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Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary discipline, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with reactions in the environment. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways, thermodynamics and kinetics. An important purpose of this Handbook, is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various countries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment; firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental Chemistry to the above mentioned toxic substances laws is to develop

laboratory test methods, or mathematical correlations and models that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the Handbook is to present, in concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including some background information such as energetics and ecology. Volume 2 is concerned with reactions and processes in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volume 1, 2 and 3 was each more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes were divided in the parts A and B. Part A of all three volumes is now being published and the second part of each of these volumes should appear about six months thereafter. Publisher and editor hope to keep materials of the volumes one to three up to date and to extend coverage in the subject areas by publishing further parts in the future. Plans also exist for volumes dealing with different subject matter such as analysis, chemical technology and toxicology, and readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Environmental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses in Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all 52 authors from 8 countries for their understanding and for devoting their time to this effort. Special thanks are due to Dr. F. Boschke of Springer for his advice and discussions throughout all stages of preparation of the Handbook. Mrs. A. Heinrich of Springer has significantly contributed to the technical development of the book through her conscientious and efficient work. Finally I like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and to some colleagues and the secretaries for technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the National Research Council of Canada, before I could devote my full time of Environmental Chemistry, here in Amsterdam. I hope this Handbook may help deepen the interest of other scientists in this subject.

Amsterdam, May 1980

O. Hutzinger

Twentyone years have now passed since the appearance of the first volumes of the Handbook. Although the basic concept has remained the same changes and adjustments were necessary.

Some years ago publishers and editors agreed to expand the Handbook by two new open-end volume series: Air Pollution and Water Pollution. These broad topics could not be fitted easily into the headings of the first three volumes. All five volume series are integrated through the choice of topics and by a system of cross referencing.

The outline of the Handbook is thus as follows:

1. The Natural Environment and the Biochemical Cycles,
2. Reaction and Processes,
3. Anthropogenic Compounds,
4. Air Pollution,
5. Water Pollution.

Rapid developments in Environmental Chemistry and the increasing breadth of the subject matter covered made it necessary to establish volume-editors. Each subject is now supervised by specialists in their respective fields.

A recent development is the accessibility of all new volumes of the Handbook from 1990 onwards, available via the Springer Homepage springeronline.com or springerlink.com.

During the last 5 to 10 years there was a growing tendency to include subject matters of societal relevance into a broad view of Environmental Chemistry. Topics include LCA (Life Cycle Analysis), Environmental Management, Sustainable Development and others. Whilst these topics are of great importance for the development and acceptance of Environmental Chemistry Publishers and Editors have decided to keep the Handbook essentially a source of information on "hard sciences".

With books in press and in preparation we have now well over 40 volumes available. Authors, volume-editors and editor-in-chief are rewarded by the broad acceptance of the "Handbook" in the scientific community.

Bayreuth, July 2001

Otto Hutzinger

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Forword

Industrial chemicals are essential to support modern society. Growth in the number and quantity of chemicals during recent decades has been extraordinary resulting in an increase in quantity and complexity of hazardous waste materials (HWMs). Many of these HWMs will remain in the environment for long periods of time, which has created a need for new methods for environmentally safe and efficient disposal including recycling and/or reuse of these complex materials. In many areas, existing landfills are reaching capacity, and new regulations have made the establishment of new landfills difficult. Disposal cost continues to increase, while the waste types accepted at solid waste landfills are becoming more and more restricted.

One answer to these problems lies in the ability of industrialized society to develop beneficial uses for these wastes as by-products. The reuse of waste by-products *in lieu* of virgin materials can relieve some of the burdens associated with disposal and may provide inexpensive and environmentally sustainable products. Current research has identified several promising uses for these materials. However, research projects concerning Environmental Impact Assessment (EIA) of various organic and inorganic contaminants in recycled complex mixtures and their leachates on surface and ground waters are still needed to insure that adverse environmental impacts do not result.

Answers to some of these concerns can be found in the present book, entitled "Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters". This book is an attempt to comprehensively understand the potential impacts associated with recycled wastes. The book is divided into three main volumes, each with specific goals.

The first volume of the book is subtitled "Concepts, Methodology and Chemical Analysis". It focuses on impact assessment and decision-making in project development and execution by presenting the general principles, methodology and conceptual framework of any EIA investigation. It discusses various sustainable engineering applications of industrial wastes, such as the reuses of various solid wastes as highway construction and repair materials, scrap tires in hydraulic engineering projects, and biosolids as soil amendments. It also evaluates several chemical and ecotoxicological methodologies of waste leachates, and introduces a unique "forensic analysis and genetic source partitioning" modeling technique, which consists of an environmental "molecular marker" approach integrated with various statistical/mathematical modeling

tools. In addition, several case studies are presented and discussed, which: (a) provide comprehensive information of the interaction between hydrology and solid wastes incorporated into highway materials; (b) assess potential ecological risks posed by constituents released from waste and industrial by-products used in highway construction; and (c) describe the processes and events that are crucial for assessing the contaminant leaching from roads where residues are used as construction material by using interaction matrices.

The second volume of the book, subtitled "Risk Analysis", is problem-oriented and includes several multi-disciplinary case studies. It evaluates various experimental methods and models for assessing the risks of recycling waste products, and ultimately presents the applicability of two hydrological models such as MIKE SHE and MACRO. This volume is also background information-oriented, and presents the principles of ecotoxicological and human risk assessments by: (a) discussing the use of the whole effluent toxicity (WET) tests as predictive tools for assessing ecotoxicological impacts of solid wastes and industrial by-products for use as highway materials; (b) providing information on the concepts used in estimating toxicity and human risk and hazard due to exposure to surface and ground waters contaminated from the recycling of hazardous waste materials; and (c) introducing an advanced modeling approach that combines the physical and chemical properties of contaminants, quantitative structure-activity and structure-property relationships, and the multicomponent joint toxic effect in order to predict the sorption/desorption coefficients, and contaminant bioavailability.

The third volume of the book is subtitled "Engineering Modeling and Sustainability". It presents, examines and reviews: (a) the fundamentals of important chemodynamic (i.e., fate and transport) behavior of environmental chemicals and their various modeling techniques; (b) the equilibrium partitioning and mass transfer relationships that control the transport of hazardous organic contaminants between and within highway construction materials and different phases in the environment; (c) several physical, chemical, and biological processes that affect organic chemical fate and transport in ground water; (d) simulation models of organic chemical concentrations in a contaminated ground water system that vary over space and time; (e) mathematical methods that have been developed during the past 15 years to perform hydrologic inversion and specifically to identify the contaminant source location and time-release history; (f) various case studies that demonstrate the utility of fate and transport modeling to understand the behavior of organic contaminants in ground water; (g) recent developments on non-aqueous phase liquids (NAPL) pool dissolution in water saturated subsurface formations; and (h) correlations to describe the rate of interface mass transfer from single component NAPL pools in saturated subsurface formations.

In addition, this volume examines various hazardous waste treatment/disposal and minimization/prevention techniques as promising alternatives for sustainable development, by: (a) presenting solidification/stabilization treatment processes to immobilize hazardous constituents in wastes by changing

these constituents into immobile (insoluble) forms; binding them in an immobile matrix; and/or binding them in a matrix which minimizes the material surface exposed to weathering and leaching; (b) providing an overview of waste minimization and its relationship to environmental sustainability; (c) portraying the causes of sustainability problems and diagnosing the defects of current industrial manufacturing processes in light of molecular nanotechnology; and (d) analyzing and extrapolating the prospect of additional capabilities that may be gained from the development of nanotechnology for environmental sustainability.

It is important to mention that information about EIA of recycled wastes on surface and ground waters is too large, diverse, and multi-disciplined, and its knowledge base is expanding too rapidly to be covered in a single book. Nevertheless, the authors tried to present the most important and valid key principles that underlie the science and engineering aspects of risk analysis, characterization, and assessment.

It is hoped that the present information help the reader continue to search for creative and economical ways to limit the release of contaminants into the environment, to develop highly sensitive techniques to track contaminant once released, to find effective methods to remediate contaminated resources, and to promote current efforts toward promoting environmental sustainability.

Seattle, Washington, USA
March, 2005

Tarek A. Kassim

Environmental Impact Assessment: Principles, Methodology and Conceptual Framework

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Abstract Public approval of an environmental analysis and impact assessment project is usually coupled with different conditions that the project is required to meet. Environmental impact assessment (EIA) constitutes an important basis for decisions regarding possible imposition of conditions. The main focus of the present chapter is to clarify the roles that EIAs can have in such decision-making processes.

The present chapter discusses and reviews the various types of environmental impacts (natural and man-made); the need for EIA data and its proper handling; the different environmental administrative procedures used in EIA projects; the EIA characteristics (in terms of their goals, impact indicators, impact estimation, applicability); the different EIA methods; and a general conceptual framework that could be applied to any environmental project.

Keywords Impact assessment · Methodology · Conceptual framework · Assessors

Abbreviations

AP	Administrative Procedures
EAIA	Environmental Analysis and Impact Assessment
EIA	Environmental Impact Assessment
IA	Impact Assessment
SIA	Social Impact Assessment

1**Introduction**

Environmental impact assessment (EIA) is an activity designed to identify and predict the impact on the biogeophysical environment and on man's health and well-being of legislative proposals, policies, programs, projects, and operational procedures, and to interpret and communicate information about the impacts [1–10]. Although the institutional procedures to be followed in the assessment process have been formalized, the scientific basis for these assessments is still rather uncertain [11–18]. The literature published on the subject is scattered through many journals, and has not been evaluated critically in ways that are useful to environmental scientists, engineers and managers. It is important to mention that the environmental assessor is sometimes unaware of the fact that the main task is not to prepare a scientific treatise on the environment, but rather to help the decision-maker select from amongst several choices for development and then to consider appropriate management strategies.

The term EIA is also used broadly to include a whole range of social and economic impacts. Social impact assessment (SIA) and economic analysis are seen as being quite distinct from an EIA in the organizations involved, professional skills used, and methodological approaches [19–23]. No matter how the terms are used, it is important to recognize that impacts on ecosystems, and biogeochemical cycles, are intimately related through complex feedback mechanisms to social impacts and economic considerations. The social impacts of any project that involves environmental changes should be studied in close association with studies of biosphere impacts [88–91].

