey.

9. Hsieh, P.A., Wingle, W., and Healy, R.W. (2000). *VS2DI—A Graphical Software Package for Simulating Fluid Flow and Solute or Energy Transport in Variably Saturated Porous Media*. Water-Resources Investigations Report 99–4130. U.S. Geological Survey.
10. Simunek, J., Sejna, M., and van Genuchten, M.Th. (1999). *The HYDRUS-2D Software Package for Simulating Two-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media. Version 2.0. IGWMC-TPS-53*. International Ground Water Modeling Center, Colorado School of Mines, Golden, CO.
11. Lin, H.-C.J., Richards, D.R., Talbot, C.A., Yeh, G.-T., Cheng, J.-R., Cheng, H.-P., and Jones, N.L. (2002). *A Three-Dimensional Finite Element Computer Model for Simulating Density-Dependent Flow and Transport in Variably Saturated Media. Version 3.0. GMS Documentation*. Environmental Modeling Systems, Inc., South Jordan, UT.
12. El-Kadi, A.I. and Ling, G. (1993). The Courant and Peclet criteria for numerical solution of the Richards equation. *Water Resour. Res.* **29**(10): 3485–3494.
13. McDonald, M.D. and Harbaugh, A.W. (1988). A modular three-dimensional finite-difference flow model. In: *Book 6, Techniques of Water Resources Investigations of the U.S. Geological Survey*.
14. Philip, J.R. (1969). Theory of infiltration. In: *Advances in Hydroscience*, Vol. 5. V.T. Chow (Ed.), Academic Press, New York, pp. 215–395.
15. El-Kadi, A.I. (1983). Modeling infiltration for water systems. GWMI 83-09, International Ground Water Modeling Center, Holcomb Research Institute, Butler University, Indianapolis, IN.
16. Green, W.A. and Ampt, G.A. (1911). Studies on soil physics, 1. The flow of air and water through soils. *J. Agric. Sci.*, 1–24.
17. Kostiakov, A.N. (1932). On the dynamics of the coefficient of water percolation in soils and on the necessity of studying it from a dynamic point of view for purpose of amelioration. *Trans. Com. Int. Soc. Sci. 6th Moscow A*, 17–21.
18. Horton, R.E. (1940). An approach towards a physical interpretation of infiltration capacity. *Soil. Sci. Soc. Am. Proc.* **5**: 399–417.
19. Philip, J.R. (1957). The theory of infiltration: 1. The infiltration equation and its solution. *Soil Sci.* **83**: 345–357.
20. Smith, R.E. and Parlange, J.Y. (1978). A parameter-efficient hydrologic infiltration model. *Water Resour. Res.* **14**: 533–538.
21. Parlange, J.Y., Lisle, I., Braddock, R.D., and Smith, R.E. (1982). The three-parameter infiltration equation. *Soil Sci.* **133**: 337–341.
22. Parlange, J.Y. and Haverkamp, R. (1989). Infiltration and ponding time. In: *Unsaturated Flow in Hydrologic Modeling: Theory and Practice*. H.J. Morel-Seytoux (Ed.), *NATO ASI Series C: Mathematical and Physical Sciences*, Vol. 275.
23. Theis, C.V. (1935). The relation between the lowering of the piezometric surface and the rate and duration of discharge of a well using groundwater storage. *Am. Geophys. Union Trans.* **16**: 519–524.
24. Freeze, R.A. and Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
25. Kruseman, G.P. and de Ridder, N.A. (1979). *Analysis and Evaluation of Pumping Test Data*, Bull. 11. International Institute for Land Reclamation and Improvements, Wageningen, The Netherlands.
26. Kruseman, G.P. and de Ridder, N.A. (1990). *Analysis and Evaluation of Pumping Test Data*, 2nd Edn. (completely revised), *ILRI Publication* 47. International Institute for Land Reclamation and Improvements, Wageningen, The Netherlands.
27. Driscoll, F.G. (1987). *Groundwater and Wells*. Johnson Division, St. Paul, MN.
28. Dominico, P.A. and Schwartz, F.W. (1990). *Physical and Chemical Hydrogeology*. John Wiley & Sons, Hoboken, NJ.
29. Walton, W.C. (1996). *Aquifer Test Analysis with WINDOWS Software*, CRC Press, Boca Raton, FL.
30. Fetter, C.W. (2001). *Applied Hydrogeology*, 4th Edn. Prentice-Hall, Upper Saddle River, NJ.
31. Boulton, N.S. (1954). *Unsteady Radial Flow to a Pumped Well Allowing for Delayed Yield From Storage*, Publication 37. International Association of Scientific Hydrology, Rome, pp. 472–477.
32. Boulton, N.S. and Streltsova, T.D. (1975). New equations for determining the formation constants of an aquifer from pumping test data. *Water Resour. Res.* **11**: 148–153.
33. Boulton, N.S., and Pontin, J.M.A. (1971). An extended theory of delayed yield from storage applied to pumping tests in unconfined anisotropic aquifers. *J. Hydrol.* **14**: 53–65.
34. Dagan, G. (1967). A method of determining the permeability and effective porosity of unconfined anisotropic aquifers. *Water Resour. Res.* **3**: 1059–1071.
35. Neuman, S.P. (1972). Theory of flow in unconfined aquifers considering delayed response of the water table. *Water Resour. Res.* **8**: 1031–1044.
36. Neuman, S.P. (1974). Effects of partial penetration on flow in unconfined aquifers considering delayed aquifer response. *Water Resour. Res.* **10**: 303–312.
37. Neuman, S.P. (1975). Analysis of pumping test data from anisotropic unconfined aquifers considering delayed yield. *Water Resour. Res.* **11**: 329–342.
38. Moench, A.F. (1995). Combining the Neuman and Boulton models for flow to a well in an unconfined aquifer. *Ground Water* **33**: 378–384.
39. Moench, A.F. (1997). Flow to a well of finite diameter in a homogeneous, anisotropic water table aquifer. *Water Resour. Res.* **33**: 1397–1407.
40. Moench, A.F., Garabedian, S.P., and LeBlanc, D.R. (2001). Estimation of hydraulic parameters from an unconfined aquifer test conducted in a glacial outwash deposit, Cape Cod, Massachusetts. Professional Paper 1629, U.S. Geological Survey.
41. Boulton, N.S. (1963). Analysis of data from non-equilibrium pumping tests allowing for delayed yield from storage. *Proc. Inst. Civ. Eng.* **26**: 469–482.
42. Waterloo Hydrogeologic, Inc. (2000). *AquiferTest User's manual*. Waterloo, Ontario, Canada.
43. Moench, A.F. (1993). Computation of type curves for flow to partially penetrating wells in water-table aquifers. *Ground Water* **31**: 966–971.
44. Cooper, H.H. and Jacob, C.E. (1946). A generalized graphical method for evaluating formation constants and summarizing well field history. *Am. Geophys. Union Trans.* **27**: 526–534.
45. Hughes, J.B. (1999). Contaminant fate processes. In: *Groundwater Contamination, Transport and Remediation*, P.B. Bedient, H.S. Rifai, and C.J. Newell (Eds.), 2nd Edn. Prentice-Hall PTR, Upper Saddle River, NJ, pp. 203–236.
46. Fetter, C.W. (1993). *Contaminant Hydrology*. Macmillan Publishing, New York.
47. Bedient, P.B., Rifai, H.S. and Newell, C.J. (1999). *Groundwater Contamination, Transport and Remediation*, 2nd Edn. Prentice-Hall PTR, Upper Saddle River, NJ.

48. Todd, D.K. (1980). *Groundwater Hydrology*, 2nd Edn. John Wiley & Sons, Hoboken, NJ.
49. Cooper, H.H. Jr. (1959). A hypothesis concerning the dynamic balance of fresh water and salt water in coastal aquifer. *J. Geophys. Res.* **64**: 461–467.
50. Drabbe, J. and Baden-Ghyben, W. (1888–1889). *Nota in verband met de voorgenomen putboring nabij Amsterdam*. Tydyschrift van het Koninkhyk Institute van Ingenieurs, The Hague, Netherlands, pp. 8–22.
51. Herzberg, B. (1901). Die Wasserversorgung einiger Nordsubader, Munch. *J. Gasbelenchtung Wasser.* **44**: 815.
52. Essaid, H.I. (1990). *The Computer Model SHARP, a Quasi-Three-Dimensional Finite-Difference Model to Simulate Freshwater and Saltwater Flow in Layered Coastal Aquifer Systems*. Water-Resources Investigations Report 90–4130. U.S. Geological Survey.
53. Jury, W.A., Russo, D., Sposito, G., and Elabd, H. (1987). The spatial variability of water and solute transport properties in unsaturated soil: I. Analysis of property variation and spatial structure with statistical models. *Hilgardia* **55**: 1–32.
54. Jury, W.A., Russo, D., Sposito, G., and Elabd, H. (1987). The spatial variability of water and solute transport properties in unsaturated soil: II. Scaling models of water transport. *Hilgardia* **55**: 33–56.
55. Hutson, J.L. and Wagenet, R.J. (1995). A multiregion model describing water flow and solute transport in heterogeneous soils. *Soil Sci. Soc. Am. J.* **59**: 743–751.
56. Flurry, M. (1996). Experimental evidence of transport of pesticides through field soils—a review. *J. Environ. Qual.* **25**: 25–45.
57. Ray C., Vogel, T., and Dusek, J. (2004). Modeling depth-variant and domain-specific sorption and biodegradation in dual-permeability media. *J. Contam. Hydrol.* **70**: 63–87.
58. Doherty, J. (1994). *PEST—Model-Independent Parameter Estimation*, Watermark Computing, Corinda, Australia.
59. El-Kadi, A.I. and Torikai, J.D. (2001). Identifying variable saturated water-flow patterns in a steep hillslope under intermittent heavy rainfall. *Hydrogeology* **9**: 231–242.
60. Durner, W. (1994). Hydraulic conductivity estimation for soils with heterogeneous pore structure. *Water Resour. Res.* **30**(2): 211–224.
61. Mohanty, B.P., Bowman, R.S., Hendrickx, J.M.H., and van Genuchten, M.T. (1997). New piecewise-continuous hydraulic functions for modeling preferential flow in an intermittent-flood-irrigated field. *Water Resour. Res.* **33**: 2049–2064.
62. Harrison, B., Sudicky, E.A., and Cherry, J.A. (1992). Numerical analysis of solute migration through fractured deposits into underlying aquifers. *Water Resour. Res.* **28**: 515–526.
63. Charbeneau, R.J. (1984). Kinematic models for soil moisture and solute transport. *Water Resour. Res.* **20**: 699–706.
64. Germann, P.F. (1985). Kinematic wave approach to infiltration and drainage into and from soil macropores. *Trans. ASAE* **28**: 745–749.
65. Duguid, J.O. and Lee, P.C.Y. (1978). Flow in fractured porous media. *Water Resour. Res.* **13**: 558–566.
66. Gerke, H.H. and van Genuchten, M.T. (1993). A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resour. Res.* **29**: 305–319.
67. Ray, C., Ellsworth, T.R., Valocchi, A.J., and Boast, C.W. (1997). An improved dual porosity model for chemical transport in macroporous soils. *J. Hydrol.* **193**: 270–292.
68. Vogel, T., Gerke, H.H., Zhang, R., and van Genuchten, M.Th. (2000). Modeling flow and transport in a two-dimensional dual-permeability system with spatially variable hydraulic properties. *J. Hydrol.* **238**: 78–89.
69. Gwo, J.P., Jardine, P.M., Wilson, G.V., and Yeh, G.T. (1995). A multi-pore concept to modeling mass transfer in subsurface media. *J. Hydrol.* **164**: 217–237.
70. Zyvoloski, G.A., Dash, G.V., and Kelkar, S. (1988). *FEHM: Finite Element Heat and Mass Transfer Code*. Report No. LA-11224-MS. Los Alamos National Laboratory, Los Alamos, NM.
71. Zyvoloski, G.A., Dash, G.V., and Kelkar, S. (1992). *FEHMN 1.0: Finite Element Heat and Mass Transfer Code*. Report No. LA-12062-MS, Rev. 1. Los Alamos National Laboratory, Los Alamos, NM.
72. El-Kadi, A.I. and Brutsaert, W. (1985). Applicability of effective parameters for unsteady flow in heterogeneous aquifers. *Water Resour. Res.* **21**: 183–198.
73. Bakr, A.A., Gelhar, L.W., Gutjahr, A.L., and McMillan, J.R. (1978). Stochastic analysis of spatial variability in subsurface flow, 1. Comparison of one- and three-dimensional flows. *Water Resour. Res.* **14**: 263–271.
74. Miller, E.E. and Miller, R.D. (1956). Physical theory for capillary flow phenomena. *J. Appl. Phys.* **27**: 354–362.
75. Dagan, G. and Bresler, E. (1979). Solute dispersion in unsaturated heterogeneous soil at field scale: I. Theory. *Soil Sci. Soc. Am. J.* **43**: 461–467.
76. Simmons, C.S. (1982). A stochastic-convective transport representation in one-dimensional porous media systems. *Water Resour. Res.* **18**: 1193–1214.
77. Jury, W.A., Stolzy, L.H., and Shouse, P. (1982). A field test of the transfer function model for predicting solute transport. *Water Resour. Res.* **19**: 369–375.
78. Hess, K.M., Wolf, S.H., and Celia, M.A. (1992). Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 3. Hydraulic conductivity variability and calculated macrodispersivities. *Water Resour. Res.* **28**: 2011–2027.
79. LeBlanc, D.R. et al. (1991). Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 1. Experimental design and observed tracer movement. *Water Resour. Res.* **27**: 895–910.
80. Garabedian, S.P., LeBlanc, D.R., Gelhar, L.W., and Celia, M.A. (1991). Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 2. Analysis of spatial moments for a nonreactive tracer. *Water Resour. Res.* **27**: 911–924.
81. Rudolph, D.L.R. et al. (1996). Infiltration and solute transport experiments in unsaturated sand and gravel, Cape Cod, Massachusetts: experimental design and overview of results. *Water Resour. Res.* **32**: 519–532.
82. El-Kadi, A.I. (2005). Validity of the generalized Richards equation for the analysis of three-dimensional test data for a coarse-material aquifer. *Vadose Zone J.*, in press.
83. Mace, A., Rudolph, D.L.R., and Kachanoski, R.G. (1998). Suitability of parametric models to describe the hydraulic properties of an unsaturated coarse sand and gravel. *Ground Water* **36**: 465–475.
84. McCobb, T.D. and LeBlanc, D.R. (2002). Detection of fresh ground water and a contaminant plume beneath Red Brook Harbor, Cape Cod, Massachusetts, 2000. Water-Resources Investigations Report 02–4166, U.S. Geological Survey.

MODELING OF DNAPL MIGRATION IN SATURATED POROUS MEDIA

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INTRODUCTION

Nonaqueous phase liquids (NAPLs) such as the homogenate hydrocarbons used in dry cleaning and industrial degreasing (DNAPLs), hydrocarbon fuels and aromatic solvents (LNAPLs), and neutrally buoyant coal tars and creosotes are widespread in our environment. Because of their low solubility, NAPL sources can emit toxic contaminants to groundwater for many decades if not managed properly. The migration of dense nonaqueous phase liquids (DNAPLs), which are immiscible with water, through the saturated porous media is an important part of contaminant hydrology and in petroleum engineering. Protection and remediation of groundwater resources require an understanding of processes that affect the fate and transport of such contaminants in the subsurface environment. To implement appropriate remedial schemes in the contaminated area, it is necessary to evaluate the extent of the contaminated area. This information can be obtained by extensive field investigation, which generally is expensive and time consuming. Field investigation can be reduced or made more cost effective, if the migration pattern of the DNAPLs can be evaluated by using numerical models accurately.