Recognizing the need for a comprehensive review, discussion and synthesis of current EIA practices, the present chapter introduces various views about EIA, its principles, methodology, and general conceptual framework which could be used for any environmental analysis and impact assessment (EAIA) project.

2**Environmental Impact**

The next few paragraphs will give information about the different terms used in environmental impact studies, the types of natural and man-made impacts, and address how to identify an environmental change.

2.1

Terminology

A number of terms have been used by several researchers and policy makers [24–25] to distinguish: (a) between natural and man-made environmental changes; and (b) between changes and the harmful and/or beneficial consequences of such changes. In one approach, a man-induced change is called an *effect*, while the harmful and/or beneficial consequences are called *impacts*. Sometimes, an impact could be beneficial to some citizens but harmful to others. Another convention is to use the term *impact* to denote only harmful effects. In still other countries, the words *effects* and *impacts* are synonymous and deleterious effects are termed *damage*. No matter how the words are defined, however, a *change/effect/impact* is usually given in terms of its nature, magnitude, and significance.

In the present chapter, the distinction will be maintained that a *change* can be natural and/or man-induced, that an *effect* is a man-induced change, and that an *impact* includes a value judgment of the significance of an *effect*.

2.2

Natural and Man-Made

Even in the absence of man, the natural environment undergoes continual change. This may be on a time-scale of: (a) hundreds of millions of years, as with continental drift and mountain-building; (b) tens of thousands of years, as with the recent Ice Ages and the changes in sea level that accompanied them; (c) hundreds of years, as with the natural eutrophication of shallow lakes; or (d) over a period of a few years, as when a colony of beavers rapidly transforms dry land into swamp.

Superimposed on natural environmental changes are those produced by man. The rate increased with the development of industry as muscle power was replaced by energy derived from fossil fuels, until during the last few decades human impacts have reached an unprecedented intensity and affect the whole world, due to a vastly increased population and higher consumption per capita.

Man's increasing control of his environment often creates conflicts between human goals and natural processes. In order to achieve greater yields, man deflects the natural flows of energy, by-passes natural processes, severs food chains, simplifies ecosystems, and uses large energy subsidies to maintain delicate artificial equilibria. In some cases, these activities may create surroundings that man considers desirable. Nevertheless, conflicts often arise between strategies that maximize short-term gains and those that maximize long-term benefits. The former sometimes require a penalty of irreversible environmental degradation.

Perceptions about environmental impacts can be rather different in diverse countries. Where poverty is widespread and large numbers of people do not have adequate food, shelter, health care, and education, the lack of develop-

ment may constitute a greater aggregate degradation to life quality than do the environmental impacts of development. The imperative for development to remedy these defects may be so great that consequent environmental degradation may be tolerated. The pervasive poverty in the underdeveloped nations has been spoken of as the *pollution of poverty*, while the widespread social and environmental erosion in the developed nations has been characterized in its advanced state as the *pollution of affluence*. While it is clear that decisions will and should be made based upon different value judgments concerning the net cost-benefit assessments about environmental, economic, and social impacts, it is now widely accepted that development can be planned to make best use of environmental resources and to avoid degradation. The process of EIA forms a part of the planning of such environmentally sound development [26–30].

In developing countries a special challenge is to stimulate development processes at the local level. If such a process can be inaugurated broadly, the fruits of development may reach more of the segments of the population than do the large, centralized schemes. Better adapted development projects and programs are apt to engender broader public support and cause less undesirable social displacement than a few large centralized projects.

The emerging recognition that sources of energy, for example, can be better utilized, that materials can be recycled more effectively, and that some pollution problems can be alleviated or largely avoided by prudent, locally scaled activity forms a basis for encouraging wider use of such objectives in development activities, both in industrialized and developing nations. The term *eco-development* has been used to describe this approach [31–33]. The success of environmentally sound development depends on proper understanding of social needs and opportunities and of environmental characteristics. For this reason, some forms of EIA are appropriate to local development as well as to large centralized projects.

Environmental problems are clearly linked to unbalanced development. This is why EIA, as a component of sound development planning, is particularly important. But these countries face a dilemma. Their need for environmental change is very great. Their resources of trained scientists to participate in environmental surveys and impact assessments are very slender. And a lack of finance, training, and infrastructure may restrict the development modes open to them. The simple transfer of the technologies now employed in the developed nations – including their methods of environmental impact assessment – may not be the best way to alleviate these problems.

Planning and management of land and water still present major problems in the industrialized countries, for example in containing urban sprawl, constructing highways and airports, maintaining the quality of lakes and estuaries, and preserving wilderness areas [34–40]. Many of these problems are associated with the massive and mounting demands for energy and water by industry and a consumer society, and are present only in embryonic form in the less developed countries.

The production of novel chemicals has introduced new environmental hazards and uncertainties. The addition of large amounts of biodegradable sub-

stances to the environment has accelerated the eutrophication of rivers and lakes, where these materials or their metabolites accumulate. Non-biodegradable compounds may be less conspicuous but more dangerous. Some are concentrated as they pass through food chains and endanger the health of man and his domestic animals, as well as that of numerous other species of wildlife.

Several crisis episodes attract much attention, but long-term exposure to moderate degrees of pollution may be a more serious threat to human health. Acute or even chronic human toxicity is only one part of the pollution problem; pollutants also have implications for the long-term maintenance of the biosphere. The short-term problems are much simpler, and are amenable in part to narrowly compartmentalized pragmatic solutions. Long-term effects of pollutants are insidious, chronic, and often cumulative. Ecologists must ask what effects these pollutants have on the structure of natural ecosystems and on biological diversity, and what such changes could mean to the long-term potential for sustaining life.

2.3

Problem Identification

When a project or a program is undertaken, it sets in motion a chain of events that modifies the state of the environment and its quality. For example, a major highway construction changes the physical landscape, which may, in turn, affect the habitat of some species, thus modifying the entire biological system in that area [1–2, 41–42]. The same highway affects land values, recreational habits, work-residence locations, and the regional economy. These various factors are interrelated, so that the net result is difficult to predict. A confounding

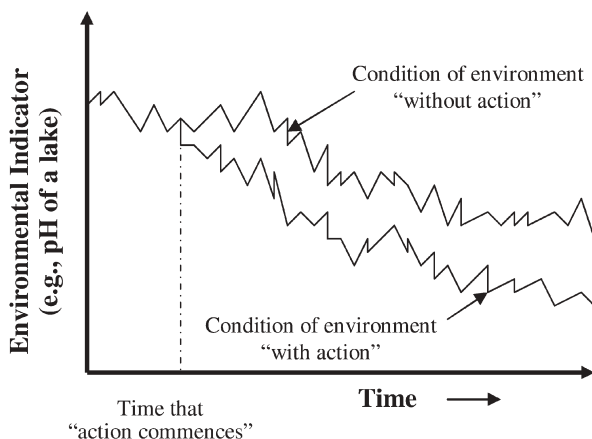


Fig. 1 Conceptual framework for assessing environmental changes. (The reference condition is the *without-action* condition and, because of naturally occurring changes, is not necessarily the present condition. The downward slope of the curves is for illustration only)

factor is that if the project were not undertaken, the environment would still exhibit: (a) great variability (due to, for instance, variations in weather and climate, natural ecological cycles and successions); (b) irreversible trends of natural origin (from the eutrophication of lakes for example); and (c) irreversible trends due to a combination of natural and man-induced factors (such as overgrazing, salinization of soils).

One of the problems for the environmental impact assessor, as indicated schematically in Fig. 1, is to identify the various components of environmental change, due to the interacting influences of man and nature. It also implies no value judgment of whether environmental change is *good* or *bad*. However, at some stage in the assessment or the decision-making process, such a judgment must be made.

3 EIA Data

Data are sets of observations of environmental elements, indicators or properties, which may be quantitative or qualitative. Scientists are accustomed to reserving judgment on environmental questions until they have adequate data [1–3, 41–45]. When preparing an EIA, however, the environmental impact assessor must often make predictions based on incomplete and sometimes irrelevant data sets. Sometimes, an over-abundance of data is available; but in undigested form. This flood of information would only confuse the readers of an EIA. The task of the assessor is, therefore, to select those observations that are relevant and sufficiently accurate for the problem under study. The selection process should be done in an objective manner. The sections that follow outline some of the problems that are commonly encountered in obtaining, assessing, and presenting data pertinent to environmental analysis and impact studies.

3.1 Needs

Many scientists, engineers, and environmental agencies are generating data. Individuals tend to be *discipline-oriented*, while agencies are *mission-oriented*. In either case, the data may seem to be deficient for use in broad interdisciplinary environmental studies. In many instances, however, the deficiency is imagined and reflects the fact that individuals are vaguely aware of available sources of data in other disciplines. The environmental impact assessor often overlooks rich sources of information resident in experienced individuals or organizations. The public, for example, is seldom invited to contribute its views about values, and needs. In general, there are two philosophies of data collection [46–49]:

- The *accounting theory* assumes that the subsequent use of data is independent of collection methods. An accountant believes that it is possible to col-

- lect data in some neutral sense, and that any subsequent manipulation can be justified if it contributes to the understanding of a problem.
- The *statistical theory* insists on the essential interdependence between the ways in which data are collected and the methods of analysis that are appropriate for these data. The collection methods limit the range of analysis methods that may be employed.

Much of the discussion on data collection and data banks assumes acceptance of the accounting theory of data manipulation. In contrast, most, if not all, of the available methods for handling numerical data assume the statistical theory of data collection, management, and manipulation.

The data sets available at the outset of an impact assessment are mostly of the first type. However, the environmental impact assessor will be guided to a certain extent in the selection of data sets by knowledge of the physical, biological, social and/or economic systems they are studying. Conversely, however, the data sources available within a region will influence the nature of the perceptual models used in the assessment. Where there are few data, the analysis will not include much detail. Supplementary data collected during the impact assessment should preferably be of the second type. The data should be sufficient to enable the prediction of an impact to be made within specified confidence limits. The amount to be collected, the frequency, precision, accuracy, and type are dependent upon the known variability of the element in space and time. Where the variability is unknown, it must be determined by a pilot study.

In general, errors in field data include those resulting from the instrument and those introduced by the observer. Unless the instrumentation is very specialized, the measured value is rarely the same as the true value. However, standardized observational procedures tend to minimize errors to the point that many data can be used directly without concern about quality. They also tend to ensure that data biases are similar from one location or time to another, so that the data, if not accurate, are at least comparable.

3.2 Interpretation

Having selected some environmental data sets, the assessor should next try to determine their information content (to search for patterns, trends, and correlations) and test for statistical significance.

The interdisciplinary nature of environmental assessments challenges the assessor and his staff. Even within the natural sciences, specialists in different fields may use a phrase in quite different ways. Even greater difficulties occur when natural and social scientists attempt to communicate with one another.

Inevitably, the varied nature of environmental problems leads scientists to use all information which does not fall within their sphere of specialization. Time and other constraints may cause them to do this without due regard for the accuracy and representativeness of the data.

3.3

Data Banks

Data banks and retrieval systems speed up the impact assessment process by optimizing the use of existing data and by helping to eliminate wasteful redundancy [50]. These systems work well if they have been designed and managed carefully. However, the limitations of data banks should be appreciated. The development of a very large, all-inclusive system could lead to a morass of data, sometimes with large amounts never being used. Furthermore, the data within such a system may contain hidden traps. A lack of an updating procedure is a related impediment.

The discipline-based data systems that have been developed for national environmental purposes provide large sources of quality controlled data. However, the observing sites may not always be representative of the proposed development site. In addition, because the acquisition of environmental data is undertaken by a variety of governmental departments, organizations, and individuals, there may be data gaps and incompatibilities amongst systems. A data system is needed wherein information from these diverse sources can be put readily at the disposal of the environmental impact assessor in the desired form. Special attention must also be given to the ways in which data are stored so that they may be recalled in sub-sets convenient for comparison and modeling.

3.4

Presentation and Exchange of Information

Data may be presented directly or in summarized form, such as on maps and graphs. However, since humans respond visually in different ways to different geometric forms and arrays, a scientifically correct diagram may sometimes be misleading. Care is therefore required to ensure that the interpretative materials convey exactly what is intended. Large data sets are sometimes reduced to small sets with the aid of empirical or physical models. Dimensional analysis often permits several variables to be collapsed to a single new parameter. In this connection, it is important to note that empirical models cannot be extrapolated with assurance to new situations [50, 51].

The mere fact that information exists does not ensure availability to prospective users. Communication links between major interest groups must therefore be established. At an early stage of an impact assessment, these groups and their respective needs must be identified as a basis for developing inventories of relevant data sources and procedures for exchanging data amongst users.

3.5

Acquisition, Analysis and Processing

The principles which must be followed by the environmental impact assessor concerning data, their acquisition, analysis, and processing should include the following points [52–56]:

- Standardization of units, sampling methods, criteria, classification, cartographic scales, and projections are essential.
- Because information required for EIAs is often widely scattered, the need for data storage and retrieval capabilities is particularly important.
- The environmental databases should always be clearly identified in terms of quantity, quality, and character to ensure that they are not misemployed or misinterpreted by the reviewer.
- Data should be consistent with respect to sampling and averaging times, time lags, and measurement locations.
- Statistical tests should be carried out to ascertain the significance, errors, frequency distributions, and other characteristics of data that are used as a basis for subsequent analysis.
- The methods of data synthesis, as well as the physical constraints on data use (like threshold effects), should be clearly identified.
- The precision and accuracy demanded for the resolution of problems should be clearly defined prior to establishing supplementary data networks.
- Empirical relationships may not be transposable. Extreme caution must be employed in using relationships that were not developed for the project; their validity should be established by pilot programs.
- New technology should not be overlooked. New systems and sensors may greatly facilitate supplementary data acquisition.

4

Administrative Procedures

Attention is directed in this part of the present chapter to the administrative procedures (APs) required to support the EIA process. The general framework to be described here is applicable to a wide range of national and international environmental laws, policies, and social customs. The procedures can be utilized in their simplest form but may be expanded according to the number of trained specialists locally available for undertaking EIAs.

The details are shown schematically in Fig. 2. The relationships between the various *players* and their *roles* vary from country to country but the *cast of players* must be designated. Those involved may include: the decision-maker, environmental impact assessor, project proponent, assessment reviewer, central and local government agencies, the public at large, special interest groups, expert advisors, and governments in adjacent jurisdictions, the legislative branch of government, and the judiciary.

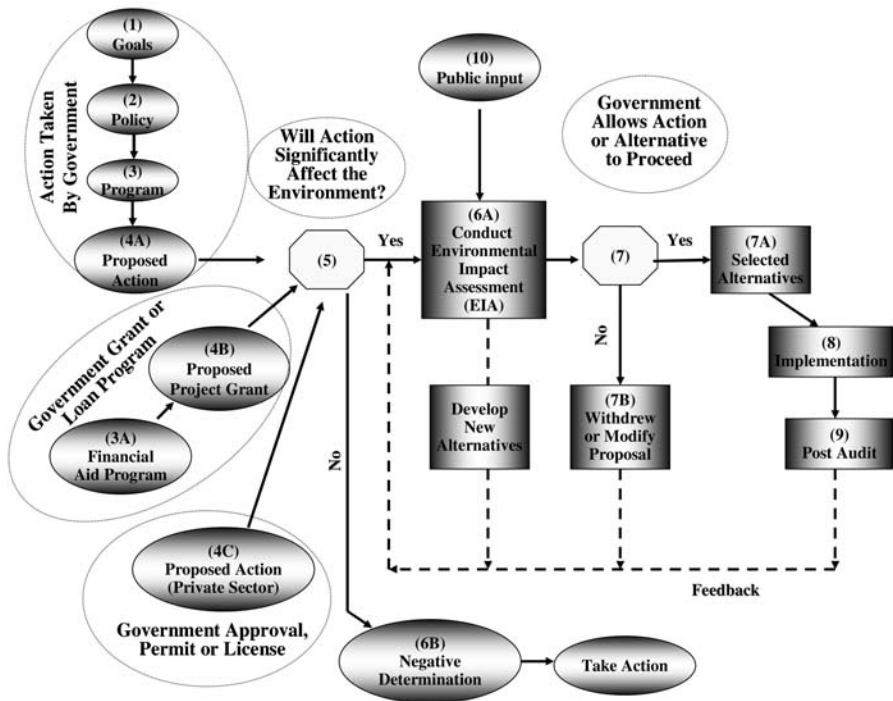


Fig. 2 EIA as an integral part of the planning and decision-making process

4.1

Administrative Design Factors

A number of points about administrative procedures (APs) should be considered when establishing an EIA process [57–59]:

- The *decision-maker* is a single point of authority or responsibility where the decision is made. The decision may be: (a) to proceed; (b) not to proceed; (c) to refer back the proposal for modification; or (d) to transfer responsibility for making a decision to a higher or to a lower level of responsibility. Clearly, there must be a decision-making process with well-defined terms of reference at the management level where the proposal is being considered.
- The decisions are often *shaped* rather than *made* or *taken*. Everyone involved in policy formulation, planning, impact assessment studies, public hearings, reviews, and legislative and media debates is in fact playing a part in shaping the decision. The final responsibility rests with a responsible person (or group) whose signature appears on the relevant document. This emphasizes that EIAs should not be considered only at the time of presentation of an impact statement to a decision-maker. Rather, environmental considerations should be included throughout the entire planning process.

- Environmental assessment should be a continuing activity, not only prior to the decision point but also afterwards. An EIA should be considered as an adaptive process, with review and updating of the EIA document periodically after the project/action has been completed.
- One defect in the way that EIAs tend to be carried out is that they are oriented to specific projects or proposals. There is often no mechanism for examination of many projects in *aggregate*. Therefore, it is possible that the impacts of an array of proposals would be found individually acceptable, although their effects, when taken together, would not. It, therefore, seems desirable to develop the concept of impact assessment at the program or policy level.
- An important question that needs to be resolved in each jurisdiction is whether EIAs should be undertaken by the *proponents* (whether they be in the public or in the private sector), by an independent body, or by a small team drawn from proponents, environmental scientists, and representatives of those with whom decisions rest.
- EIAs need to be *reviewed* by an independent body for relevance, completeness, and objectivity. The reviewer may be a government department or separate body. But whatever mechanism is chosen, the objective is to ensure compliance, with the spirit as well as the fine print of the environmental law, with established procedures and guidelines, including appropriate time-tables.
- The review process could include study by specialists on the staff of the review authority, study by other designated experts, or both. Public participation is often desirable, as the perceptions of specialists may differ markedly from those of the public. Ways in which this might be accomplished include the: (a) appointment of private citizens to the review authority; (b) establishment of regional planning committees to include members of the public; (c) canvassing of elected representatives; (d) public hearings; and (e) seminars or workshops.
- APs should include a provision for post-auditing of actions, to ensure compliance with the requirements and to test the validity of the predictions contained in the EIA.
- Guidelines concerning APs should be prepared and made public.