The movement of DNAPLs through an initially saturated porous medium is represented as the two-phase flow of water and DNAPLs simultaneously in the porous medium (1). One of the fluids may wet the porous medium more than the other. A large number of experiments for multiphase processes have been carried out (2–4) and these have shown that Darcy's velocity for each phase in the porous medium can be described by the generalized Darcy's law. Darcy's law is extended to multiphase flow by postulating that the gradient in phase pressure of each phase is causing that fluid phase to flow in the porous medium and the effective premeability of each phase is a function of saturation of that respective phase. The continuity equations for immiscible two-phase flow of DNAPLs and water in the porous medium is given by (5,6):

$$\frac{\partial}{\partial x_i}\left[\frac{\rho_\alpha k_{ij} k_{r\alpha}(S_\alpha)}{\mu_\alpha}\left(\frac{\partial P_{ij\alpha}(S_\alpha)}{\partial x_j}+\rho_\alpha g\right)\right] \pm q_{ij\alpha} = \frac{\partial}{\partial t}(\phi \rho_\alpha S_{ij\alpha}), \alpha = \{w, nw\} \quad (1)$$

where x_i and x_j are the Cartesian coordinates in the x and z directions, t is the time, i and j are the direction indices, μ [$ML^{-1}T^{-1}$] is the viscosity, ρ [ML^{-3}] is the density, k is intrinsic permeability, k_α [LT^{-1}] is the relative permeability of the phase, and z [L] is the vertical distance taken as positive upward. The α represents both DNAPL and water phases, S is the phase saturation, φ is the medium porosity, q_α [LT^{-1}] is the phase source or sink term, g [LT^{-2}] is the acceleration due to gravity, and P_α is the phase pressure.

When two immiscible fluids are in contact, a discontinuity in phase pressures exists at the interface separating the fluids by the consequence of the interfacial tension, which exists between two phases in contact. The magnitude of the pressure difference depends on the interface curvature at that point, which in turn depends on the saturation of phases. The phase pressures are coupled through the capillary pressure P_C and are a function of saturation:

$$P_C(S_\alpha) = P_{nw} - P_w, \quad \alpha = \{w, nw\} \quad (2)$$

The governing equations have strong nonlinearities such as the dependence of the relative permeabilities $k_{r\alpha}$ and P_C on the respective phase saturations. Parameterization of capillary pressure saturation and the relative permeability saturation relations widely used for the two phases are given by Brooks and Corey (7) and van Genuchten (8).

STATUS OF LITERATURE

The governing equations of multiphase flow are highly nonlinear. Numerical methods of multiphase flow mainly depend on the formulation of the governing equations used for the numerical modeling. The numerical and analytical approaches of the multiphase flow are difficult due to its high nonlinearity and the coupling between the phases. Buckley and Leverett (9) were the first to analyze the multiphase fluid displacement in one dimension by a simplified mathematical model by suppressing the capillary derivative term. Fokas and Yortsos (10) developed a closed form analytical solution for one-dimensional flow with capillary drive by restricting the capillary hydraulic functions. McWhorter and Sunada (11) developed an exact quasianalytical solution using the concept of fractional flow functions known as the flux concentration relations.

A number of numerical models have been developed to simulate the migration of dense nonaqueous phase liquids (DNAPLs) in groundwater. All the models are based on one or another type of primary variables. The multiphase flow equations are highly nonlinear and it requires powerful techniques to handle the coupled equations. The choice of method for solution of multiphase flow is very important. Peaceman (12) used the explicit method and Peaceman and Rachford (13) used the alternating direction implicit (ADI) method. Results showed that the ADI method is unstable for multiphase simulations especially in heterogeneous porous media.

The simultaneous solution (SS) method was first proposed by Douglas and Rachford (14) and later extended and further analyzed by Coats et al. (15), Coats (16), and Sheffield (17) for the petroleum simulation problems. Explicit and alternating direction implicit methods are not stable for two-phase immiscible fluid problems; hence, a

simultaneous implicit method was introduced (13) and was the first implicit method to be used successfully for problems in two dimensions. The first convergence analysis of the SS method was presented for two-phase flow by Douglas (18) and later by Coats (16), who analyzed the stability of both the SS and IMPES methods. The implicit pressure explicit saturation (IMPES) method was proposed by Sheldon et al. (19) and Stone and Gardner (20). The basic idea behind this method was to obtain a single pressure equation by a combination of the flow equations. Peaceman and Rachford (21) proposed the leapfrog sequential method, which gives satisfactory results in a limited number of calculations and the truncation error is larger than the simultaneous method. This method leads to an anomalous situation where one of the relative permeabilities becomes zero. Fagin and Stewart (22) developed another type of sequential method and this method is described in detail by Coats et al. (23), in which pressure of one of the phases was taken as one primary variable and was calculated implicitly and the saturation was calculated either explicitly or implicitly using the present value of pressure. This method was also subjected to saturation creep where the relative permeability of one of the phases becomes zero. Aziz and Settari (1) developed a sequential method consisting of two steps. The first step was to obtain an implicit pressure for saturation simulation. In this method, the equations of two phases were combined into one, like in the IMPES method, to obtain a single pressure equation in one phase pressure and the saturation was calculated implicitly using new phase pressures.

Kueper and Frind (5,6) carried out experiments and developed a two-dimensional finite difference model to study the simultaneous movement of DNAPLs and water in heterogeneous porous media. Numerical simulation of DNAPLs infiltration processes in the saturated heterogeneous porous media was studied by means of numerical simulations using the finite element method (24). The two-phase simulator MUFTE developed by Helmig (25) was based on a semidiscrete finite element formulation using a modified Petrov–Galerkin technique, and the nonlinearization was carried out using the Newton–Raphson method. Difference in parameterization of the constitutive relations was studied by Croise et al. (24) for homogeneous media, and the results show that the constitutive relations have significant impact on DNAPLs migration in homogeneous media. Also, the study is carried out for DNAPLs infiltration into heterogeneous media and it shows that the infiltration of DNAPLs is highly dependent on the capillary resistance at the interface between the media.

A comparative study was made between the numerical methods such as fully upwind Galerkin method, which belongs to the classical finite element method, and a mixed hybrid finite element method based on an implicit pressure explicit saturation (IMPES) approach (26). The results show that the control volume finite element approach based on coupled pressure and a saturation scheme is mass conserved locally over each control volume. Also, they observed that the IMPES method was not suited to simulate processes where high changes of capillary pressure with respect to saturation occur.

Coupling of different numerical algorithms for two-phase flow in saturated porous media was carried out using both fully implicit and sequential formulations (27). The influence of field scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formulation was studied by Timothy et al. (28). Three node centered finite volume discretizations for multiphase flow in porous media have been developed by Huber and Helmig (26) to study the extent of heterogeneity at the interfaces and their associated interface conditions. Finite volume methods such as the Box method (BOX), control volume finite element method (CVFE), IFDM method, and different combinations of these methods such as BOXIFDM and CVBOXIFDM have been compared. The results show that the CVFE has difficulty generating meshes, which obey the positive transmissibility constraint. The BOX, IFDM, BOXIFDM, and CVBOXIFDM do not have any restriction on the user grid. Also, the results show that the BOX discretization may generate spurious oscillations at the corners of heterogeneities if the Brooks and Corey model is employed. Combinations of all three methods are applicable for any mesh without generating a physical saturation profile at the heterogeneities. The study of effective parameters for two-phase flow in a porous medium with periodic heterogeneities to investigate the feasibility of replacing a porous medium containing heterogeneities with an equivalent homogeneous medium was done by Ashtiani et al. (29). Selecting the proper primary variables for the efficient modeling of the highly nonlinear problems of multiphase flow in a heterogeneous porous fractured medium is carried out by Yu-Shu Wu et al. (30).

ADAPTIVE MODIFIED SEQUENTIAL METHOD

Thomas and Thurnan (31) and Forsyth (32) have described an adaptive implicit method. This involve solving implicit formulations of the governing equations in part of the domain where changes in the primary variables were large, while in the rest of the domain, which is computationally less intensive, the less robust IMPES method was employed. In most practical multiphase simulation problems, large changes in fluid pressure and saturations do not occur throughout the spatial domain at a given time step. Computational effort is therefore inefficiently spent on solving equations in areas where less activity occurs. However, the locations of active zones change with time. A study of an adaptive solution using a fully implicit method is incorporated for the two-phase simulation in the saturated porous medium by Unger et al. (33). They observed that the adaptive solution using a simultaneous method requires extensive checks for the applicability of this procedure at each node and this leads to a negligible computational benefit.

In this work, an adaptive solution using a modified sequential method is used for the modeling. The linearization of the governing equations is carried out using a modified Newton–Raphson method. The modified sequential method developed by Mini Mathew for the simulation of DNAPLs–water in the saturated zone is used in the adaptive solution. The modified sequential method

consists of two steps. In the first step, the linearized equation of wetting fluid is used for the simulation of wetting fluid pressure by taking the primary variable of saturation of wetting fluid at the previous iteration on the right-hand side. The Jacobian matrix of wetting fluid pressure is a five-banded matrix and the equation is given by

$$[A_1][P_W]^{n+1/2} = [R_1]^n \tag{3}$$

where $[A_1]$ is an $N \times N$ (N is the number of nodes) Jacobian matrix, $[P_W]$ is a column vector of N unknowns of P_W, and R_1 is the column vector consisting of Eq. 4:

$$R_1 = -[[BS_{Wi(j-1)}] + [D''S_{W(i-1)j}] + [E''S_{Wij}] + [F''S_{W(i+1)j}] + [H''S_{Wi(j+1)}]] \tag{4}$$

where B'', D'', E'', F'', and H'' are the partial derivatives of the governing equation of wetting fluid with respect to the wetting fluid saturation. At the first time step for the wetting fluid pressure simulation, the simulation was carried out for the full domain. The active nodes were identified for the simulation of wetting fluid saturation. The nodes were categorized as either active or inactive in each iteration. For the simulation of wetting fluid pressure, the active nodes were selected in such a way that the difference in saturation of water (wetting fluid) between the present and the previous iteration at that particular node or any one of its surrounding four nodes is less than the specified tolerance level of water saturation. Other nodes, except the active nodes, are taken as inactive nodes for the pressure calculation. On inactive nodes the pressure of wetting fluid is taken from the previous iteration.

In the second step, the wetting fluid saturation is calculated using the nonwetting phase equation. The equation in matrix form is given by

$$[A_2][S_W] = [R_2]^{n+1/2} \tag{5}$$

where $[A_2]$ is an $N \times N$ (N is the number of nodes) Jacobian matrix, $[S_W]$ is a column vector of N unknowns of S_W, and R_2 is the column vector consisting of Equation 6:

$$R_2 = -[[B''''P_{W_i(j-1)}] + [D''''P_{W(i-1)j}] + [E''''P_{Wij}] + [F''''P_{W(i+1)j}] + [H''''P_{Wij+1}]] \tag{6}$$

where B'''', D'''', E'''', F'''', and H'''' are the partial derivatives of the governing equation of nonwetting fluid with respect to the wetting fluid pressure. For the simulation of wetting fluid saturation, the active nodes were selected in such a way that the difference in water pressure between the present and the previous iteration at that particular node or at any one of its surrounding four nodes is less than the specified tolerance level of water pressure. The computation for the saturation was carried out only for the active nodes and the saturation of inactive nodes was taken from the previous iteration. This procedure was continued in each iteration until the simulation ends.

DNAPLS MIGRATION IN

In this section, an effort is made to study the effect of DNAPLs migration in randomly heterogeneous porous media. The simulation is carried out using ASMSEM model to study the handling power of the numerical method for the DNAPLs simulation on the randomly heterogeneous porous media. The properties of the fluid and medium and the domain properties are: wetting fluid density, 1000 kg·m^{-3}; nonwetting fluid density, 1460 kg·m^{-3};

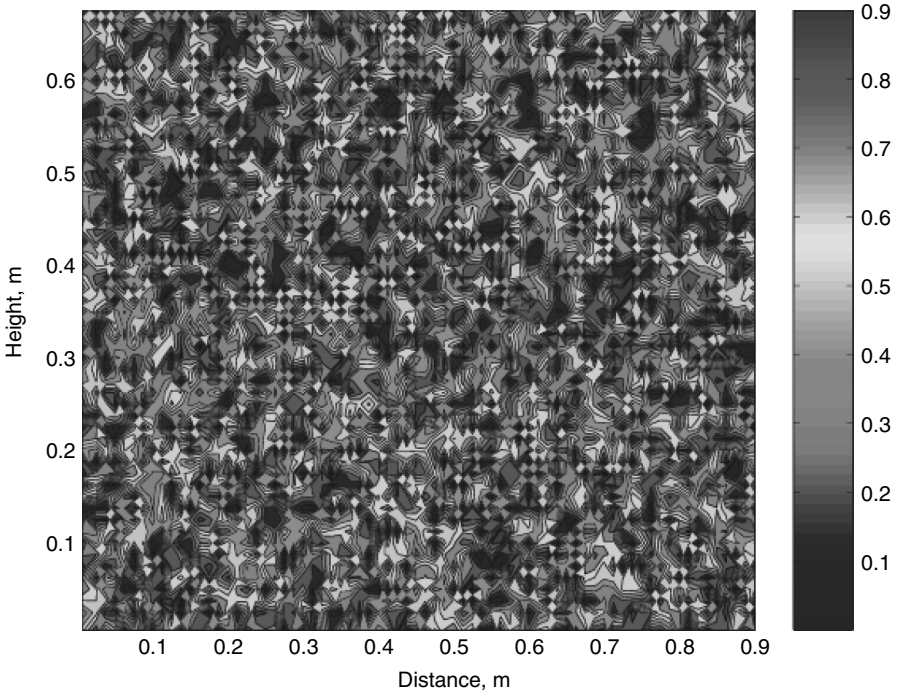


Figure 1. Random permeability field.