4.2

Sequence of Environmental Planning/Decision-Making

In Fig. 2, individual functions in the planning/decision-making process are numbered, 1 through 10. These are not necessarily separate operations in time or place, nor are they necessarily performed by separate individuals or institutions. It is emphasized that the detailed way in which the environmental planning system operates depends upon the approach taken within a particular jurisdiction. The diagram (Fig. 2) is presented mainly to show the relationship of one function to the next, particularly the relationship of the assessment

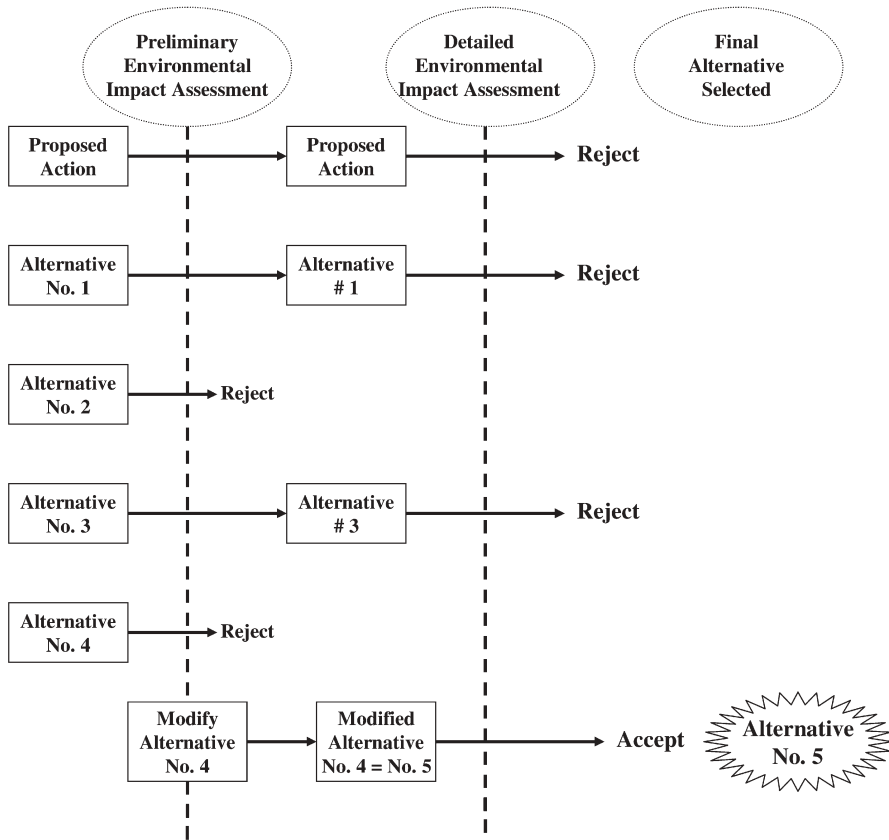


Fig. 3 The consideration of alternatives to achieve a goal

procedure to the overall decision-making process. Figure 3 shows an iterative procedure for the consideration of alternatives to achieve certain goals. In addition, Table 1 discusses the various sequences of environmental planning and decision-making.

The main focus of the present book, entitled *Environmental Impact Assessment of Recycled Wastes on Surface and Groundwaters*, is mainly on functions 5–7, but it is necessary to consider the entire sequence in order to fully appreciate the linkages and relationships.

4.3

The Players

The responsibilities of individuals and groups of individuals who participate in the EIA process vary. In each case, the roles should be explicitly delineated, and the procedure to be followed should be understood by all the players,

Table 1 Sequence of environmental planning and decision-making (schematically shown in Fig. 2)

Process step	Purpose	Description (see also Fig. 2)
Step 1	Goals establishment	- Governments and their officials set goals - These goals, general or specific, would establish the framework within which environmental policies, programs, and actions are implemented - If one goal is to ensure that environmental considerations receive adequate attention in the planning and implementation of actions, an EIA procedure is a way in which this can be achieved
Steps 2 and 3	Policy and program establishment	- The goal-setting process must be translated into actions <i>via</i> policy and program activities - It is important to ensure that environmental considerations are raised and taken into account by the decision-maker as early as possible in the planning process and not almost as an afterthought, just before a final decision is taken (in Step 7) - This can be accomplished with a formal EIA of goals, policies, or programs, in addition to the more usual EIAs of <i>action</i>
Step 4	Actions	Actions may originate in several ways: - (4A): solely through programs of the central government - (4B): through programs initiated by local levels of government or in the private sector, but supported financially through grants or loans from the central government - (4C): through programs initiated by local levels of government or in the private sector, but subject to approval or licensing by the central government
Step 5	Significant impact determination	- The evaluation of whether a proposal will significantly affect the environment is a first screening of the proposal to decide whether or not a detailed EIA will be required, and to ensure that a range of alternatives is examined - This may be a simple judgment by the responsible official or advisory body, or it may be based on a formal document, brief but relevant, prepared by a small group of specialists

Table 1 (continued)

Process step	Purpose	Description (see also Fig. 2)
Step 5	Significant impact determination	- If the responsible person or group decides that a proposed action will not significantly affect the environment, then a so called <i>negative determination</i> is made (Step 6B) which may involve a public notice or explanation; steps are then taken to proceed with the proposed action responsible person a group simply identifies such cases
Step 6	Environmental impact assessment	- If a proposed action is believed to have potentially significant impacts on the environment, then an EIA is performed on the proposed action and on feasible alternatives (Step 6A) - It is at this point that the public may provide input into the process in many countries (Step 10) - An important potential result of the EIA process is the development of new alternatives that may lessen the environmental impacts - These will be fed back into Step 6, so that an iterative process may eventually allow the project to proceed to Step 8
Step 7	Decision-making	- After review of the EIA (Step 6), the decision-maker may decide that the action should proceed (Step 7A) or that it is environmentally unsatisfactory (Step 7B) - In the latter case, the proposed action may either be withdrawn, or be modified and fed back again into the EIA process - The decision-maker will make a wise decision, although the task is not easy because of the large number of political, environmental, and other factors which often conflict with one another - Sometimes the EIA itself will contain conflicting objectives (such as the maintenance of water quality at the expense of air quality) - The environmental impact assessor will usually assign a system of weights when he makes his recommendations

Table 1 (continued)

Process step	Purpose	Description (see also Fig. 2)
Step 7	Decision-making	- However, the various components should be clearly separated in order that the reviewer and the decision-maker may change these weights to accommodate other considerations such as the relative political sensitivities of neighboring countries to releases of air versus water pollutants
Step 8	Implementation	- Implementation involves several functions: detailed planning, design, and operation - Implementation may be carried out by a designated government agency or by others - In the case of non-governmental implementation, there is still a responsibility within government to ensure compliance with regulations and standards
Step 9	Post-audit	- The whole implementation process (including planning, initiation, and operation) should remain under review to ensure that the designated environmental quality standards are achieved by continued monitoring of certain features of the environment - Such data be used to verify the predictions made for the selected alternative, and also may contribute to the improvement of future assessments - The continuing review may improve the goal-setting and decision-making processes by providing information on the environmental effectiveness of each action - It is recommended that reasonably comprehensive post-audits of EIAs be made a year or so after completion of the actions, to determine the accuracy of the pre-assessment process and to advance the scientific basis for impact assessments

including the public. The following points should be taken into consideration about the various players in EIA process [60–62]:

- *Decision-maker*: can be a head of state, a group of ministers, an elected body, or a single designated individual.
- *Assessor*: is the person, agency or company with responsibility for preparing the EIA.
- *Proponent*: can be a government agency or a private firm wishing to initiate the project.
- *Reviewer*: is the person, agency or board with responsibility for reviewing the EIA and assuring compliance with published guidelines or regulations.
- *Other government agencies*: are agencies with a special interest in the project. They may be components of the national government services or they may be associated with provinces, states, cities or villages.
- *Expert advisors*: are persons with the specialized knowledge required to evaluate the proposed action. They may come from within or outside the government service.
- *Public at large*: includes citizens and the press.
- *Special interest groups*: includes environmental organizations, labor unions, professional societies, and local associations.
- *International*: refers to neighboring countries or intergovernmental bodies, and indicates the need in some cases for consultations with these bodies.

5

EIA Characteristics

The next few paragraphs discuss the general characteristics of EIAs, their goals, impact indicators, impact estimation and applicability.

5.1

Goals

An EIA should: (a) describe the proposed *action*, as well as alternatives; (b) estimate the nature and magnitudes of the likely environmental changes; (c) identify the relevant human concerns; (d) estimate the significance of the predicted environmental changes (estimate the *impacts* of the proposed action); (e) make recommendations for either acceptance of the project, remedial action, acceptance of one or more alternatives, or rejection; (f) make recommendations for inspection procedures to be followed after the action has been completed. An EIA should contain three subsections relating to environmental effects (Fig. 1), as follows [3–10, 63–65]:

5.1.1

Establishing the Initial Reference State

Assessment of environmental change pre-supposes knowledge about the present state. It will be necessary to select attributes that may be used to estimate this state. Some of these will be directly measurable; others will only be capable of being recorded within a series of defined categories, or ranked in ascending or descending order of approximate magnitude. At worst, it will be necessary to record the state of the environment by the presence or absence of some of the attributes. Difficult decisions will need to be made about the population (in a statistical sense) which is to be represented by the measured variables, and the extent to which sub-division of this population into geographical regions, ecosystems, and so on, is either feasible or necessary. In fact, it must be emphasized that the establishment of an initial reference state is difficult; not only are environmental systems dynamic but they contain cyclical and random components. An initial state cannot therefore be described satisfactorily with a once-off survey; even with a regular monitoring program, a description of an existing environmental state still contains a degree of subjectivity and uncertainty.

5.1.2

Predicting the Future State in the Absence of Action

In order to provide a fair basis for examining human impacts, future environmental states in the absence of action must be estimated. The populations of a species of animal or fish may already be declining (which can be schematically represented in Fig. 1), due to over-grazing or over-fishing, even before a smelter is built. This part of the analysis is largely a scientific problem, requiring skills drawn from many disciplines. The prediction will often be uncertain, but the degree of uncertainty should be indicated in qualitative terms at least.

Predictions of the behavior of biological sub-systems and their responses to environmental stresses are also subject to uncertainty. Fortunately, there are mathematical techniques for describing these uncertainties and subjecting them to critical analysis. The decision-maker should be aware of the degree of uncertainty that surrounds the predicted state of the environment and have some understanding of the methods by which this uncertainty is calculated.

5.1.3

Predicting the Future State in the Presence of Action

For each of the proposed actions, and for admissible combinations of these actions, there will be an expected state of the environment which is to be compared with the expected state in the absence of action. Consequently, predictions similar to those outlined in the subsection above must be derived for

each of the proposed alternatives. Forecasts will be required for several time-scales, both for the *with* and the *without* action cases.