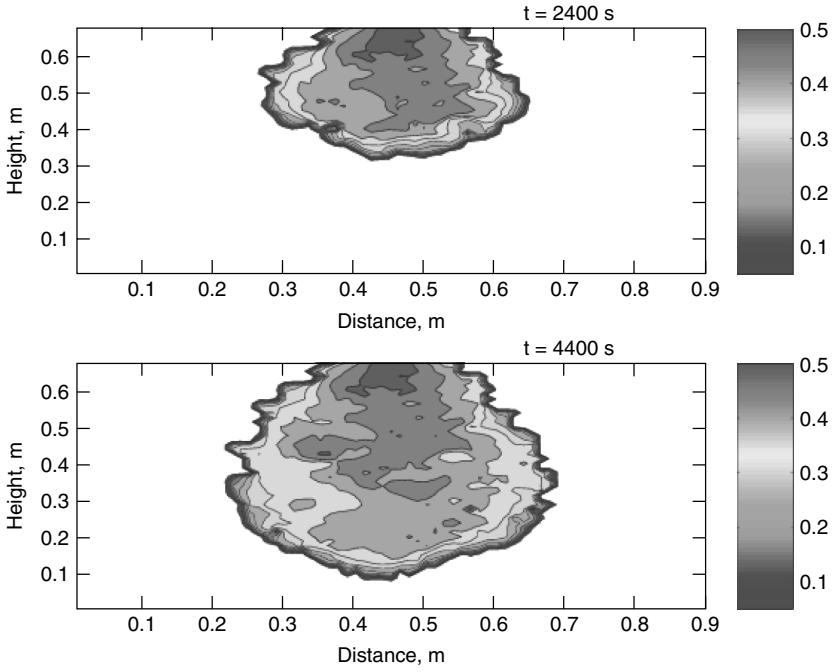


Figure 2. DNAPL migration profiles.

wetting fluid viscosity, 0.001 Pa·s; nonwetting fluid viscosity, of 0.0009 Pa·s; intrinsic permeability, 6.64E-11 m^2; porosity, 0.4; wetting phase residual saturation, 0.09; displacement pressure, 755 Pa; and pore size distribution index, 2.70. In the random porous media, the capillary pressure curve depends on the local value of the absolute permeability and is given by

$$P_C(S_W) = P_d[k^*/k]^{1/2} S_{ew}{}^{-1/\lambda}$$

where k^* is the mean value of the permeability field and the parameters P_d and λ are the Brooks and Corey parameters. The main aim of this study is to verify the handling power of the model using the adaptive modified sequential method for the DNAPLs simulation on randomly heterogeneous porous media. Figure 1 shows the permeability field, which is generated for the present study. The permeability field was generated in such a way that the mean value of the permeability field is equal to the intrinsic permeability of the medium. Figure 2 shows the DNAPLs migration profile after 2400 s and 4400 s.

CONCLUSION

The main mechanisms of DNAPLs migration in porous media have been discussed. Several works in this area, especially about modeling, have been discussed in detail. The main approaches for modeling of DNAPLs migration is presented. The advantage of the adaptive modified sequential method has been pointed out. The developed model is applied on a randomly heterogeneous porous medium to establish DNAPLs migration patterns. Such simulation models will be very useful in planning field experiments for prediction and remediation due to DNAPLs contamination.

BIBLIOGRAPHY

1. Aziz, K. and Settari, A. (1979). *Petroleum Reservoir Simulation*. Applied Science, London.
2. Wyckoff, R.D. and Botset, H.G. (1936). The flow of gas–liquid mixtures through unconsolidated sand. *Physics* **7**: 325–345.
3. Leverett, M.C. (1938). Flow of oil–water mixtures through unconsolidated sands. *Trans. Am. Inst. Min. Metall. Pet. Eng.* **132**: 149–171.
4. Scheidegger, A.E. (1974). *Physics of Flow Through Porous Media*. 3rd Edn. University of Toronto Press, Toronto, Canada.
5. Kueper, B.H. and Frind, E.O. (1991). Two phase flow in heterogeneous porous media 1. Model development. *Water Resour. Res.* **27**(6): 1049–1057.
6. Kueper, B.H. and Frind, E.O. (1991). Two phase flow in heterogeneous porous media 2. Model application. *Water Resour. Res.* **27**(6): 1059–1070.
7. Brooks, R.H. and Corey, A.T. (1964). *Hydraulics Properties of Porous Media*. Hydrol., Pap. 3. Civil Engineering Department, Colorado State University, Fort Collins, CO.
8. van Genuchten, M.T. (1980). A closed form solution for predicting the hydraulic conductivity in soils. *Soil Sci. Am. J.* **44**: 892–898.
9. Buckley, S.E. and Leverett, M.C. (1942). Mechanism of fluid displacement in sands. *Trans. Am. Inst. Min. Metall. Pet. Eng.* **146**: 107–116.
10. Fokas, A.S. and Yortsos, Y.C. (1982). On the exactly solvable equation $S_t = [(\beta S + \gamma)^{[-2]} S_x]_x + \alpha(\beta S + \gamma)^{[-2]} S_x$ occurring in two phase flow in porous media. *SIAM J. Appl. Math.* **42**(2): 318–332.
11. McWhorter, D.B. and Sunada, D.K. (1990). Exact integral solutions for two phase flow. *Water Resour. Res.* **26**(3): 399–414.
12. Peaceman, D.W. (1967). *Numerical Solution of the Nonlinear Equations for Two Phase Flow Through Porous Media, Nonlinear Partial Differential Equations—Methods of Solutions*. Academic Press, New York, pp. 79–91.

13. Peaceman, D.W. and Rachford, H.H. (1962). The numerical calculation of multidimensional miscible displacement. *Trans. SPE AIME* **225**: 327–329.
14. Douglas, J., Jr. and Rachford, H.H., Jr. (1959). On the numerical solution of heat conduction problems in two and three space variables. *Am. Math. Soc. Trans.* **82**(2): 421–439.
15. Coats, K.H., Nielsen, R.L., Terhune, M.H., and Weber, A.G. (1967). Simulation of three dimensional two phase flow in oil and gas reservoir. *Trans. SPE AIME* **240**: 377–388.
16. Coats, K.H. (1968). *Elements of Reservoir Simulation*. Lecture notes, University of Texas, reprinted by Intercomp Resources Development and Engineering, Inc., Houston, TX.
17. Sheffield, M. (1969). Three phase fluid flow including gravitational, viscous and capillary forces. *Soc. Pet. Eng. J.* **9**: 232–246.
18. Douglas, J., Jr. (1960). A numerical method for the solution of a parabolic system. *Numer. Math.* **2**: 91–98.
19. Sheldon, J.W., Zondek, B., and Cardwell, W.T. (1959). One dimensional incompressible non capillary two phase fluid flow in porous medium. *Trans. SPE AIME* **216**: 290–296.
20. Stone, H.L. and Gardner, A.O., Jr. (1961). Analysis of gas cap or dissolved gas reservoirs. *Trans. SPE AIME* **222**: 92–104.
21. Peaceman, D.W. and Rachford, H.H. (1955). The numerical solution of parabolic and elliptic differential equations. *SIAM J. Appl. Math.* **3**: 28–41.
22. Fagin, R.G. and Stewart, C.H. (1966). A new approach to the two dimensional multiphase reservoir simulator. *Soc. Pet. Eng. J.* **6**: 175–182.
23. Coats, K.H., Dempsey, J.R., and Henderson, J.H. (1970). A new technique for determining reservoir description from field performance data. *Trans. SPE AIME* **249**: 66–74.
24. Croise, J., Helmig, R., and Sheta, H. (1995). Numerical simulation of DNAPL infiltration processes in saturated heterogeneous porous media. In: *Proceedings of GQ Conference*, May 15–18.
25. Helmig, R. (1995). *Theory and Numerical Methods for Multiphase Flow in Porous Medium*. Technical report, Institute for Wasserbau, University of Stuttgart, Stuttgart, Germany.
26. Huber, R. and Helmig, R. (1999). Multiphase flow in heterogeneous porous media: a classical finite element method versus an implicit pressure explicit saturation based mixed finite element–finite volume approach. *Int. J. Numer. Methods Fluids* **29**: 899–920.
27. Peszynska, M., Lu, Q., and Wheeler, M.F. (1999). Coupling different numerical algorithms for two phase fluid flow. In: *The Mathematics of Finite Elements and Applications X*. J.R. Whiteman (Ed.). Brunel University, Uxbridge, Middlesex, UK, pp. 205–214.
28. Dekker, T.J. and Abriola, L.A. (2000). The influence of field scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formulations. *Journal of Contaminant Hydrology* **42**(2): 187–218.
29. Ataie–Ashtiani, B. et al. (2001). Effective parameters for two phase flow in a porous medium with periodic heterogeneities. *J. Contam. Hydrol.* **49**: 87–109.
30. Yu-Shu, W., Zhang, K., and Pruess, K. (2002). Massively parallel simulation of flow and transport in variably saturated porous and fractured media. In: *Proceedings of the XIVth International Conference on Computational Methods in Water Resources* (CMWR XIV), June 23–28, Delft, The Netherlands, Vol. 1, pp. 289–297.
31. Thomas, G.W. and Thurnan, D.H. (1983). Reservoir simulation using an adaptive implicit method. *Soc. Pet. Eng. J.* **23**: 750–768.
32. Forsyth, P.A. (1989). Adaptive implicit criteria for two phase flow with gravity and capillary pressure. *SIAM J. Sci. Static Comput.* **10**: 227–252.
33. Unger, A.J.A, Forsyth, P.A., and Sudicky, E.A. (1998). Influence of alternative dissolution methods and subsurface heterogeneity on DNAPL disappearance times. *J. Contam. Hydrol.* **30**: 217–242.

THE USE OF SEMIPERMEABLE MEMBRANE DEVICES (SPMDs) FOR MONITORING, EXPOSURE, AND TOXICITY ASSESSMENT

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INTRODUCTION

Semipermeable Membrane Devices (SPMDs) constitute an innovative approach for sequestering trace/ultra-trace levels of waterborne hydrophobic chemicals and for accurate exposure estimates (1,2). Bioavailable hydrophobic organic contaminants usually occur at trace (<1 ppb) or ultra-trace (<1 ppt) concentration levels in water. The traditional active sampling methods such as liquid-liquid extraction (LLE) or solid phase extraction (SPE) are only partially successful in sequestering these pollutants from water because of the very large water volumes required for processing/analysis. The concentrations of aquatic contaminants can change daily or even hourly, therefore, a great number of samples are required to get a true picture of contaminants present. The limitations in the direct determination of such low concentrations in water have often prompted the use of biomonitoring organisms for exposure estimates. However, the organism-based approach also has inherent problems, including biotransformation and depuration of contaminants, and inapplicability in many exposure situations because of the effects of stress on the biomonitoring organisms that often lead to a lack of proportionality between biomonitoring organism tissue concentrations and ambient exposure concentrations. The SPMDs are lipid-containing polymeric membranes, which function as passive *in situ* samplers of hydrophobic organic pollutants and as physical models of the bioconcentration process (Fig. 1).

Triolein (glyceryl trioleate, $C_{57}H_{104}O_6$) containing SPMDs made of low-density polyethylene (LDPE) were first developed by scientists of the U.S. Geological Survey's Columbia Environmental Research Center (1,3), although similar membranes containing *n*-hexane were previously used by Soedergren (4,5) for simulation of the uptake of pollutants by aquatic organisms. In general, SPMDs can be advantageously used in the following broad areas of application (1):

1. Determination of pollution point sources
2. Estimation of time-weighted average dissolved or vapor phase chemical concentrations

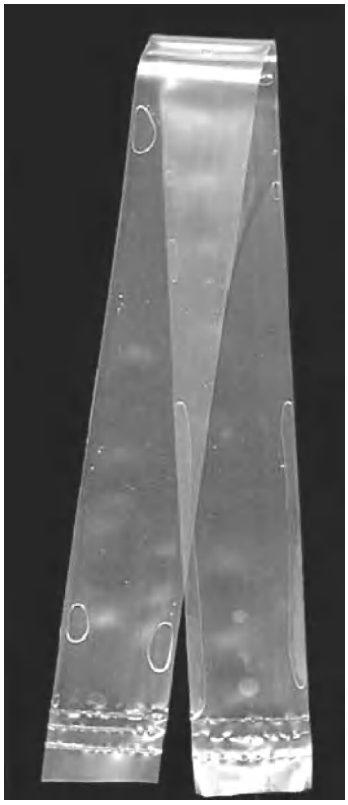


Figure 1. Photo of a semipermeable membrane device (SPMD).

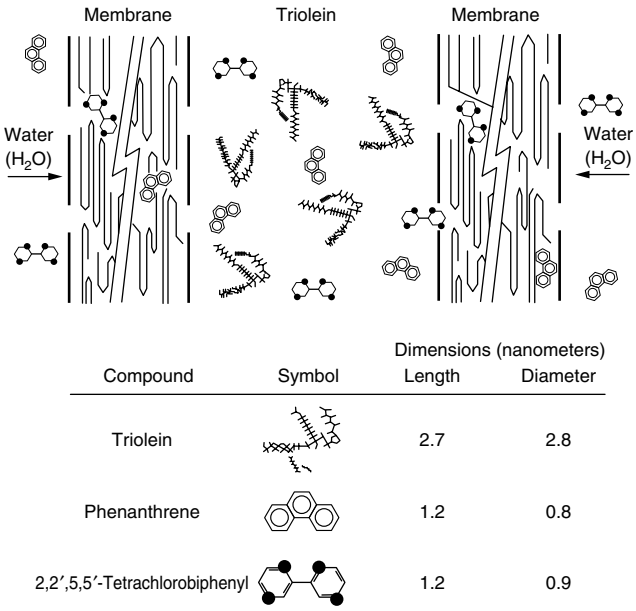


Figure 2. Schematic cross section of an SPMD in an aqueous environment (7).

3. *In situ* mimetic concentration of bioavailable chemicals for bioindicator or immunoassay tests
4. Contaminant sequestration in toxicity identification and evaluation (TIE) procedures
5. Estimation of organisms' exposure and bioconcentration potential
6. Determination of the readily bioavailable fraction (dissolved or vapor phase) of a chemical in an environmental compartment for predicting transport, fate, and residue toxicity

SPMD-BIOMEMBRANE SIMILARITIES

The organism-based bioconcentration studies are associated with several problems, such as biotransformation and depuration of contaminants, stress effects caused by noncontaminant stressors or the target contaminants, etc. The SPMD-based approach may offer significant advantages, including: (a) SPMDs do not need to be fed, (b) they do not eat each other or die from disease, lack of oxygen, or from the target contaminants, (c) an SPMD does not move around, will not escape, reproduce, and create an introduced species problem, (d) an SPMD can be used in almost any aquatic environment (cold mountain water, warm desert water, sea water, groundwater), (e) fish can actively depurate some kinds of hydrophobic contaminants, SPMDs don't, and (f) SPMDs can be used to back-calculate the concentration of a waterborne contaminant, but that usually cannot be done with fish.

SPMDs are designed to mimic the parts of animals that cause bioconcentration. The special plastic of SPMDs (LDPE) allows contaminants to pass through to the lipid while excluding water-like membranes of animal cells. The lipid inside (triolein) is similar to a highly purified fish fat. Although the composition of polymeric membranes differ substantially from that of gill membranes (i.e., bilayers of phospholipids and proteins), the diffusion of many lipophilic organic compounds through so-called "nonporous" polymeric membranes appears to simulate diffusion through biomembranes (6). Low-density polyethylene and gill membranes appear to exhibit similar steric exclusion limits with respect to the uptake of hydrophobic organic contaminants (3). Molecules greater than about 600 da (about 10 Åcross-sectional diameter in terms of molecular breadth) are excluded (Fig. 2). Contaminants larger than the exclusion limit or adsorbed on suspended particles (not dissolved) are neither bioconcentrated nor SPMD-available (2,6).

Herve et al. (8) and Prest et al. (9) compared SPMDs and mussels as monitors of bioconcentrating organochlorine compounds. Mussel-SPMD comparisons were species-specific and depended on noncontaminant stressors. However, mussels and SPMDs were found to be complementary in that mussels alone concentrated some compounds, whereas SPMDs alone concentrated others. A comparison between Green-Lipped mussels and SPMDs in Hong Kong coastal waters showed that SPMDs failed to rank the sites in the same order as mussels in terms of organochlorine contaminant concentrations, nevertheless, in localities where mussels cannot survive, SPMDs may be valuable in providing an indication of potentially bioavailable lipophilic pollutants (10). SPMDs and caged channel catfish were also compared for uptake of polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and polychlorinated biphenyls (PCBs). Higher concentrations of analytes were

found in SPMDs than in catfish (11). On the contrary, concentrations of DDT and its metabolites detected in SPMD extracts were approximately 1000 times smaller than those measured in fish (*Cyprinus caprio*) tissues in the Mississipi Delta (7).