5.2

Impact Indicators

An *impact indicator* is an element or parameter that provides a measure of the significance of the effect (in other words of the *magnitude* of an environmental impact). Some indicators, such as mortality statistics, have associated numerical scales. Other impact indicators can only be ranked on simple scales such as *good-better-best* or *acceptable-unacceptable*.

The selection of a set of indicators is often a crucial step in the impact assessment process, requiring an input from the decision-maker. In the absence of relevant goals or policies, the assessor may suggest some indicators and scales, but he should not proceed with the assessment until his proposals are accepted.

The most widely used impact indicators are those such as air and water quality standards that have statutory authority. These standards integrate in some sense the worth that a jurisdiction places on clean air and clear water [66–70]. The numerical values have been derived from examination of the available toxicological data relating pollutant dosages to health and vegetation effects, combined with a consideration of best practical technology. Admittedly the evidence is sometimes incomplete and controversial, but the assessor should accept the derived standards. The impact assessment process is not the appropriate forum for debates on the validity of numerical values. A possible exception occurs when, in the absence of national standards, a local decision-maker or an overseas engineering firm decides to employ standards borrowed from another jurisdiction. Toxicological evidence based on temperate-zone studies cannot always be confidently extrapolated to the tropics or to the arctic.

After the impact indicators and their scales are selected, their values must be estimated from the predicted values of the environmental effects for each project alternative and for several time-scales.

5.3

Impact Estimation

In some defined way, the description of the environment must be collapsed to the behavior of a few variables, which must then be related to the impact indicators. An objective, although not always achievable, is that for each of the proposed actions and for each of the human concerns, the expected outcomes can be compared on numerical scales.

The original measurement units for the impact indicators will normally be quite different: some may be numerical, while others are in the form of a series of classes. At this point in the analysis, therefore, the environmental impact assessor should convert the scale into a comparable set using some system of

normalization. In the most primitive system, each indicator is rated as being *significant-positive*, *insignificant*, or *significant-negative*; the numbers of positive and of negative counts are then compared [5–8]. Because some human concerns are frequently more important than others, however, a series of weights may be assigned to the concerns.

Having estimated the environmental impacts of the proposed action, the assessor next needs to make recommendations. The wisdom of these recommendations depends greatly on the extent to which there is discussion spanning many disciplines among the assessor's staff and advisors. This group of people should include scientists, engineers, sociologists, and economists, each of whom feels a personal commitment and sense of excitement.

5.4

Applicability

EIAs have been most widely used in the industrialized countries, but they have general applicability, provided that they take into account not only the physical and biological characteristics of a particular region but also its local socio-economic priorities and cultural traditions. Countries, and often different provinces within a country too, are at different stages of economic development, and have different priorities, policies, and preoccupations. The probable adverse consequences of any development must be weighed against estimated socio-economic benefits. What is unacceptable will vary greatly from one country or situation to another.

In developing countries particularly, the process of elaborating EIAs must in no way be viewed as a brake or obstacle to economic development, but rather as a means for assisting in planning the rational use of the country's natural resources. This is because the economic development and prosperity of whole nations are tied to the successful long-term management of natural resources. The cost of an EIA will usually be much less than that of remedial measures that may subsequently be necessary.

Apart from any consideration of possible adverse effects on the quality of life, the environmental effects on many development projects may well be crucial for their economic viability [71–73].

6

EIA Methods

The variety of methods used to assess impacts is very large [1–10, 15–19, 31–38], however, in this chapter; we cannot attempt to include all of the existing methods. Instead, a few representative types are described. These can be used at almost every stage in the preparation of an EIA.

In order to choose a suitable EIA method, various desirable properties should be taken into consideration. Such properties are discussed in Table 2.

Table 2 Desirable properties for EIA methods

Properties	Description
Comprehensiveness	– Sometimes a method is required that will detect the full range of important elements and combinations of elements, directing attention to novel or unsuspected effects or impacts, as well as to the expected ones
Selectiveness	– Sometimes a method is required that focuses attention on major factors – It is often desirable to eliminate unimportant impacts that would dissipate effort if included in the final analysis as early as possible – To some degree, screening at the identification stage requires a tentative pre-determination of the importance of an impact, and this may on occasion create subsequent bias
Mutual exclusiveness	– The task of avoiding double counting of effects and impacts is difficult because of the many interrelationships that exist in the environment – In practice, it is permissible to view a human concern from different perspectives, provided that the uniqueness of the phenomenon identified by each impact indicator is preserved – The point can be illustrated by noting that there could be several impacts of some action affecting recreation; the major human concern might be economic (for those whose income is derived there from), social (for those who use the area), and ecological (for those concerned with the effects on wildlife)
Confidence limits	– Subjective approaches to uncertainty are common in many existing methods and can sometimes lead to quite useful predictions – Explicit procedures are generally more acceptable, as their internal assumptions are open to critical examination, analysis, and alteration – In statistical models, measure of uncertainty is typically given as the standard deviation or standard error – Ideally, the measure of uncertainty should be in a form common to the discipline within which the prediction is made – Having estimated the range of uncertainty, the environmental impact assessor should undertake three separate analyses whenever possible, using the most likely, the greatest plausible (like two standard deviations away from the mean), and the smallest plausible numerical values of the element being predicted – When the resulting range of predicted values proves to be unacceptably wide, the assessor is alerted to the need for further study and/or monitoring

Table 2 (continued)

Properties	Description
Objectiveness	– This property is desirable to minimize the possibility that the predictions automatically support the preconceived notions of the promoter and/or assessor – These prejudgments are usually caused by a lack of knowledge of local conditions or insensitivity to public opinion – A second reason is to ensure comparability of EIA predictions amongst similar types of actions – An ideal prediction method contains no bias
Interactiveness	– Environmental, sociological, and economic processes often contain feedback mechanisms – A change in the magnitude of an environmental effect or impact indicator may then produce unexpected amplifications or dampening in other parts of the system – Prediction methods should include a capability to identify interactions and to estimate their magnitudes

6.1
General Types

The present section outlines information about the general types of EIA methods, such as those for the identification of effects and impacts, the prediction of effects, the interpretation of impacts, communication, and the determination of inspection procedures. The following is a summary.

6.1.1
Methods for Identification of Effects and Impacts

There are three principal methods for identifying environmental effects and impacts [5, 7, 10–15], as follows:

- **Checklists:** Checklists are comprehensive lists of environmental effects and impact indicators designed to stimulate the analyst to think broadly about possible consequences of contemplated actions. This strength can also be a weakness, however, because it may lead the analyst to ignore factors that are not on the lists. Checklists are found in one form or another in nearly all EIA methods.
- **Matrices:** Matrices typically employ a list of human actions in addition to a list of impact indicators. The two are related in a matrix that can be used to identify, to a limited extent, cause-and-effect relationships. Published guidelines may specify these relationships or may simply list the range of

possible actions and characteristics in an open matrix, which is to be completed by the analyst.

- **Flow diagrams:** Flow diagrams are sometimes used to identify action-effect-impact relationships. An example is given in Fig. 4, which shows the connection between a particular environmental impact (decrease in growth rate and size of commercial shellfish) and coastal urban development. The flow diagram permits the analyst to visualize the connection between action and impact. The method is best suited to single-project assessments, and is not recommended for large regional actions. In the latter case, the display may sometimes become so extensive that it will be of little practical value, particularly when several action alternatives must be examined.

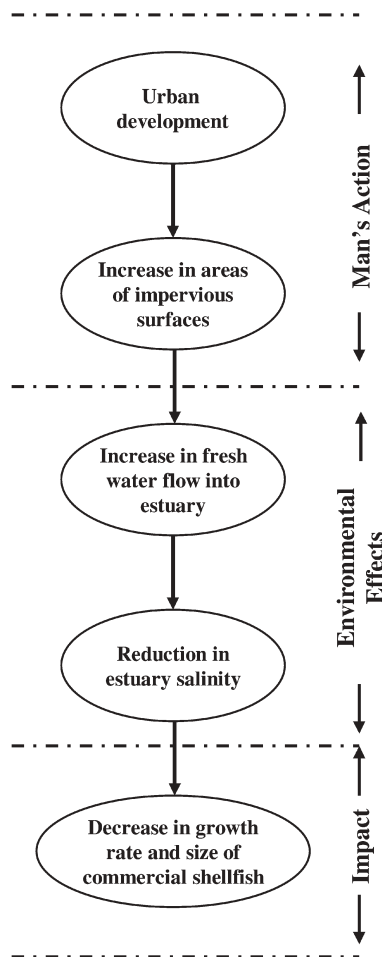


Fig. 4 Example of a flow-chart used for impact identification

6.1.2

Methods for Prediction of Effects

Methods for prediction cover a wide spectrum and cannot readily be categorized. All predictions are based on conceptual models of how the universe functions; they range in complexity from those that are totally intuitive to those based on explicit assumptions concerning the nature of environmental processes [5–10]. Provided that the problem is well formulated and not too complex, scientific methods can be used to obtain useful predictions, particularly in the biogeophysical disciplines.

Methods for predicting qualitative effects are difficult to find or to validate. In many cases, the prediction indicates merely whether there will be degradation, no change, or enhancement of environmental quality. In other cases, qualitative ranking scales (from 1 to 5, 10 or 100) are used.

Because some methods are better or more relevant than others, a listing of recommended methods for solving specific environmental problems would seem to be desirable. However, a compendium of methods is likely to be a snare for the unwary non-specialist. The environment is never as well-behaved as assumed in models, and the assessor is to be discouraged from accepting off-the-shelf formulae.

6.1.3

Methods for Interpretation of Impacts

There are three methods for comparing impact indicators, as follows:

6.1.3.1

Display of Sets of Values of Individual Impact Indicators

One way to avoid the problem of synthesis is to display all of the impact indicators in a checklist or matrix [6, 10]. For a relatively small set, and provided that some thought is given to a sensible grouping of similar kinds of indicators into subsets, a qualitative picture of the aggregate impact may become apparent by the clustering of checkmarks in the diagram.