BASICS OF SAMPLING USING SPMDS

SPMDs will, in general, concentrate from water all neutral hydrophobic chemicals having molecular masses <600 da (10 Å in terms of molecular breadth). No other sampling approach offers this broad a range of applicability with respect to chemical class or molecular mass (1,6). Examples of environmental contaminants that have been effectively sampled by SPMDs include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), moderately polar organophosphate pesticides, alkylated phenols, pyrethroid insecticides, nitroaromatic compounds, neutral organometallic compounds, and certain heterocyclic compounds (1,2,6,7,12–15). Other neutral chemicals that have been found in dialysates from field-deployed SPMDs include polybrominated diphenyl ethers, trifluralin, pendimethalin, etc. (7,12). The SPMDs are not designed to concentrate ionic species such as ionic metals, salts of organic acids, or very polar chemicals (1).

SPMDs have been applied successfully not only in natural aquatic environments, but also in sewerage systems and waste water treatment plants (2,14,16,17), as well as in the air phase of soils (18) and in the atmosphere (19,20).

The uptake of organic compounds by SPMDs is in accordance with polymer permeability and equilibrium partition theory. As chemical partitioning coefficients between membrane and water (K_{MW}) and between lipid and water (K_{LW}) increase with the lipophilic indicator (K_{OW}), the SPMD sampling rate is expected to rise proportionally. At saturation, the capacity of the SPMD for a hydrophobic chemical is generally related with the compound's K_{OW}, i.e., the higher a compound's K_{OW}, the greater the capacity of the SPMD for that chemical. Neutral organic chemicals that are hydrophobic (i.e., with log $K_{OW} \geq 3$) will be concentrated by the SPMD, but for compounds with log $K_{OW} \leq 3$, no significant advantage exists in using SPMDs in preference to other sampling procedures (2).

The uptake of HOCs by SPMDs is linear (or integrative) for the first days of deployment, then it becomes curvilinear (partly integrative) and, finally, when it reaches equilibrium, the amount of HOCs taken up is exactly equal to the amount of HOCs lost (Fig. 3). One of the main principals in using SPMDs in sampling is to operate only in the kinetic phase of uptake, where contaminant uptake is linear. Exposure time must therefore be optimized because, during longer exposure periods, equilibrium between the SPMD and sampling media may be approached for certain contaminants (6). The uptake of HOCs with log K_{OW}s > 4.9 is usually linear during exposure times <30 days, whereas for compounds with log K_{OW} < 4.9, equilibrium concentrations of analytes may be reached or approached in ≤30 days (22). A compound with log $K_{OW} = 6$ would need 200 days at a constant water concentration and at an effective sampling rate of 10 L/d to reach 90% equilibrium. However, during the initial period, the uptake rate by the SPMD is linear and first-order (23).

In the linear uptake phase, the concentration of a contaminant in the SPMD will be proportional to the concentration in water as a time-weighted average according to the Eq. 1:

$$C_{SPMD} = C_W R_S t / M_{SPMD} \quad (1)$$

where C_{SPMD} is the concentration of the analyte in the SPMD, C_W is the concentration of the analyte in water, t is the exposure time in days, M_{SPMD} is the mass of the SPMD, and R_S is the SPMD sampling rate (21). Briefly, the analyte sampling rate (R_S) for a given analyte is determined from laboratory or field exposures conducted under controlled conditions. As field-deployed SPMDs often become biofouled, the potential impedance to analyte uptake because of aufwuchs layers needs to be accounted for, thus the environmental sampling rate (R_{SC}) is given by Eq. 2:

$$R_{SC} = R_S F \quad (2)$$

where F is 1 minus the fractional reduction in uptake flux or sampling rate because of fouling (2). Typically, for no or little biofouling, no correction is made. For mild, medium, and heavy biofouling, uptake impedances of 10%, 30%, and 50%, respectively, are assumed.

The SPMD sampling rates have been demonstrated to be independent of water concentrations and salinity. Sampling rates increase with temperature and log K_{OW} (i.e., sampling rates increase with increasing hydrophobicity) up to a log K_{OW} of about 5.5 (1,21,24). A decrease in uptake rates for compounds with log $K_{OW} > 6$ has been observed in similarity to bioconcentration rates in fish (2). Using the above approach and available R_{SC} values (15,21,24), the bioavailable waterborne concentrations

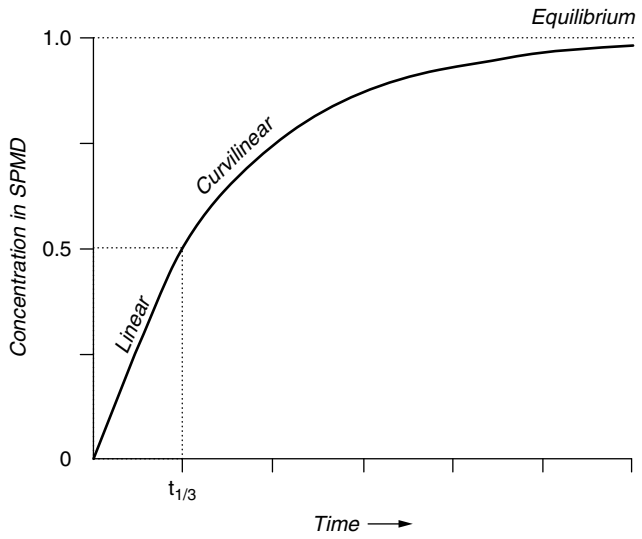


Figure 3. The three phases of SPMD uptake (21).

of typical hydrophobic contaminants have been calculated in many field locations (1,13,25–28).

Any length SPMD with a constant surface area/volume ratio (SA/V) of about 460 cm^2 per ml of triolein, an approximate 0.2 lipid-to-membrane mass ratio, and a 75–90 μm wall thickness is considered to be a "standard SPMD." The uptake rates of specific HOCs by standard SPMDs are presented in Table 1.

SPMDs are great for identifying sources of contamination on small geographical and temporal scales, i.e., when in the study area, the water flow velocities and exposure temperatures are essentially unchanged. A higher observed amount for a particular compound usually indicates a higher exposure concentration. Things become more complicated, however, when between-compound comparisons have to be made (e.g., low K_{OW} compounds may have higher aqueous concentrations, and yet have smaller absorbed amounts because the SPMD sorption capacity is limited) or when substantial between-site differences exist in water flow velocities and temperatures. A third difficulty is that the "SPMD absorbed amount" is not a quantity that is easy to use in environmental fate modeling and in monitoring programs (2). The use of Permeability/Performance Reference Compounds (PRCs) helps to identify and eliminate these problems, establishing a firm link between the absorbed amounts and the aqueous concentrations of contaminants. PRCs are analytically noninterfering compounds, such as perdeuterated PAHs, with moderate to fairly high SPMD fugacity, that are added to SPMD prior to deployment. Their losses during the field exposure compared with losses under controlled laboratory conditions are used to correct for the effects of variations of temperature, diffusion layer thickness, and degree of biofouling on SPMD uptake rates (2,29).

Table 1. R_S Values for Selected HOCs by Standard SPMDs (l/d, 18 °C)

Compound	R_S	Compound	R_S
HCB	2.6[a]	PCB-153	4.2[b]
α-HCH, β-HCH	0.9[a]	PCB-138	4.9[b]
Lindane	0.7[a]	PCB-180	7.7[b]
Heptachlor	3.6[a]	Naphthalene	0.9[a]
Heptachlor epoxide	2.9[a]	Acenapthene	2.3[a]
Endosulfan	1.1[a]	Fluorene	1.7[a]
p-p′-DDE	5.5[a]	Phenanthrene	3.4[a]
Dieldrin	1.8[a]	Pyrene	5.2[a]
Endrin	3.1[a]	Benzo[a]pyrene	4.3[a]
p-p′-DDD	3.1[a]	2,3,7,8-TCDD	3.8[a]
p-p′-DDT	3.2[a]	2,3,7,8-TCDF	3.7[a]
PCB-28	2.3[b]	1,2,3,7,8-PeCDD	3.4[a]
PCB-52	1.8[b]	1,2,3,7,8-PeCDF	3.8[a]
PCB-101	3.0[b]	1,2,3,4,7,8-HxCDD	4.0[a]
PCB-118	4.2[b]	1,2,3,4,7,8-HxCDF	2.7[a]

[a](21).
[b](24).

DEPLOYMENT, PROCESSING, AND ANALYSIS OF SPMDS

SPMDs are available commercially, but they can also be prepared in the laboratory. Once SPMDs are acquired or prepared, they should remain in vapor-tight tins until deployment, and, ideally, they should be stored to −15 °C (1). Several deployment devices have been proposed for the passive sampling with SPMDs (25,27,30), which usually are made of stainless steel or other metals. Use of plastic is not suggested, as it can be a potential interference because of the possible presence of leachable organics. Hardware must be designed so as to minimize abrasion of the membrane, especially

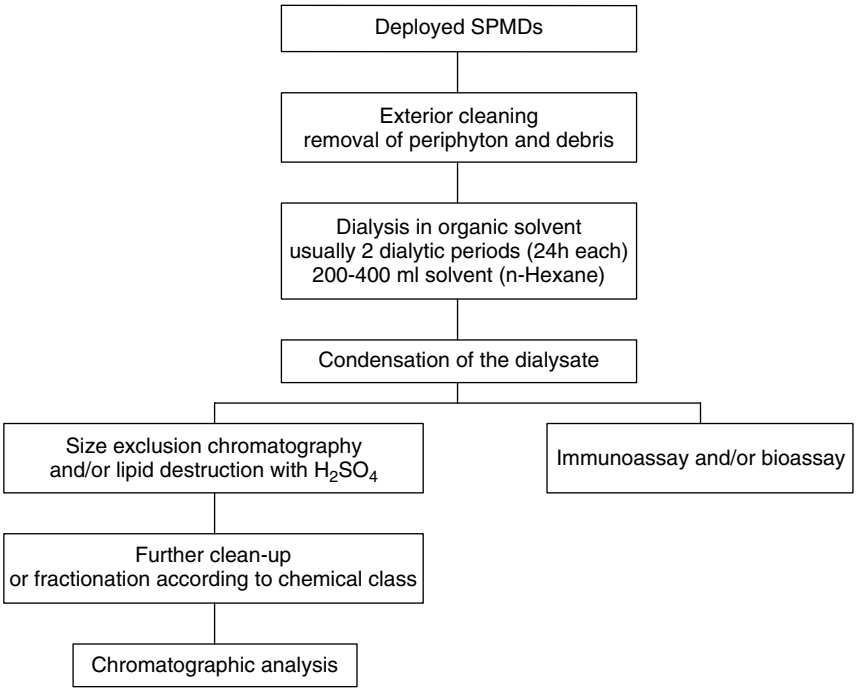


Figure 4. Analytical scheme for the processing of SPMDs.

in turbulent environments (1), and they should also be deployed in such a way that the maximum exposure of membrane surface is ensured. When the deployment period is over, the SPMDs should again be put in vapor-tight tins and kept frozen until analysis.

SPMDs that have been exposed to the aquatic environment can contain a diversity of lipophilic contaminants other than those specifically targeted (3). Also, the outsides of exposed SPMDs are often biofouled by aufwuchs (attached microscopic or macroscopic organisms) and must be cleaned before the targeted residues can be determined (6,13,14,31). Contaminants concentrated in SPMDs are easily recovered by dialysis into organic solvents such as n-hexane, cyclopentane, or cyclohexane (6,14,16,17,19,25–27,30–33). Dialysates from exposed SPMDs can conceivably contain biogenic material from aufwuchs, codialyzed triolein, methyl oleate, and impurities and oligomers from polyethylene (2,3,6). Analytical procedures are therefore required to overcome these impediments. Size exclusion chromatography (SEC) is usually employed to remove interferences, especially codialyzed polyethylene oligomers, oleic acid, and methyl oleate, although oleic acid may be present even after SEC-treatment (1). A solution to this problem may be the application of a destruction technique, like hydrolysis or acidic treatment. The problem with these treatments is that a part of target compounds may also be destroyed. Compounds that resist strongly to acidic treatment are PCBs and some OCPs (34). Fig. 4 is a generalized representation of the analytical scheme.

Quality control of sampling employing SPMDs requires the use of field and trip blanks accounting for contamination of SPMDs by airborne chemicals during the time between opening the can and deployment, and for potential interferences introduced during transport. Laboratory blanks may also be used, together with reagent blanks and duplicate samples, to ensure the quality of results.

The range of concentrations in which HOCs are present in SPMDs can vary from a few pg $SPMD^{-1}$ (14) to μ g $SPMD^{-1}$ (2) or higher depending on the concentration of the specific chemical in water, the size of the SPMD deployed, the uptake rate, and the detection limit of the analytical technique employed. In any case, the concentration of a chemical in the SPMD will be higher than in the ambient water, which is one of the major advantages of the use of SPMDs.

BIBLIOGRAPHY

1. Petty, J.D. et al. (2000). An approach for assessment of water quality using semipermeable membrane devices (SPMDs) and bioindicator tests. *Chemosphere* **41**: 311–321.
2. Petty, J.D. et al. (2000). Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminats. *J. Chromatogr A.* **879**: 83–95.
3. Huckins, J.N., Tubergen, M.W., and Manuweera, G.K. (1990). Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.
4. Soedergren, A. (1987). Solvent-filled dialysis membranes simulate uptake of pollutants by aquatic organisms. *Environ. Sci. Technol*. **21**(9): 855–859.
5. Soedergren, A. (1990). Monitoring of persistent, lipophilic pollutants in water and sediment by solvent-filled dialysis membranes. *Ecotox. Environ. Safe* **19**(2): 143–149.
6. Lebo, J.A. et al. (1992). Use of semipermeable membrane devices for *in situ* monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere* **25**: 697–718.
7. Zimmerman, L.R., Thurman, E.M., and Bastian, K.C. (2000). Detection of persistent organic pollutants in the Mississippi Delta using semipermeable membrane devices. *Sci. Tot. Environ.* **248**: 169–179.
8. Herve, S. et al. (1995). Lipid-filled semipermeable membrane devices and mussels as samplers of organochlorine compounds in lake water. *Environ. Sci. Pollut. Res.* **2**: 24–30.
9. Prest, H.F., Richardson, B.J., Jacobson, L.A., Vedder, J., and Martin, M. (1995). Monitoring Organchlorines with semi-permeable membrane devices (SPMDs) and Mussels (Mutilus-Edulis) in corio Bay, Victoria, Australia. *Mar. Pollut. Bull.* **30**: 543–554.
10. Richardson, B., Zheng, G., and Lam, P. (2000). Are SPMDs as good as mussels? A comparison of the Green-Liped Mussel (*Perna Viridis*) and SPMDs for monitoring organochlorine contaminats in Hong-Kong coastal waters. 6th *International SPMD Workshop and Symposium*, Columbia, MO.
11. Gale, R.W. etal. (1997). Comparison of the uptake of dioxin like compounds by caged channel catfish and semipermeable membrane devices in the Saginaw River, Michigan. *Environ. Sci. Technol.* **31**: 178–187.
12. Petty, J.D., Huckins, J.N., Martin D.B., and Adornato, T.G. (1995). Use of semipermeable membrane devices (SPMDs) to determine bioavailable organochlorine pesticide residues in streams receiving irrigation drainwater. *Chemosphere* **30**: 1891–1902.
13. Wang, Y., Wang, Z., Wang, C.X., and Wang, W.H. (1999). Uptake of weakly hydrophobic nitroaromatics from water by semipermeable membrane devices (SPMDs) and by goldfish (Carassius auratus). *Chemosphere* **38**(1): 51–66.
14. Wang, Y. et al. (2001). Monitoring priority pollutants in a sewage treatment process by dichloromethane extraction and triolein-semipermeable membrane device. *Chemosphere* **43**: 339–346.
15. Rantalainen, A.L., Cretney, W.J., and Ikonomou, M.G. (2000). Uptake rates of Semipermeable membrane devices (SPMDs) for PCDDs, PCDFs and PCBs in water and sediment. *Chemosphere* **40**: 147–158.
16. Stuer-Laudridsen, F. and Kjolholt, J. (2000). Identification of selected hydrophobic organic contaminants in wastewater with semipermeable membrane devices (SPMDs). *Wat. Res.* **34**: 3478–3482.
17. Samara, C. and Katsoyiannis, A. (2002). Evaluation of Persistent Organic Pollutants (POPs) in wastewater by means of Semipermeable Membrane Devices (SPMDs). *Proceedings of the* 2nd *European Conference on Pesticides and Related Organic Contaminants*, September 25–29, Corfu, Greece, pp. 109–116.
18. Rantalainen, A.L., Paasivirta, J., and Herve, S. (1998). Uptake of chlorohydrocrbons from soil by lipid-containing semipermeable membrane devices (SPMDs). *Chemosphere* **36**: 1415–1427.
19. Petty, J.D., Huckins, J.N., and Zajicek, J.I. (1993). Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* **27**: 1609–1624.

20. Prest, H.F., Jacobson, L.A., and Huckins, J.N. (1995). Passive sampling of water and coastal air via semipermeable membrane devices. *Chemosphere* **35**: 1351–1361.
21. Huckins, J.N., Petty, J.D., Prest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., and Johnson, B.T. (2000). *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samples of Waterborne Hydrophobic Contaminats*. Edition of Columbia Environmental Research Center, USGS, USDI, and California Analytical Division, Agilent Technologies, Inc., Palo Alto, CA.
22. Huckins, J.N. et al. (1999). Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons in water. *Environ. Sci. Technol.* **33**: 3918–3923.
23. Huckins, J.N. et al. (1993). Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.
24. Meadows, J.C. et al. (1998). Estimation of uptake rate constatnts for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.
25. Petty, J.D. et al. (1995). Determination of waterborne bioavailable organochlorine pesticide residues in the lower Missouri river. *Environ. Sci. Technol.* **29**: 2561–2566.
26. Petty, J.D. et al. (1998). Determination of bioavailable contaminats in the lower Missouri River following the flood of 1993. *Environ. Sci. Technol.* **32**: 837–842.
27. Lebo, J.A. et al. (1995). Use of Semipermeable membrane devices as an in-situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-parts-per-quadrillion concentrations. *Environ. Sci. Technol.* **29**(11): 2886–2892.
28. Echols, K.R. et al. (2000). Comparing polychlorinated biphenyl concentrations and patterns in the Saginaw River using sediment, caged fish, and semipermeable membrane devices. *Environ. Sci. Technol.* **34**: 4095–4102.
29. Huckins, J.N. et al. (2002). Development of the permeability/performance reference compound approach for *in situ* calibration of semipermeable membrane devices. *Environ. Sci. Technol.* **36**: 85–91.
30. Ellis, G.S. et al. (1995). Evaluation of lipid-containing semipermeable membrane devices for monitoring organochlorine contaminants in the upper Mississippi river. *Environ. Sci. Technol.* **14**: 1875–1884.
31. Rantalainen, A.L., Ikonomou, M.G., and Roge, I.H. (1998). Lipid containing semipermeable mebrane devices (SPMDs) as concentrators of toxic chemicals in the lower Fraser River, Vancouver, British Coloumbia. *Chemosphere* **37**(6): 1119–1138.
32. Lebo, J.A. et al. (1996). Use of the semipermeable membrane device (SPMD) to sample polycyclic aromatic hydrocarbon pollution in a lotic system. *Polycycl. Arom. Comp.* **8**(1): 53–65.
33. Van Stee, L.L.P. et al. (2002). Use of semi-permeable membrane devices and solid phase extraction for the wide-range screening of microcontaminants in surface water by GC-AED/MS. *Water Res.* **36**: 4455–4470.
34. USEPA. (1998). *Standard operating procedure for acid cleanup of organic extracts for PCB analysis*. CRL Method 3600—Acid. *CRL SOP GC016*.

READING LIST

Chiou, C.T. (1995). Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* **19**: 57–62.

RIVER-CONNECTED AQUIFERS: GEOPHYSICS, STRATIGRAPHY, HYDROGEOLOGY, AND GEOCHEMISTRY

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GENERAL

When water wells are constructed in aquifers that occur adjacent to rivers, pumping from the wells commonly causes infiltration of river water toward the wells, thereby increasing the total available water yield. This type of water production has been used extensively in many European countries (1) and, to a lesser extent, in North America.

The flow of river water through permeable riverbed and aquifer sediments, commonly referred to as riverbank filtration, can provide filtration and general purification benefits. Riverbank filtration provides some protection to water supplies from persistent and shock-loaded biological and chemical contaminants that may be present in the river water (2), and commonly provides a first step in the treatment of water supplies (1,3,4); however, in some cases, water quality problems associated with the river water may be transmitted through the aquifer to break through to the wells (5). Riverbank filtration can completely or partially remove suspended solids and pathogens from the infiltrating river water (1,6–11). In addition, the infiltrating river water undergoes chemical modifications, some of which may be beneficial, such as adsorption of metals (6), denitrification (12–15), and biodegradation of organic compounds (15,16). Some chemical changes may be detrimental such as increased hardness (10) and increased concentrations of dissolved iron and manganese (10,12,13,17–19).

In the development and management of river-recharged aquifer systems, the two most important considerations are the sustainability of water quantity and water quality. The quantity of water available is dependent on the river discharge and on the hydrostratigraphy between the riverbed and adjacent pumping wells. The quality of water extracted from the wells is influenced by the quality of the river water, the nature of flow paths from the river to the wells, the travel time in the riverbed sediments and aquifer (9), and the geochemical and mineralogical characteristics of the riverbed and aquifer sediments (19). Development of an understanding of these characteristics is therefore a prerequisite for managing well fields that use induced infiltration of river water.

In 2001, a multidisciplinary investigation of the Fredericton Aquifer was initiated with the objectives of determining:

- stratigraphic controls on the flow path and infiltration flux for river water entering the aquifer,
- the travel time between the river and the pumping wells, and
- the spatial and temporal variation in geochemical reactions that occur as river water infiltrates the aquifer, leading to changes in water quality.

In this contribution, the Fredericton Aquifer, which is considered typical of many alluvial-valley water-supply aquifers, is used as a case study to illustrate possible approaches to the characterization of river-recharged aquifer systems, and describe some of the important stratigraphic, hydrogeologic, and geochemical features of these systems. The combined use of geophysical, hydrogeological, and geochemical methods of investigation has led to a more complete understanding of river water infiltration toward municipal wells and the resulting water quality implications.

FREDERICTON AQUIFER CASE STUDY

The study area is located in Fredericton, New Brunswick, Canada (Fig. 1) (45.87 °N, 66.53 °W). The Saint John River at Fredericton lies in a broad bedrock valley that is partially filled with up to 65 m of unconsolidated sediments. The City of Fredericton obtains its entire water supply (approximately 25,000 m^3/day) from a semiconfined aquifer that lies within the river valley. As shown in Fig. 2, drilling has revealed that the coarse-grained sediments that make up the aquifer have the morphology of a buried esker ridge that runs approximately SE-NW underneath the city and is thought to follow the general drainage direction of the bedrock valley floor. The ridge is up to 30-m thick and contains a large range in particle sizes from sand to boulders (20). The deposit thins as it spreads along the north and south valley walls.

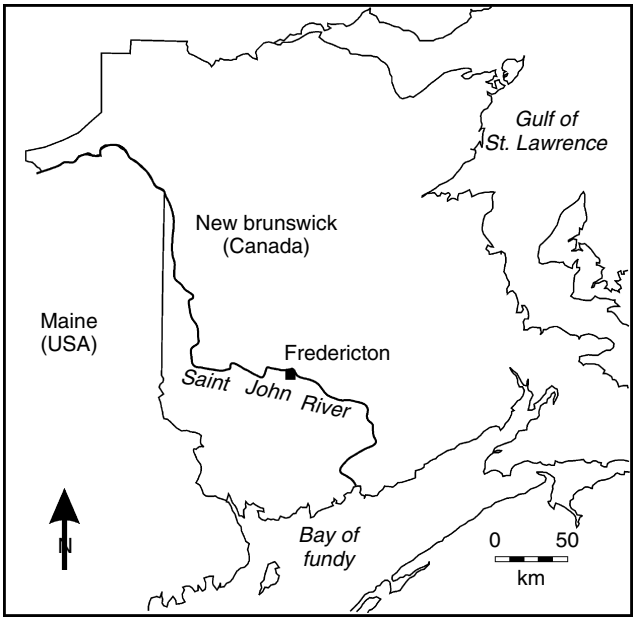


Figure 1. Location of the Fredericton Aquifer case study.

The city currently has eight wells located on the south side of the Saint John River (Fig. 2), and all wells are completed in a sand and gravel aquifer with screen depths between 25 m and 48 m below ground level. Four of the eight wells are located within 150 m of the river. A discontinuous silt/clay unit overlies the aquifer, and in locations where it is discontinuous, referred to as windows, the aquifer is recharged by the river or by precipitation. The aquifer may also be recharged by an upward flux of groundwater from the underlying bedrock.

A history of elevated Mn concentrations has existed in several of the Fredericton supply wells, and Mn concentrations in groundwater from some of the production

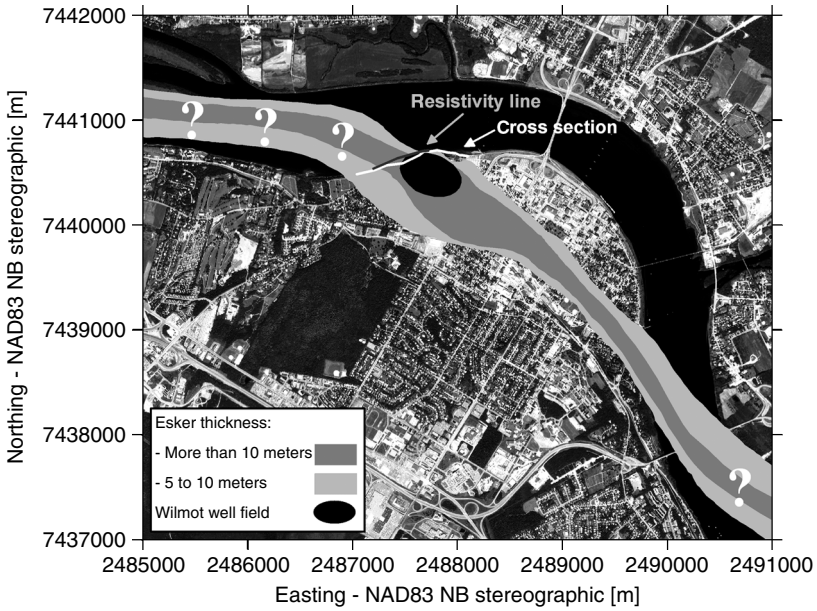


Figure 2. Satellite photo with superimposed map of the buried esker ridge that forms the main part of the aquifer underlying the City of Fredericton and adjacent Saint John River. The well field is highlighted in black [from (21)].

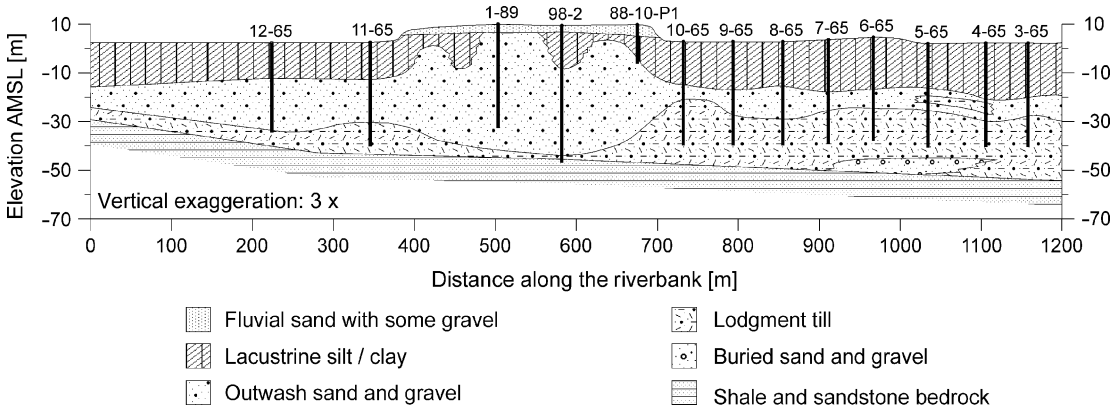


Figure 3. Cross section located along the south shore of the Saint John River and passing obliquely over the buried esker at the edge of the well field as shown in Fig. 2. The rise in surface elevation over the esker ridge reflects the fact that boreholes in that area were drilled atop the river's bank whereas most others were drilled at the river's edge. Borehole logs are from (22) and the City of Fredericton. Undulations in the esker surface are inferred from the resistivity imaging results in Fig. 4.

wells exceed the Canadian Drinking Water Guideline of 0.05 mg/L by up to 3 mg/L. Previous work (19,21) has demonstrated that dissolved organic carbon (DOC) present in the infiltrating river water promotes biogeochemical reactions in the adjacent aquifer, leading to elevated Mn concentrations.

Stratigraphic Controls on River Water Infiltration

In the approximately 50 years since the first water wells were developed in the Fredericton Aquifer, there have been over 700 drill holes completed to sample the unconsolidated glacial and postglacial deposits in the bedrock valley. The information obtained from these drilling activities is extremely useful in developing a general understanding of the glacial stratigraphy, including the aquifer and its enclosing geologic units (Fig. 3). However, despite the large amount of drill-hole data available, the detailed knowledge of stratigraphy below the river that is required to identify discrete flow paths from the river to the wells could not be derived from the drill-hole data. A very large number of additional drill holes would have been required to obtain the necessary geologic information, and such a conventional approach was not feasible because of financial constraints. Consequently, an alternative approach was taken using a variety of near-surface geophysical techniques to determine the subsurface distribution of important stratigraphic units.

Shoreline Resistivity Imaging. The clay content of the silt/clay aquitard unit creates a contrast in electrical conductivity/resistivity with the surrounding sands and gravels. This contrast allows for the effective use of electrical and electromagnetic geophysical techniques for mapping discontinuities (windows) in the aquitard that overlies the aquifer. Resistivity data were first acquired along a 500-m profile located on the shoreline of the river beside the Wilmot Well Field (Fig. 2). The data were acquired in dipole-dipole mode using 10-m dipoles and five apparent resistivity measurements for every current injection location (i.e., $a = 10$ m, $n = 5$) in order to provide a dataset suitable for two-dimensional inversion.