This approach is used in numerous methods. Because the assessor intends to be all-inclusive, however, the sets are usually much too large for visual comprehension. In the Leopold matrix [10, 74–75], for example, 17,600 pieces of information are displayed. Such an array may confuse the decision-maker, particularly if a separate checklist or matrix is prepared for each alternative. Effort may be wasted if the environmental impact assessor conscientiously tries to fill in a high proportion of the boxes, and he may be swamped with excessive information if he succeeds.

6.1.3.2

Ranking of Alternatives Within Impact Categories

A second and better method for estimating relative importance is to rank alternatives within groups of impact indicators [4, 10]. This permits the determination of alternatives that have the least adverse, or most beneficial, impact on the greatest number of impact indicators. No formal attempt is made to assign weights to the impact indicators; hence the total impacts of alternatives cannot be compared.

6.1.3.3

Normalization and Mathematical Weighting

In order to compare indicators numerically and to obtain aggregate impacts for each alternative: (a) the impact indicator scales must be in comparable units, and (b) an objective method for assigning numerical weights must be selected.

Various normalization techniques are available to achieve the first objective [1, 2, 10, 76–78]. For example, environmental quality is scaled from 0 (very bad) to 1 (very good) by the use of *value functions*. *Very bad* and *very good* can be defined in various ways. For a qualitative variable such as water clarity that has been ranked from 1 to 5 or from 1 to 10 by the environmental impact assessor, the scales are simply transformed arithmetically to the range from 0 to 1. For quantitative variables such as water or air quality, *very bad* could be the maximum permissible concentrations established by law, while *very good* could be the background concentrations found at great distances from sources.

Finally, a method of weighting may be required in order to obtain an aggregate index for comparing alternatives [3, 41–42, 79–80]. This is undoubtedly a controversial part of the analysis. The following schemes are listed in increasing order of complexity:

- a. Count the numbers of negative, insignificant, and positive impacts, and sum in each class.
- b. When the impact indicators are in comparable units, assign equal weights.
- c. Weight according to the number of affected persons.
- d. Weight according to the relative importance of each impact indicator.

Scheme (a) is a special case of (b), both of which are to be discouraged. Scheme (d) may implicitly include (c). In either case, the criteria for weighting should be obtained from the decision-maker or from national goals. The number of weights will often be rather small, as few as two positive and two negative.

6.1.4

Methods for Communication

Communication is sometimes the weakest component in the EIA process [10]. The assessor may not have direct access to the decision-maker, in which case

preparation of the EIA Executive Summary or Statement is probably the most important part of the EIA document. Every effort should be made to avoid incomprehensibility and/or ambiguity, which may occur in several ways, as follows: (a) if scientific jargon is used without explanation; (b) if uncommon measurement units or scales are used to predict impacts; (c) if the explicit criteria and assumptions used in connection with value judgments and trade-offs are not given; or (d) if the *affected parties* are not clearly indicated. Generally, affected parties should be clearly indicated. A good communication method should indicate the link in space and time between the expected impact and the affected parties.

6.1.5

Methods for Determining Inspection Procedures

After an action has been completed, environmental quality may fall below design criteria [81–83] because of: (a) an incorrect or incomplete impact assessment; (b) a rare environmental event or episode; (c) an accident or structural failure of a component; or (d) human error.

The inspection procedures should take account of these four possibilities and may include periodic examination of equipment and safety procedures. In some cases, recommendations for regular monitoring programs may be necessary. The procedures to be followed in most cases can be derived from the predictions of effects and impacts that have already been made.

6.2

Analysis of Three General Approaches

Three general approaches, selected because they represent a range of options for impact assessment, are discussed in this section. These include the Leopold Matrix, Overlays, and the Battelle environmental evaluation system. The following is a summary.

6.2.1

The Leopold Matrix

6.2.1.1

Description

The pioneering approach to impact assessment, the Leopold Matrix, was developed by Dr. Luna Leopold and others of the United States Geological Survey [6, 10, 74–75]. The matrix was designed for the assessment of impacts associated with almost any type of construction project. Its main strength is as a checklist that incorporates qualitative information on cause-and-effect relationships, but it is also useful for communicating results.

The Leopold system is an open-cell matrix containing 100 project actions along the horizontal axis and 88 environmental *characteristics* and *conditions* along the vertical axis. These are listed in Table 3. The list of project actions in

Table 3 The Leopold Matrix (Part I lists the project actions, arranged horizontally in the matrix; and Part 2 lists the environmental characteristics and conditions, arranged vertically in the matrix)

Part 1: Project actions

A. <i>Modification of regime</i> a. Exotic flora or fauna introduction b. Biological controls c. Modification of habitat d. Alteration of ground cover e. Alteration of ground-water hydrology f. Alteration of drainage g. River control and flow codification h. Canalization i. Irrigation j. Weather modification k. Burning l. Surface or paving m. Noise and vibration	C. <i>Resource extraction</i> a. Blasting and drilling b. Surface excavation c. Sub-surface excavation and retorting d. Well drilling and fluid removal e. Dredging f. Clear cutting and other lumbering g. Commercial fishing and hunting
B. <i>Land transformation and construction</i> a. Urbanization b. Industrial sites and buildings c. Airports d. Highways and bridges e. Roads and trails f. Railroads g. Cables and lifts h. Transmission lines, pipelines and corridors i. Barriers, including fencing j. Channel dredging and straightening k. Channel revetments l. Canals m. Dams and impoundments n. Piers, seawalls, marinas, & sea terminals o. Offshore structures p. Recreational structures q. Blasting and drilling r. Cut and fill s. Tunnels and underground structures	D. <i>Processing</i> a. Farming b. Ranching and grazing c. Feed lots d. Dairying e. Energy generation f. Mineral processing g. Metallurgical industry h. Chemical industry i. Textile industry j. Automobile and aircraft k. Oil refining l. Food m. Lumbering n. Pulp and paper o. Product storage E. <i>Land alteration</i> a. Erosion control and terracing b. Mine sealing and waste control c. Strip mining rehabilitation d. Landscaping e. Harbor dredging f. Marsh fill and drainage F. <i>Resource renewal</i> a. Reforestation b. Wildlife stocking and management c. Ground-water recharge d. Fertilization application e. Waste recycling
-

Table 3 (continued)

Part 1: Project actions

G. <i>Changes in traffic</i> a. Railway b. Automobile c. Trucking d. Shipping e. Aircraft f. River and canal traffic g. Pleasure boating h. Trails i. Cables and lifts j. Communication k. Pipeline H. <i>Waste emplacement and treatment</i> a. Ocean dumping b. Landfill c. Emplacement of tailings, spoil and overburden d. Underground storage e. Junk disposal f. Oil-well flooding g. Deep-well emplacement	h. Cooling-water discharge i. Municipal waste discharge j. Irrigation k. Liquid effluent discharge l. Stabilization and oxidation ponds m. Septic tanks, commercial and domestic n. Stack and exhaust emission o. Spent lubricants I. <i>Chemical treatment</i> a. Fertilization b. Chemical deicing of highways c. Chemical stabilization of soil d. Weed control e. Insect control (pesticides) J. <i>Accidents</i> a. Explosions b. Spills and leaks c. Operational failure

Part 2: Environmental “characteristics” and “conditions”

A. Physical and chemical characteristics

1. <i>Earth</i> a. Mineral resources b. Construction materials c. Soils d. Landform e. Force fields and background radiation f. Unique physical features 2. <i>Water</i> a. Surface b. Ocean c. Underground d. Quality e. Temperature f. Snow, ice, and permafrost	3. <i>Atmosphere</i> a. Quality (gases, particulates) b. Climate (micro, macro) c. Temperature 4. <i>Processes</i> a. Floods b. Erosion c. Deposition (sedimentation, precipitation) d. Solution e. Sorption (ion exchange, complexing) f. Compaction and settling g. Stability (slides, slumps) h. Stress-strain (earthquake) i. Recharge j. Air movements

Table 3 (continued)

Part 2: Environmental “characteristics” and “conditions”

B. Biological conditions

1. *Flora*

- a. Trees
- b. Shrubs
- c. Grass
- d. Crops
- e. Microflora
- f. Aquatic plants
- g. Endangered species
- h. Barriers
- i. Corridors

2. *Fauna*

- a. Birds
- b. Land animals including reptiles
- c. Fish and shellfish
- d. Benthic organisms
- e. Insects
- f. Microfauna
- g. Endangered species
- h. Barriers
- i. Corridors

C. Cultural factors

1. *Land use*

- a. Wilderness and open spaces
- b. Wetlands
- c. Forestry
- d. Grazing
- e. Agriculture
- f. Residential
- g. Commercial
- h. Industrial
- i. Mining and quarrying
- j. Presence of misfits

- c. Open space qualities
- d. Landscape design
- e. Unique physical features
- f. Parks and reserves
- g. Monuments
- h. Rare and unique species or ecosystems
- i. Historical/archaeological sites and objects
- j. Presence of misfits

2. *Recreation*

- a. Hunting
- b. Fishing
- c. Boating
- d. Swimming
- e. Camping and hiking
- f. Picnicking
- g. Resorts

4. *Cultural Status*

- a. Cultural patterns (life style)
- b. Health and safety
- c. Employment
- d. Population density

3. *Aesthetics and Human Interest*

- a. Scenic views and vistas
- b. Wilderness qualities

5. *Man-made facilities and activities*

- a. Structures
- b. Transportation network
- c. Utility networks
- d. Waste disposal
- e. Barriers
- f. Corridors

D. Ecological relationships such as:

- a. Salinization of water resources
- b. Eutrophication
- c. Disease-insect vectors

- d. Food chains
- e. Salinization of surficial materials
- f. Brush encroachment
- g. Other

Table 3 is comprehensive, but the environmental impact assessor will find that many of the cells will not be used in any individual case. The *characteristics* and *conditions* in Table 3 are a combination of environmental effects and impacts.

6.2.1.2 Identification

The Leopold Matrix is comprehensive in covering both the physical-biological and the socio-economic environments. The list of 88 environmental characteristics is weak, however, from the point of view of structural parallelism and balance.