Figure 4 shows the minimum structure resistivity model obtained by inversion (23). The model indicates that the aquitard is laterally continuous near either end of the line and confirms the presence of a window zone in the area where we would expect it based on the cross section in Fig. 3. The interpreted thicknesses of clay/silt on either side of the window ($\sim$12–15 m) are in agreement with geologic logs from three boreholes that had previously been drilled on the shore. Below the high resistivity layer that is interpreted to represent the aquifer sand and gravel, a slight decrease occurs in resistivity depths greater than 30 m, which may represent the glacial till layer; however, the depth of penetration and/or resistivity contrast are not sufficient to conclusively define this contact. Most notably, the resistivity image reveals the presence of two silt/clay pods within the window, neither of which had been well defined by drilling. These pods reduce the area available for river water infiltration through the window into the aquifer.

Figure 4 also shows a profile of apparent electrical conductivity as measured along the shoreline with an electromagnetic terrain conductivity meter (Geonics EM31) having an effective depth of exploration of approximately 6 m (24). Comparison of this profile to the resistivity inversion result shows that apparent conductivities are relatively high in areas underlain by the clay/silt aquitard and low where it is absent. The EM method's speed as a reconnaissance tool and sensitivity to the presence of the aquitard window encouraged us to try adapting it for use on the river in the search for the river bottom recharge area.

Riverine Electromagnetic and Seismic Surveys. Although the resistivity survey revealed the width of the potential recharge zone along the shore and its two-dimensional morphology, a need still existed to define this zone underneath the river where the majority of recharge was

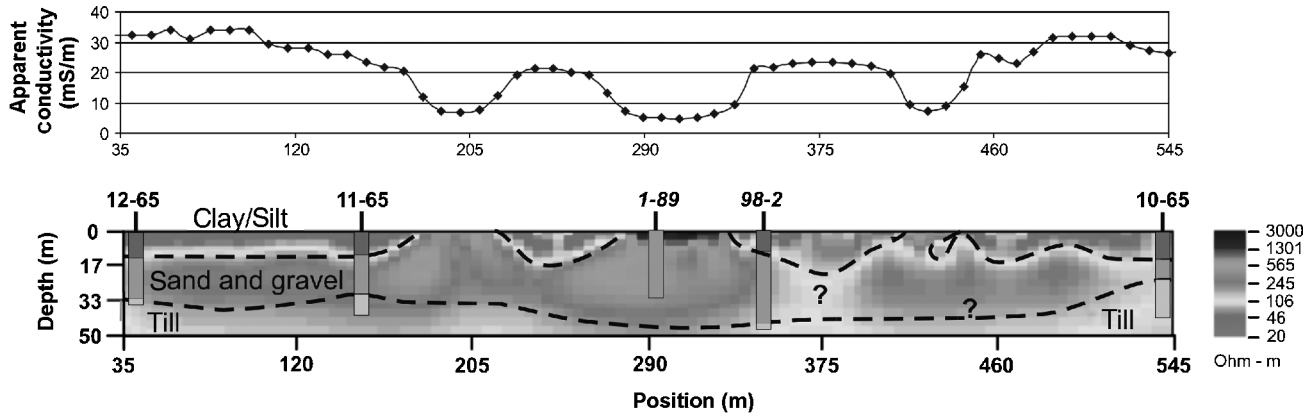


Figure 4. EM31 apparent conductivity profile (top), and resistivity depth section model (bottom) for a 500-m transect located along the shoreline of the Saint John River at the edge of the well field as shown in Fig. 2. Low resistivity zones (30 to 60 ohm-m) indicated by hot colors are interpreted as the conductive silt/clay aquitard, whereas the higher resistivities (>200 ohm-m) are interpreted as sand and gravel. In comparison, the measured resistivity of the river water was approximately 100 ohm-m.

expected to occur. Riverine EM and seismic reflection surveys were carried out for that purpose.

Electromagnetic Surveys. EM31 and deeper penetrating EM34 terrain conductivity meters were adapted for use on the water by deploying them in a nonmetallic canoe and inflatable raft. A DGPS was used to navigate along survey lines and record the locations of measurements made at 2–5 second intervals as the craft moved slowly along the water surface. In order to compensate for variations in apparent conductivity related to variations in water depth (~0.5 to 6 m), we devised an approximate bathymetric correction based on a one-dimensional earth model (23). A measurement of the river water's conductivity (10.3 mS/m) and a bathymetric map extracted from the seismic data described below were used as the basis for these corrections. Finally, the bathymetry-corrected apparent conductivity data were "leveled" to remove small miss-ties at the line intersections that were attributed to temporal drift in the instrument's response.

Figure 5 is a map of the leveled, bathymetry-corrected apparent conductivity measured using the EM34 in such a way as to achieve an effective depth of penetration of approximately 15 m (i.e., vertical dipole mode measurements with a transmitter-receiver coil separation of 10 m). The map created from EM31 data was similar but more strongly influenced by the varying thickness of fluvial sands (~0 to 6 m) overlying the aquitard. The most striking feature in Fig. 5 is the oblong, low conductivity zone trending under the river in a northwesterly to westerly direction. Based on a comparison of the EM31 and EM34 maps, this zone is interpreted as a window in the aquitard where sand and gravel extends upward through the surrounding silt/clay layer. The two elongated high conductivity anomalies within the window were previously detected by the shoreline resistivity survey and are interpreted as silt/clay pods that were deposited within depressions on the paleo-surface of the esker. The strong, erratic anomalies centered 250 m NE of the window are probably caused by metal cables that are known to have been discarded on the riverbed.

Single Channel Seismic Reflection Surveys. Single channel seismic reflection surveys were carried out with the expectation that the interface between aquitard and aquifer would be detectable because of differences in the seismic velocities or densities of the silt/clay and sand lithologies. The instrumentation consisted of an IKB Seistec sub-bottom profiler with an electrodynamic boomer source and integrated hydrophone receiver that was well suited for operation in the shallow riverine environment. Depth penetration was dependent on river bottom type, but many areas yielded excellent records showing reflections with dominant frequencies of 2–2.5 kHz from depths as great as 50 m (23).

Seismic profile C1040, shown in Fig. 6, lies subparallel to the river edge, 100–200 m offshore (Fig. 5). The eastern half of the line, where we expected aquitard material to be present, exhibits excellent reflectivity extending to two-way times as great as 30 ms, which corresponds to a depth of 24 ± 1 m using the average P-wave velocity of 1600 ± 50 m/s deduced for this depth range from borehole seismic surveys carried out on shore (25).

There are two prominent reflectors in this and most other records. The shallower one appears to come from the middle of the silt/clay aquitard where an abrupt increase in P-wave velocity was observed in borehole seismic records (25). The deeper one is thought to be the contact between the aquitard and underlying sand and gravel aquifer. Vestiges of slightly deeper reflectors exist in the record, one of which may represent the contact between the aquifer and glacial till. However, the relatively high frequencies employed in this survey were unable to penetrate far through the coarse-grained sediments underlying the aquitard, and no evidence exists of a reflection from bedrock.

In the central part of the seismic profile below position 460 m, the prominent aquitard reflectors terminate

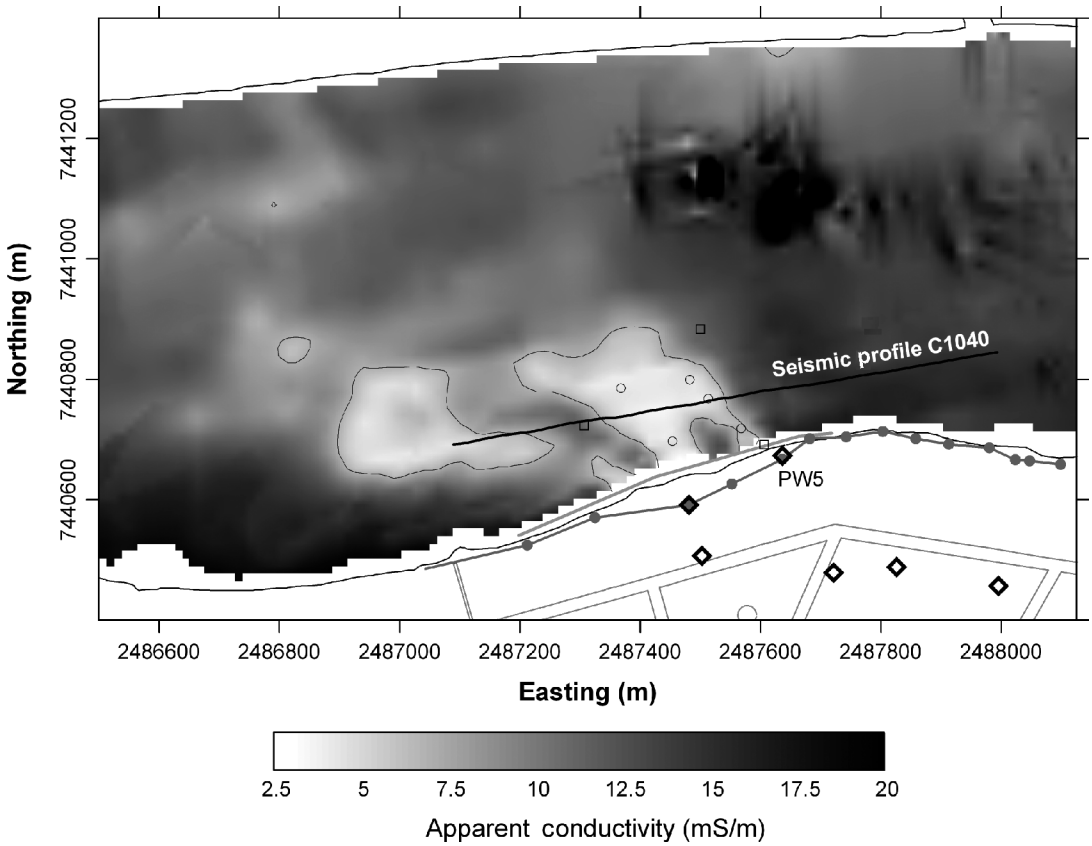


Figure 5. Bathymetry-corrected apparent conductivity map for the bottom of the Saint John River based on data collected with an EM34 terrain conductivity meter having an effective exploration depth of ~15 m. The map reveals a low conductivity zone of irregular shape (approximated by the 7 mS/m contour) interpreted as an aquitard window. The open circles and squares represent eight boreholes, three of which encountered aquitard (squares) and five of which did not. The locations of pumping wells (diamonds) and of the shoreline resistivity transect and cross section are also shown.

abruptly against a zone of low reflectivity. The coincident drops in EM31 and EM34 apparent conductivities shown in Fig. 6 lead us to conclude that an electrically conductive and laminated aquitard is here draped on the edge of the more resistive and massive-textured sand and gravel esker ridge. The region of shallow reflectivity and elevated conductivity observed in the western half of the profile, below positions 140 to 280 m, is similarly attributed to the presence of a silt/clay pod embedded in the top of the esker.

Confirmation of the Geophysical Interpretation. Confirmation of the presence of the aquitard window was provided by a drilling program on the river designed to core the aquifer and install piezometers for hydrogeological and hydrogeochemical investigations. The locations of eight holes drilled from a floating barge are shown in Fig. 5. The five holes identified as open circles were sampled continuously using a split-spoon through uninterrupted sands and gravels to depths ranging from 6 to 25 m below the river bottom. The absence of clay/silt is in agreement with the low bathymetry-corrected apparent conductivities obtained at those locations. In contrast, the three holes shown as open squares in Fig. 5 all encountered clay/silt aquitard material, consistent with their location in areas of elevated apparent conductivities.

Water Travel Times

Travel times between the riverbed and the wells can be assessed using tracer tests; however, because of the logistical difficulties of using artificial tracers in a large river such as the Saint John River, we have used two natural tracers, ^{222}Rn and water temperature. Velocities obtained from these tracers were compared with velocities in engineered slow-sand filtration systems, which are very effective for the removal of micro-organisms and pretreatment of drinking water (26). It must be noted that the velocities obtained to date are based on the assumption of vertical infiltration of river water into the underlying sediments; the actual flow paths will also have a horizontal component that has not been considered. The actual flow paths will therefore be longer, and the corresponding resultant velocities higher, than the vertical velocities we present here.

Water Temperature. The water temperature tracer technique is based on the occurrence of temporal temperature contrasts between the river water and the

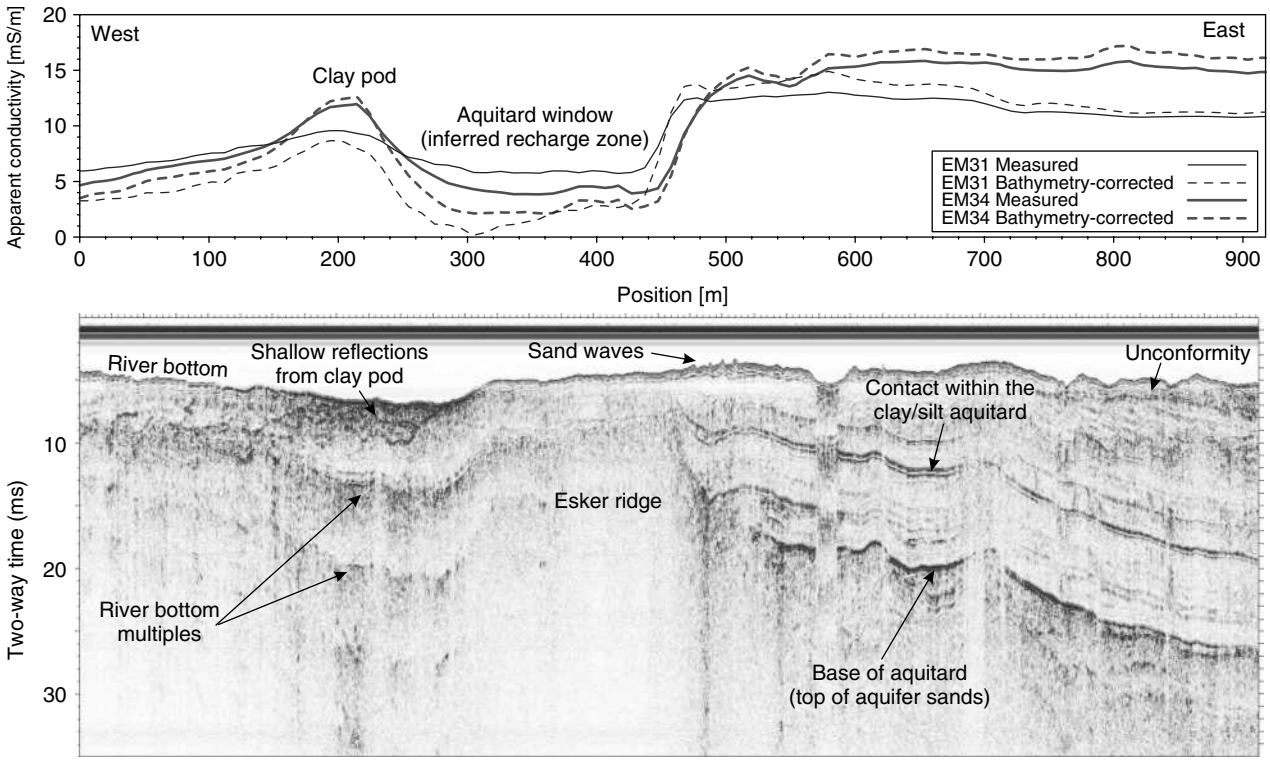


Figure 6. Seismic section and apparent conductivity profiles along the 920-m line C1040 shown in Fig. 5. The seismic record extends to approximately 28-m depth and is displayed with a vertical exaggeration of 12 times. Two strong reflectors, corresponding to interfaces within and at the base of the aquitard, are evident in the seismic data and are draped on the flank of the esker ridge below position 460 m. The apparent conductivity profiles reveal the same contact as well as the presence of a clay pod incised into the esker.

underlying aquifer. The method requires time-series measurements of the groundwater temperature along a flow path from the river toward the wells, and numerical modeling of these time series to determine groundwater flow velocities (27).