The Leopold Matrix is not *selective*, and includes no mechanism for focusing attention on the most critical human concerns. Related to this is the fact that the matrix does not distinguish between immediate and long-term impacts, although separate matrices could be prepared for each time period of interest.

The principle of a *mutually exclusive* method is not preserved in the Leopold Matrix, and there is substantial opportunity for double counting. This is a fault of the Leopold Matrix in particular rather than of matrices in general.

6.2.1.3 Prediction

The method can accommodate both quantitative and qualitative data. It does not, however, provide a means for discriminating between them. In addition, the magnitudes of the predictions are not related explicitly to the *with-action* and *without-action* future states.

Objectivity is not a strong feature of the Leopold Matrix. Each assessor is free to develop his own ranking system on the numerical scale ranging from 1 to 10.

The Leopold Matrix contains no provision for indicating *uncertainty* resulting from inadequate data or knowledge. All predictions are treated as if certain to occur. Similarly, there is no way of indicating environmental variability, including the possibility of *extremes* that would present unacceptable hazards if they did occur, nor are the associated probabilities indicated.

The Leopold Matrix is not efficient in identifying *interactions*. However, because the results are summarized on a single diagram, interactions may be perceived by the reader in some cases.

6.2.1.4 Interpretation

The Leopold Matrix employs weights to indicate relative importance of effects and impacts. A weakness of the system is that it does not provide explicit criteria for assigning numerical values to these weights.

Synthesis of the predictions into aggregate indices is not possible, because the results are summarized in an 8,800 (88×100) cell matrix, with two entries in each cell – one for magnitude and one for importance. Therefore, the decision-maker could be presented with as many as 17,600 items for each alternative proposal for action.

6.2.1.5

Communication

By providing a visual display on a single diagram, the Leopold Matrix may often be effective in communicating results. However, the matrix does not indicate the main issues or the groups of people most likely to be affected by the impact.

6.2.1.6

Inspection Procedures

The matrix has no capability for making recommendations on inspection procedures to be followed after completion of the action.

In summary, although the matrix approach has a number of limitations, it may often provide helpful initial guidance in designing further studies. In this connection, the assessor can modify the matrix to meet certain particular needs. For initial screening of alternatives, it is recommended that the number of cells be reduced, and that a series of matrices be prepared: (a) one set for environmental effects and another for impact indicators; (b) one set for each of two or three future times of interest; (c) one set for each of two or three alternatives. Particular cells could be flagged if the assessor felt that an extreme condition might occur, even though the probability was very low, and footnotes could be used where appropriate. A set of 8 or 12 such matrices might be a useful tool at the outset of an assessment, or whenever the resources of the assessor are limited.

6.2.2

Overlays

6.2.2.1

Description

The overlay approach to impact assessment on a series of transparencies is used to identify, predict, assign relative significance to, and communicate impacts in a geographical reference frame larger in scale than a localized action would require [5–7, 10].

The study area is subdivided into convenient geographical units, based on uniformly-spaced grid points, topographic features or differing land uses [84, 85]. Within each unit, the assessor collects information on environmental

factors and human concerns, through aerial photography, topological and government land inventory maps, field observations, public meetings, discussions with local science specialists and cultural groups, or by random sampling techniques. The concerns are assembled into a set of factors, each having a common basis. Regional maps (transparencies) are drawn for each factor, the number of maps having a practical limitation of about 10. By a series of overlays, the land-use suitability, action compatibility, and engineering feasibility are evaluated visually, in order that the best combination may be identified.

The overlay approach can accommodate both qualitative and quantitative data. There are, however, limits to the number of different types of data that can be comprehended in one display. A computerized version has greater flexibility. Although in this case the individual cartographic displays may be too complex to follow in sequence, the final maps are readily prepared and understood.

6.2.2.2 Identification

The approach is only moderately *comprehensive* because there is no mechanism that requires consideration of all potential impacts. When using overlays, the burden of ensuring comprehensiveness is largely on the analyst.

The approach is *selective* because there is a limit to the number of transparencies that can be viewed together.

The Overlays approach may be *mutually exclusive* provided that checklists of concerns, effects, and impacts are prepared at the outset and a simplified matrix-type analysis is undertaken.

6.2.2.3 Prediction

Because predictions are made for each unit area, the overlay method is strong in predicting spatial patterns, although weak in estimating magnitudes: a rather elaborate set of rules is often required to reveal differences in severity of impacts from place to place.

In some regions, the assessor may be able to find cartographic charts of future environmental states, which have been prepared recently for some other purpose. The *with-action* and *without-action* conditions can then be readily compared.

The *objectivity* of the overlay method is high with respect to the spatial positioning of effects and impacts, but is otherwise low. Overlays are not effective in estimating or displaying *uncertainty* and *interactions*.

Extreme impacts with small probabilities of occurrence are not considered. A skilled assessor may indicate in a footnote or on a supplementary map, however, those areas near proposed corridors where there is a possibility of landslides, floods or other unacceptable risks.

6.2.2.4 Interpretation

Two methods [6–10] are used to obtain aggregate impacts from overlays: (a) *conventional weighting*, the weights being a measure of relative importance; (b) *threshold technique*, in which a unit square is excluded from further consideration whenever a designated number of impacts are forecast to occur, or whenever an individual impact is unacceptably high.

A weighted average tends to give too little emphasis to impacts that are extreme for only a few people; the decision-maker may wish to be alerted to these extremes, and may wish to receive recommendations for remedial actions.

Overlays are strong in synthesis and in indicating trade-offs whenever spatial relationships are important. Although the analysis is limited to the total area represented by the transparencies, several levels of detail may be examined by preparing: (a) a set of overlays for a geographical scale much larger than the area covered by the action, and in only modest detail; or (b) a set of overlays for part of the region on an expanded scale, and in much greater detail than the other set.

6.2.2.5 Communication

The overlay approach can be used to communicate clearly where the types and numbers of affected parties are to be found. Other advantages include: (a) the possibility of displaying magnitudes by color, coding or shading; and (b) the ease with which the system can be programmed on a computer to provide composite charts that can be readily understood.

6.2.2.6 Inspection Procedures

The overlay method provides guidance on the spatial design of inspection procedures to be followed.

In summary, the overlay system cannot be considered ideal, but despite its limitations it is useful for illuminating complex spatial relations. It is recommended for large regional developments and corridor selection problems, provided that the assessor views his analysis with at least a modest degree of skepticism.

6.2.3

The Battelle Environmental Evaluation System

6.2.3.1

Description

The environmental evaluation system [7, 10] was designed by the Battelle Columbus Laboratories in the United States to assess impacts of water-resource developments, water-quality management plans, highways, nuclear power plants, and other projects.

The Battelle environmental evaluation system for water resources is described in Table 4. The human concerns are separated into four main categories: (a) ecology; (b) physical/chemical; (c) aesthetics; and (d) human interest/social. Each category contains a number of components that have been selected specifically for use in all U.S. Bureau of Reclamation water-resource development projects.

6.2.3.2

Identification

The approach is *comprehensive* and at the same time *selective*. The assessor may select an appropriate level of detail. The system is not *mutually exclusive* in the strict sense of the phrase. Impacts are not counted twice; nevertheless, the same impact may sometimes appear in different parts of the system. For example, the water-quality problems caused by high concentrations of suspended particulate matter are contained in the physical/chemistry category (turbidity), while the associated aesthetic problems are to be found in the aesthetic category (appearance of water).

6.2.3.3

Prediction

The method provides *prediction of magnitudes* on normalized scales, from which differences between the states with and without action can readily be determined.

The *objectivity* is high in terms of comparisons between alternatives and between projects. The value-function curves have been standardized, and the rationale for the shapes of these curves is public knowledge.

The system contains no effective mechanism for estimating or displaying *interactions*. However, the assessor is alerted to the possibility of *uncertainty* and of *extremes* by red flags.

6.2.3.4

Interpretation

The numerical weighting scheme is explicit, permitting calculation of a project impact for each alternative. Although any type of weighting scheme is contro-

Table 4 The Battelle environmental classification for water-resource development projects (the numbers in parentheses are relative weights)

Ecology	Physical/chemical
<i>Terrestrial species and populations</i>	<i>Water quality</i>
Browsers and grazers (14)	Basin hydrologic loss (20)
Crops (14)	Biochemical oxygen demand (25)
Natural vegetation (14)	Dissolved oxygen (31)
Pest species (14)	Fecal coliforms (18)
Upland game birds (14)	Inorganic carbon (22)
	Inorganic nitrogen (25)
<i>Aquatic species and populations</i>	Inorganic phosphate (28)
Commercial fisheries (14)	Pesticides (16)
Natural vegetation (14)	pH (18)
Pest species (14)	Stream flow variation (28)
Sport fish (14)	Temperature (28)
Water fowl (14)	Total dissolved solids (25)
	Toxic substances (14)
<i>Terrestrial habitats and communities</i>	Turbidity (20)
Food web index (12)	
Land use (12)	<i>Air quality</i>
Rare and endangered species (12)	Carbon monoxide (5)
Species diversity (14)	Hydrocarbons (5)
	Nitrogen oxides (10)
<i>Aquatic habitats and communities</i>	Particulate matter (12)
Food web index (12)	Photochemical oxidants (5)
Rare and endangered species (12)	Sulfur oxides (10)
River characteristics (12)	Other (5)
Species diversity (14)	
	<i>Land pollution</i>
	Land use (14)
	Soil erosion (14)
	<i>Noise pollution</i>
	Noise (4)
Aesthetics	Human interest/social
<i>Land</i>	<i>Education/Scientific</i>
Geologic surface material (6)	Archeological (13)
Relief and topographic character (16)	Ecological (13)
Width and alignment (10)	Geological (11)
	Hydrological (11)
<i>Air</i>	<i>Historical</i>
Odor and visual (3)	Architecture and styles (11)
Sounds (2)	Events (11)
	Persons (11)
<i>Water</i>	Religions and cultures (11)
Appearance of water (10)	Western Frontier (11)
Land and water interface (16)	

Table 4 (continued)

Aesthetics	Human interest/social
<i>Water</i>	<i>Cultures</i>
Odor and floating material (6)	Indians (14)
Water surface area (10)	Other ethnic groups (7)
Wooded and geologic shoreline (10)	Religious groups (7)
<i>Biota</i>	<i>Mood/Atmosphere</i>
Animals: domestic (5)	Awe/inspiration (11)
Animals: wild (5)	Isolation/solitude (11)
Diversity of vegetation types (9)	Mystery (4)
Variety within vegetation types (5)	"Oneness" with nature (11)
<i>Man-made objects</i>	<i>Life patterns</i>
Man-made objects (10)	Employment opportunities (13)
<i>Composition</i>	Housing (13)
Composite effect (15)	Social interactions (11)
Unique composition (15)	

versial, this one has been developed from systematic studies and its rationale is documented. The designers of the system believe strongly that the weights should not be allowed to vary within project alternatives.