Seasonal time-series temperature data were collected at three locations (Fig. 7) within the aquitard window that was identified by EM surveys. At each location, data were collected with temperature loggers located at five or six depths distributed between 1.2 m and 18 m below the riverbed. In addition, one temperature logger was located at the riverbed to record the river water temperature changes.

Figure 8 presents representative data from location T1. The river water temperature decreases in the fall, approaches 0 °C during winter ice cover, and then gradually increases after ice break up reaching a maximum in midsummer. Groundwater temperatures recorded at T1 also exhibit significant seasonal variation with temperatures ranging from slightly greater than 0 °C to 22 °C. With increasing depth below the riverbed, groundwater temperature time series display an increasing lag relative to river water temperature. The lag reflects the time required for infiltration-induced transport of heat from the riverbed to the underlying sediments, and confirms the initial stratigraphic interpretation that, at this location, river water

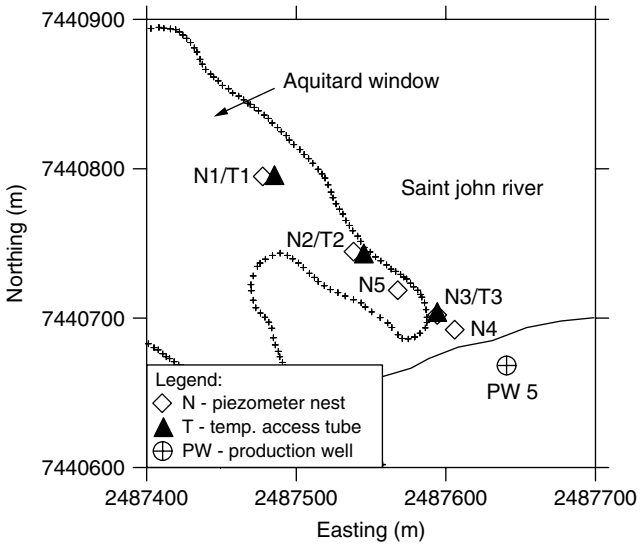


Figure 7. Location map of eastern portion of aquitard window showing the position of multilevel piezometer nests, temperature access tubes, and production well PW5.

moves downward into the aquifer. Similar trends were also observed in data from locations T2 and T3.

A finite-element solution (28) for the one-dimensional partial differential equation for heat convection and

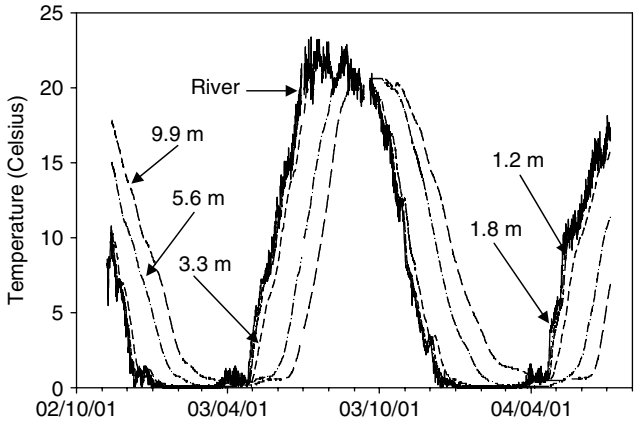


Figure 8. Saint John River and subsurface temperature time series for location T1. Locations T2 and T3 have similar temperature trends.

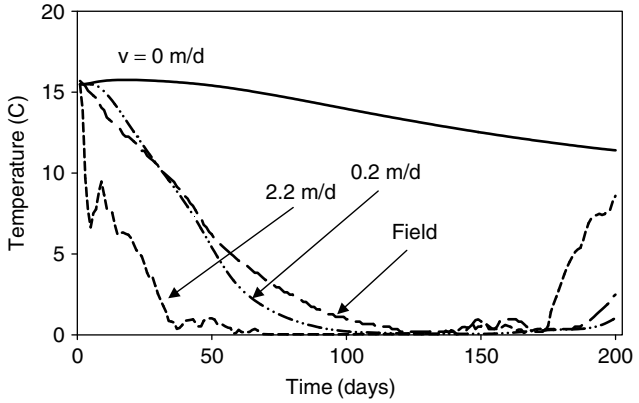


Figure 9. Comparison of simulated and measured temperatures at a depth of 4.7 m below the riverbed at location T3. To demonstrate the sensitivity to the infiltration velocity, simulation results are shown for three average linear velocity values, with v = 0 m/d representing pure heat conduction.

conduction:

$$[\varepsilon\rho^f c^f + (1-\varepsilon)\rho^s c^s]\frac{\partial T}{\partial t} + \rho^f c^f q^f \frac{\partial T}{\partial z} - \frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right) = 0 \quad (1)$$

where T is the system temperature, ε is the porosity, $\rho^f c^f$ is the volumetric heat capacity of the fluid, $\rho^s c^s$ is the volumetric heat capacity of the solids, q^f is the vertical Darcy flux, and λ is the thermal conductivity, was used to simulate temperatures in the recharge zone. Using the measured river water temperatures as the upper boundary condition, downward Darcy velocities were obtained by trial-and-error adjustment of the hydraulic head boundary conditions to reproduce the temperature time series observed beneath the riverbed. Thermal parameters were derived from correlations between sediment physical properties and thermal properties (27). An example of a comparison between simulated and measured temperature time series for several Darcy velocity values is presented in Fig. 9. For this particular location and depth (T3, 4.7 m depth), a velocity of 0.2 m/day provides a good agreement with the field data. Using this approach, vertical groundwater velocities have been estimated from each of the time-series records at locations T1, T2, and T3, and the results are summarized in Table 1.

Radon. The use of ^{222}Rn as a tracer for determining groundwater travel times is based on the knowledge that soluble ^{222}Rn is formed by the radioactive decay of ^{226}Ra. Given that ^{222}Rn is a gas that partitions readily from water into the air, and that ^{226}Ra is present dominantly in the mineral constituents of rocks and sediments, the activity of ^{222}Rn is generally very low in surface water and increases with travel time after infiltration of surface water into sediments. Steady-state activities are generally reached in saturated groundwater flow systems after residence times of approximately 30 days (29).

Water samples were collected for ^{222}Rn analyses from nested piezometers installed in the riverbed sediments to depths of between 4 and 25 m (Fig. 7). To estimate the steady-state ^{222}Rn activity for the aquifer, samples were also collected from several on-land monitoring wells.

Assuming that ^{222}Rn progenitors (e.g., uranium and radium) are homogeneously distributed throughout the aquifer sediments and that a steady-state ^{222}Rn activity, A_e, is attained, the residence time for infiltrated water can be estimated using (29):

$$t = \ln(1 - A_t/A_e)/\lambda' \quad (2)$$

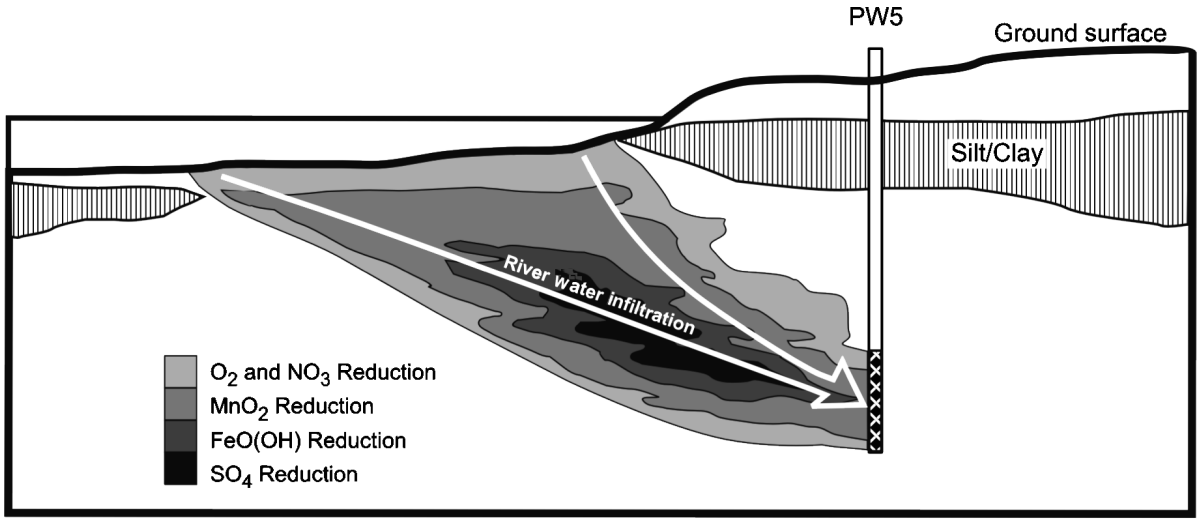
where t is the residence time, A_t is the measured ^{222}Rn activity in each piezometer, A_e is the steady-state ^{222}Rn activity, and λ' is the radioactive decay constant for ^{222}Rn.

A steady-state value of $A_e = 36$ Bq/L was used in Eq. 2 because this was the highest activity found in a series of on-land monitoring wells adjacent to the river. Activities of ^{222}Rn varied with depth and location from 13 to 23 Bq/L at N1, 14 to 22 Bq/L at N2, and 23 to 29 Bq/L at N3. These activities correspond to residence times of 2.4 to 5.5 days at N1, 2.8 to 5.3 days at N2, and 5.5 to 8.8 days at N3. Downward flow velocities were calculated by dividing the piezometer screen (sample) depth by the corresponding residence time, which resulted in a total of eleven estimates of vertical velocity in the infiltration area, which are summarized in Table 1. Heat transport-derived velocities and those based on ^{222}Rn activity are similar in magnitude.

Comparison with Slow-Sand Filtration. Average linear velocities for slow-sand filters are typically in the range of 5 to 20 m/day with sand bed thicknesses of approximately one meter (26). The vertical velocity estimates we have obtained are generally lower that slow-sand filtration

Table 1. Ranges of Vertical Average Linear Velocity (m/day)

Method	T1/N1	T2/N2	T3/N3
Temperature	1.5–2.6	0.2–1.3	0.1–0.2
^{222}Rn	1.1–4.0	1.6–5.0	0.7–2.7



O_2 Reduction
$CH_2O + O_2 \Rightarrow HCO_3^- + H^+$

NO_3 Reduction
$5CH_2O + 4NO_3^- + 4H^+ \Rightarrow 5HCO_3^- + 2N_2 + 2H_2O + 5H^+$

MnO_2 Reduction
$^1/_2CH_2O + MnO_{2(s)} + {}^1/_2H^+ \Rightarrow Mn^{(II)} + {}^1/_2HCO_3^- + OH^-$

FeO(OH) Reduction
$^1/_4CH_2O + FeO(OH)_{(s)} + {}^7/_4H^+ \Rightarrow Fe^{(II)} + {}^1/_4HCO_3^- + {}^3/_2H_2O$

SO_4 Reduction
$2CH_2O + SO_4^{2-} + H^+ \Rightarrow 2HCO_3^- + HS^- + 2H^+$

Figure 10. Thermodynamically based conceptual model for the redox zonation that is expected to develop in groundwater along the infiltration flow path from the river to wells. In these reactions, CH_2O is used to represent labile DOC.

velocities, and the aquifer sediments under investigation have a much larger "bed" thickness (>20 m) than engineered systems. These characteristics suggest that, in this case, riverbank filtration is conducive to providing pretreatment of the drinking water supply. However, it has also been noted (26) that cold water temperatures (near 1 °C) inhibit biological processes such as the production of natural polymers that are important for micro-organism removal during slow-sand filtration. We have observed such cold temperatures to significant depths in this case study, and therefore it might be expected that micro-organism removal during riverbank filtration will also be seasonally variable.

Groundwater Geochemistry

In order to improve the knowledge of the long-term geochemical evolution of groundwater from wells adjacent to the river, hydrogeochemical investigations were designed to provide an understanding of the influence of the DOC flux from the river on the redox conditions within the aquifer. The approach was to monitor the geochemical conditions along a flow path from the river toward supply well PW5 (Fig. 10). The monitoring was intended to identify spatial and temporal (seasonal) variations in the concentrations of redox-sensitive solutes such as dissolved O_2 (DO), NO_3, Mn, Fe, and SO_4. Aqueous geochemical sampling was conducted during the spring, summer, and fall at piezometers installed in the aquifer below the river bed (Fig. 7).

Thermodynamic principles suggest that the infiltration of DOC to an aquifer system would result in a sequential or stepwise decline in redox conditions, with reactions that provide the greatest energy advantage to microbial catalysts proceeding first, followed by reactions that provide less energy. The general sequence that is expected (30,31) would be the oxidation of DOC coupled sequentially to the reduction of O_2, NO_3, Mn(IV) oxide, Fe(III) oxide, SO_4, and finally CO_2. The O_2, NO_3, and SO_4 would generally be supplied by the infiltrating river water, and the Mn(IV) and Fe(III) are present as oxide or oxyhydroxide minerals in the aquifer sediment, with Fe(III) minerals usually in greater abundance. In accordance with thermodynamic principles, a conceptual model for the redox zonation that may be expected to develop along the flow path during river bank filtration is presented in Fig. 10.

Seasonal Geochemical Variations. The DOC concentration in the Saint John River ranges from 7.9 mg/L in July to 10.9 mg/L in September. Along the infiltration pathway, a general decrease occurs in DOC concentration with depth and distance toward the well, which is greatest (30–50%) in August and September. The concentrations of DO, NO_3,

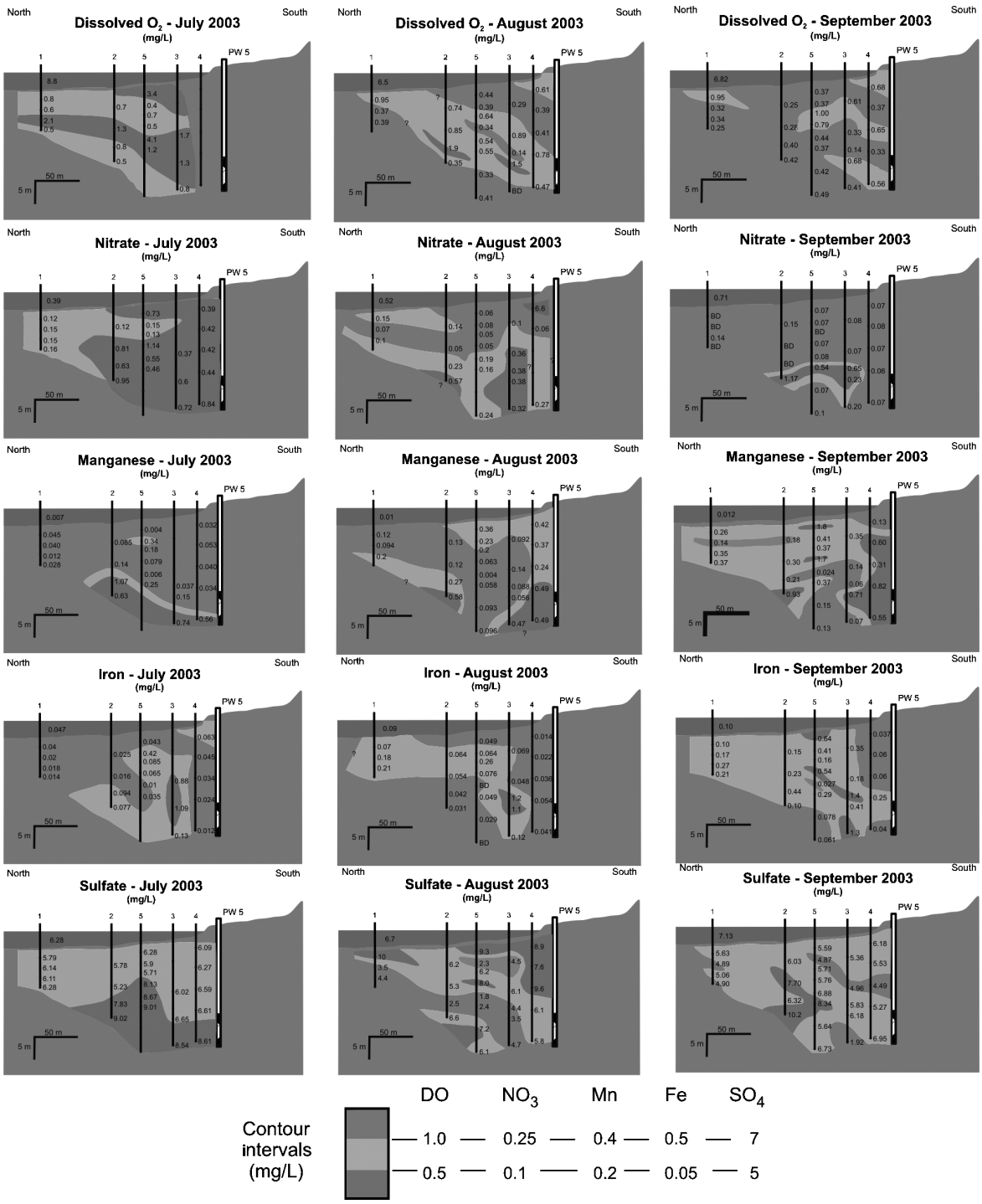


Figure 11. Seasonal (left to right) and spatial variations in redox-sensitive geochemical parameters along the flow path between the Saint John River and City of Fredericton municipal well PW5. Piezometer nests are indicated by vertical lines and individual piezometers (sample locations) are indicated by points on the lines.

Mn, Fe, and, to some extent, SO_4 display significant seasonal variations (Fig. 11). The redox conditions cycle on a seasonal time scale, likely in response to temperature changes in the infiltrating river water. Through the spring and into midsummer, the aquifer temperature is generally less than 5 °C (Fig. 8). The cold temperatures inhibit microbiologically mediated redox reactions between DOC and electron acceptors such as O_2, NO_3, Mn(IV), and Fe(III). As a result, conditions are relatively oxidizing with elevated concentrations of dissolved O_2 and NO_3, and low concentrations of Mn and Fe. Toward late summer and into the fall, the aquifer temperature increases and

the system tends toward more reducing conditions, with concentrations of dissolved O_2 and NO_3 declining, and concentrations of Mn and Fe increasing. Localized zones of elevated HS concentrations suggest that SO_4 reduction occurs; however, the seasonal trend toward reducing conditions is not manifest by a widespread decline in SO_4 concentrations as it is for O_2 and NO_3 (Fig. 11).

Spatial Geochemical Variations. Although the decline in dissolved O_2 and NO_3 concentrations and increase in the concentrations of Mn and Fe toward late summer and fall suggests that the reactions noted in Fig. 10 occur, the substantial overlap of the reactions in space that is observed (Fig. 11) indicates that they do not proceed sequentially as suggested by equilibrium thermodynamics, on the contrary, the data suggest that the system is far from equilibrium, which is likely attributable to a combination of variable reaction kinetics for the respective reactions (probably related to mineralogy and microbiological abundance and activity) and a heterogeneous grain-size or permeability distribution that may lead to the development of localized redox gradients at a scale that can not be resolved by the sampling.

With sustained pumping over several decades, the flux of DOC from the river will lead to depletion of the Mn(IV) and Fe(III) oxide minerals in the sediment. The pattern of depletion will be a function of the initial mineral abundance and distribution, the respective rates of oxide-mineral reductive dissolution, and the spatial variations in groundwater flux within the aquifer. However, over time, there should be a general trend toward depletion of Mn-oxides, followed by depletion of Fe oxides. The distribution of dissolved Mn and Fe in August 2003 is consistent with this expectation in that Mn concentrations are highest in the down-gradient region closest to the well, suggesting that Mn-oxide minerals have been depleted along an interface that migrates toward the well with time. The trend in concentrations of dissolved Mn in the water extracted from well PW5 (Fig. 12) is also consistent with the expectation that Mn-oxide mineral depletion will occur in the aquifer sediments.

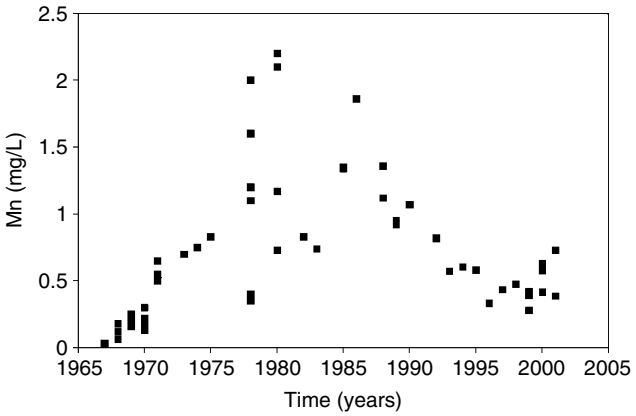


Figure 12. Manganese concentrations in the groundwater extracted from municipal well PW5.

SUMMARY

The Fredericton Aquifer is a typical semiconfined river-valley aquifer composed of glaciofluvial sand and gravel that is recharged by infiltration of water from a large river. Geophysical surveys have revealed a hydraulic connection to the Saint John River through an irregular-shaped window zone where the aquitard overlying the aquifer has been removed by erosion. Continuous profiling, using electromagnetic terrain conductivity meters deployed in small boats, proved to be the most effective way to delineate the window zone. The river water's moderately low conductivity (10 mS/m) and the relatively shallow depth to the aquitard, contributed to the method's high spatial resolution. Single channel seismic reflection profiles and a shoreline resistivity imaging survey provided important stratigraphic information and evidence to support the electromagnetic interpretation.

Two natural tracers, water temperature and ^{222}Rn, were used to determine downward flow velocities within the aquitard window located beneath the riverbed. Temperature data was collected continuously to determine seasonal variations and interpreted using heat transport modeling. ^{222}Rn activities for water samples from piezometers nests gave estimates of residence time, which were then used to compute infiltration velocities. The velocities derived from heat transport modeling and ^{222}Rn activities compared well with vertical average linear velocities ranging from 0.1 m/day to 5 m/day. Although these velocities are relatively high for subsurface flow, they are lower than typical velocities in engineered slow-sand filtration systems. As such, it is expected that filtration in the sediments located between the riverbed and production wells will be effective in removing micro-organisms. However, the seasonal occurrence of cold water temperatures in the sediments may cause a lower removal of micro-organisms during certain periods of the year.

The groundwater velocities and seasonal temperature variations measured in the aquifer below the river have a significant influence on the redox reactions that control the concentrations of DO, NO_3, Mn, Fe, and SO_4. The high velocities result in a large flux of reactants (DOC, DO, NO_3, and SO_4), thereby minimizing the potential that reaction rates will be reactant limited. The seasonal temperature fluctuations in the groundwater influence the reaction kinetics for chemical and microbiologically mediated reactions. The seasonal variations in temperature are considered the controlling influence on the aquifer redox conditions, with elevated temperature in late summer and fall contributing to increased reaction rates and a trend toward more reducing conditions. The data suggest that reductive dissolution of Mn oxide minerals as a consequence of sustained pumping over the past 40 years has resulted in the near depletion of Mn oxides along the infiltration flow path to well PW5.

This case study demonstrates the use of near-surface geophysical methods to define stratigraphic complexity in three dimensions, which controls spatial variability of the recharge flux. The geophysical results were especially useful for optimizing the layout of multilevel piezometer

nests and mini-piezometers used in the subsequent hydrogeological and hydrogeochemical investigations. The use of the natural tracers, temperature and ^{222}Rn, provides important information about the travel time between the river and the wells. This information allows for an assessment of risk associated with possible contamination events in the river. In addition, the temperature data are important in the interpretation of seasonal variations in groundwater chemistry. In general, riverbank filtration provides a reliable source of recharge to the wellfield in Fredericton. The filtration velocities in the aquifer sediments in the vicinity of PW5 are comparable with those in engineered slow-sand filtration systems. The principle disadvantage of riverbank filtration in this case study is elevated Mn concentrations that are related to the modification of redox conditions in the aquifer as a result of the infiltration of DOC from the river.

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BIBLIOGRAPHY

1. Kuehn, W. and Mueller, U. (2000). Riverbank filtration, an overview. *J. Amer. Water Works Assoc.* **92**: 60–69.
2. Ray, C., Soong, T.W., Lian, Y.Q., and Roadcap, G.S. (2002). Effect of flood-induced chemical load on filtrate quality at bank filtration sites. *J. Hydrol.* **266**: 235–258.
3. Malzer, H.-J., Gerlach, M., and Gimbel, R. (2000). Transport and fate of organic compounds during riverbank filtration. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 117–126.
4. Rismal, M. and Kopac, I. (2000). Riverbank filtration as pre-treatment of river water for artificial recharge of groundwater in Slovenia. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 183–196.
5. Duncan, D., Pederson, D.T., Shepherd, T.R., and Carr, J.D. (1991). Atrazine used as a tracer of induced recharge. *Ground Water Mon. Rev.* **11**: 144–150.
6. Bourg, A.C.M., Darmendrail, D., and Ricour, J. (1989). Geochemical filtration of riverbank and migration of heavy metals between the Deûle River and the Ansereuilles Alluvion-Chalk Aquifer (Nord, France). *Geoderma*. **44**: 229–244.
7. Waber, U.E., Lienert, C., and von Gunten, H.R. (1990). Colloid-related infiltration of trace metals from a river to shallow groundwater. *J. Contam. Hydrol.* **6**: 251–265.
8. Medema, G.J., Juhasz-Holterman, M., and Luijten, J.A. (2000). Removal of micro-organisms by bank filtration in a gravel-sand soil. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 161–168.
9. Wang, J.Z., Song, R., and Hubbs, S.A. (2000). Particle removal through riverbank filtration process. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 127–137.
10. Hiscock, K.M. and Grischek, T. (2002). Attenuation of groundwater pollution by bank filtration. *J. Hydrol.* **266**: 139–144.
11. Ray, C. (2002). Effect of biogeochemical, hydrogeological, and well construction factors on riverbank filtrate quality. In: *Riverbank Filtration: Understanding Contaminant Biogeochemistry and Pathogen Removal*. C. Ray (Ed.). Kluwer Academic Publishers, the Netherlands, pp. 1–16.
12. Jacobs, L.A., von Gunten, H.R., and Keil, R. (1988). Geochemical changes along a river-groundwater infiltration flow path: Glattfelden, Switzerland. *Geochim. Cosmochim. Acta*. **52**: 2693–2706.
13. Bourg, A.C.M. and Bertin, C. (1993). Biogeochemical processes during the infiltration of river water into an alluvial aquifer. *Environ. Sci. Technol.* **27**: 661–666.
14. Doussan, C., Ledoux, E., and Detay, M. (1998). River-groundwater exchanges, bank filtration, and groundwater quality: ammonium behaviour. *J. Environ. Qual.* **27**: 1418–1427.
15. Grischek, T., Worch, E., and Nestler, W. (2000). Is bank filtration under anoxic conditions feasible?. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 57–66.
16. Sacher, F., Brauch, H.-J., and Kuhn, W. (2000). Fate studies of hydrophyllic organic micro-pollutants in riverbank filtration. In: *Proceedings of the International Riverbank Filtration Conference, November 2000*. W. Jülich and J. Schubert (Eds.). IAWR, Amsterdam, the Netherlands, pp. 139–148.
17. von Gunten, H.R. et al. (1991). Seasonal biogeochemical cycles in riverborne groundwater. *Geochim. Cosmochim. Acta*. **55**: 3597–3609.
18. Bourg, A.C.M. and Bertin, C. (1994). Seasonal and spatial trends in manganese solubility in an alluvial aquifer. *Environ. Sci. Technol.* **28**: 868–876.
19. Thomas, N.E., Kan, K.T., Bray, D.I., and MacQuarrie, K.T.B. (1994). Temporal changes in manganese concentrations in water from the Fredericton Aquifer, New Brunswick. *Ground Water* **32**: 650–656.
20. Violette, G.G. (1990). *The application of a computer model to assess the potential effects of groundwater withdrawals from the Fredericton Aquifer*. Fredericton, N.B., MScE Thesis, University of New Brunswick, Department of Civil Engineering, Fredericton, NB, Canada.
21. TerrAtlantic Engineering Limited. (2000). *Development of the Groundwater Resource*. Fredericton, NB—status report: Unpublished report prepared for the City of Fredericton.
22. Petrunic, B.M., MacQuarrie, K.T.B., and Al, T.A. (2004). Reductive dissolution of Mn oxides in river-recharged aquifers: a laboratory column study. *J. Hydrol.* In press.
23. Butler, K.E., Nadeau, J.-C., Parrott, R., and Daigle, A. (2004). Delineating recharge to a river valley aquifer by riverine seismic and EM methods. *J. Env. Eng. Geophys.* **9**: 95–109.
24. McNeill, J.D. (1980). *Technical note TN-6, Electromagnetic Terrain Conductivity Measurements at Low Induction Numbers: Geonics Limited*. Mississauga, Ontario, Canada.
25. Nadeau, J.-C., Butler, K.E., Hunter, J.A., Burns, R., Douma, M., Good, R., and Veillette, N. (2004). Reflection and

Downhole Seismic Studies of a Glaciofluvial River Valley Aquifer. In: *Proceedings of 17th Symposium on Application of Geophysics to Engineering and Environmental Problems*. EEGS, pp. 1408–1419.

26. Logsdon, G.S., Kohne, R., Solomon, A., and LaBlonde, S. (2002). Slow sand filtration for small water systems. *J. Envir. Eng. Sc.* **1**: 339–348.
27. Lapham, W.W. (1989). *Use of temperature profiles beneath streams to determine rates of vertical ground-water flow and vertical hydraulic conductivity*. US Geol. Survey Water Supply Paper 2337.
28. Diersch, H.-J.G. (2004). *WASY Software FEFLOW® 5.1 Finite Element Subsurface Flow & Transport Simulation System User's Manual*. WASY, Berlin, Germany.
29. Hoehn, E. and von Gunten, H.R. (1989). Radon in groundwater: a tool to assess infiltration from surface waters to aquifers. *Water Resour. Res.* **25**: 1795–1803.
30. Champ, D.R., Gulens, J., and Jackson, R.E. (1979). Oxidation-reduction sequences in groundwater flow systems. *Can. J. Earth Sci.* **16**: 12–23.
31. Stumm, W. and Morgan, J.J. (1981). *Aquatic Chemistry*. John Wiley & Sons, New York.

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Water Encyclopedia: Oceanography; Meteorology; Physics and Chemistry; Water Law; and Water History, Art, and Culture (Vol. 4)
Water Encyclopedia: Ground Water (Vol. 5)

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