The Battelle system of determining weights is a useful example to discuss [10, 18]. The human concerns are divided into a few *categories*, each of which has *components*, for which there are separate sets of *impact indicators*. For example, pollution is a category, water pollution is a component, and pH is one of a set of impact indicators. The system for selecting weights contains nine steps, as follows:

- Step 1: Select a group of individuals and explain to them in detail the weighting concept and the use of their rankings and weights.
- Step 2: List the categories, components, and impact indicators, and ask each individual independently to rank each member of each set in decreasing order of importance.
- Step 3: Each individual assigns a value of 1 to the first category on his list, and then decides how much the second is worth compared to the first, expressing his estimate as a decimal between 0 and 1.
- Step 4: Each individual makes similar comparisons for all consecutive pairs of categories.
- Step 5: Steps 3 and 4 are repeated for all of the sets of components and impact indicators.
- Step 6: Averages are computed over all individuals for all categories, components, and indicators, the weights being adjusted in the cases of com-

ponents and indicators to take account of the weights obtained for the larger groupings.

Step 7: The group results are revealed to the individuals.

Step 8: The experiment is repeated with the same group of individuals.

Step 9: The experiment is repeated with a different group of individuals to check for reproducibility.

6.2.3.5

Communication

The approach does not link impacts to *affected parties* or to *dominant issues*. However, the system is effective in its *summary format*, which is usually a table listing individual and aggregate impacts as well as flagging impacts in need of future study. The summary format is designed for the specialist and may sometimes require explanation.

6.2.3.6

Inspection Procedures

The approach provides modest guidance on the development of future inspection procedures. Particularly for value functions that are related to national standards or criteria, the system indicates the parameters that will require monitoring.

In summary, the Battelle methodology, although not ideal, has much to recommend it wherever the assessor has sufficient resources.

6.2.4

Critical Evaluation

Table 5 summarizes the strengths and weaknesses of the three general approaches presented in this chapter. The environmental impact assessor may have difficulty in choosing from amongst the range of approaches and of methods. The choice that wins depends upon the nature of the action and upon the available resources. Indeed, the assessor may sometimes intend to use more than one approach, either: (a) *consecutively* at different stages and levels of detail of the assessment; or (b) *concurrently* at a single stage. In the latter case, the assessor may wish to test whether two approaches yield the same results.

6.3

The Problem of Uncertainty

An EIA contains four kinds of uncertainty, due to the: (a) natural variability of the environment; (b) inadequate understanding of the behavior of the environment; (c) inadequate data for the region or country being assessed; and (d) socio-economic uncertainties.

Table 5 Comparison between the Leopold Matrix, Overlays and Battelle environmental evaluation approaches

	Leopold	Overlays	Battelle
<i>Capability</i>			
Identification	Medium	Medium	High
Prediction	Low	Low	High
Interpretation	Low	Low-medium	High
Communication	Low	High	Low-medium
Inspection procedures	Low	Medium	Low-medium
<i>Action complexity capability</i>			
	Incremental alternatives	Fundamental and incremental alternatives	Incremental alternatives
<i>Risk assessment capability</i>			
	Nil	Nil	Nil
<i>Capability of flagging extremes</i>			
	Low	Low	Medium
<i>Replicability of results</i>			
	Low	Low-medium	High
<i>Level of detail</i>			
Screening of alternatives	Incremental	Fundamental and incremental	Incremental
Detailed assessment	Yes	Yes	Yes
Documentation stage	Yes	Yes	Yes
Money	Low	Maps low; computer high	High
<i>Resource requirements</i>			
Time	Low	Maps low; computer high	High
Skilled manpower	Medium	High	High
Computational	Low	Maps low; computer high	Medium
Knowledge	Medium	Medium	Medium

Methods are available for predicting the first kind of uncertainty [86–87]. Frequency distributions of the numerical values of physical and biological elements can be estimated in many cases, and can be used to predict the probabilities of rare events. Although prediction of the exact date of occurrence of a rare environmental event is not possible, the environmental engineer can design a structure so that its risk of failure is smaller than any value specified in national environmental codes or standards.

The second and third types of uncertainty are more difficult to manage. The degree of knowledge and data varies from discipline to discipline, and this leads to mismatches, not only in the confidence to be placed in a prediction but also in the philosophies advocated by members of the assessment team.

The fourth kind of uncertainty, socio-economic, is the most difficult to quantify. Externalities such as wars, and changes in international trade relations are impossible to predict. But even when national and international conditions remain relatively stable, the construction of a highway may sometimes produce unexpected adjustments by the local population [41–42]. For example, there is always uncertainty in predicting the ways in which a community will respond after a highway has been constructed: in terms of employment, housing, recreational, and other kinds of patterns. Furthermore, the strong feedback loops between socio-economic and biophysical impacts can result in corresponding uncertainty in the long-term biophysical impacts.

It should be noted that uncertainty increases as a prediction is made for times further and further into the future. In some cases, predictions of long term consequences may be so uncertain that the decision-maker has no option but to make a decision on the basis of the expected short-term impacts. Accordingly, an EIA should be considered as an *investigation into*, rather than a *determination of* impacts. At present, an EIA is one of several considerations leading to a decision to implement a proposed action. Once the decision has been taken, the EIA is generally filed, and the assessment team is disbanded. A modest monitoring program may be established by the proponent or by a designated government agency.

7

Conceptual Framework

Generally, a conceptual framework needs to be formulated before the EIA methods are applied [1–3, 10, 92–94]. If the environmental impact assessor simply follows existing, pre-packaged methods, the results will fall short of their potential. An outline for such a framework is presented in this section. This begins by defining a simulation model, describing its essential characteristics, and identifying the criteria that will establish the need for such a model in an EIA. Then, assuming that the use of a simulation is appropriate, the sections give advice on how to start, and on what the decision-maker will need to do. After a brief description of a simple policy analysis that will determine whether or not it is worth continuing with the development of the simulation, the processes of model and validation are outlined so that the administrator will know what the technical experts concerned with these stages are doing. The use of simulations in complex policy analysis and possible ways that the results from the analysis can be presented are then described [95–96]. Finally, a very brief description is given of possible developments in simulation techniques relevant to EIAs.

7.1

Model Classes

The models used in EIAs are simplified representations of reality. Models can be sub-divided into three main classes:

- A scaled-down copy of a physical object (for instance, a ship).
- A mathematical representation of a physical or biological process (such as the spread of pollution from a chimney, or the movement of a weather disturbance across a region).
- An exploratory representation of complex relationships amongst physical, biological, and socio-economic factors or indicators (quantitative or qualitative).

Section 7 of this chapter is mainly about the third class of model, often called a *simulation* or a *scenario*. In its simplest form, this kind of representation is extremely useful in the first stages of an EIA, helping to synthesize the widely diverse information reaching the environmental impact assessor through many specialists. As the simulation model becomes more and more complex, it becomes less and less relevant to the EIA process. In fact, the tendency towards complexity, leading to the construction of mathematical extravaganzas, has given the modeler a poor public image in some cases.

7.2

Simulation Model

The essential feature of an EIA is the provision of choice between a range of alternatives. Any choice will affect several heterogeneous *elements*: physical, ecological, and sociological [2, 10]. Further, these elements are usually inter-related in complicated ways and there is a mass of information. This mass may be small; it may have obvious and not so obvious gaps in it.

7.2.1

Complexity

The interconnected nature of the elements in the environment poses special problems for impact assessment, because the linkages between these elements are often far from simple. If there are two related elements, representing an *action* and an *impact*, the simplest assumption to make is that when an alteration to one element slightly occurs, the other element will change slightly and proportionately (Fig. 5a). The technical term for such relationships is *linear*. Very often in natural or social systems, however, the assumption of linear relationships is false. An *action* may produce an *impact*, but increasing the action may not significantly increase the impact (Fig. 5b). Alternatively, a gradually increasing action may produce negligible change until a point is reached at which dramatic alterations in impact occur (Fig. 5c). Both of these relation-

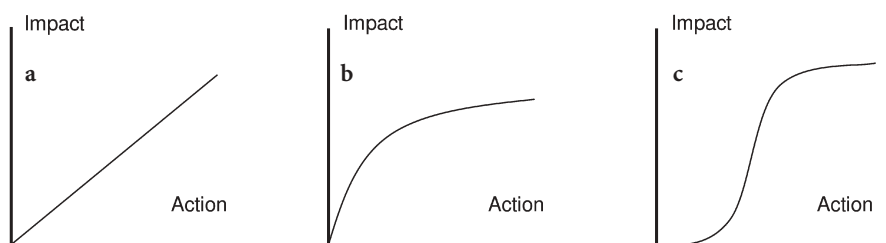


Fig. 5a–c Typical forms of relationships between action and impact: **a** linear; **b** non-linear; and **c** complex non-linear

ships are technically described as *non-linear*. In the former, the probable impact of increased action may be over-estimated by assuming linearity; in the latter, a potential catastrophe may not be foreseen. Further, these responses may be displaced by the system and appear as impacts at points structurally or geographically distant from the action.

7.2.2

Time-Dependent Relations

The natural world is not static. Flows of energy and matter, and changes in these flows, are not only usual but also sometimes necessary for the maintenance of viable ecosystems [97]. Conditions that appear to be static may be slowly changing or may represent only a temporary equilibrium condition between several processes acting in opposite ways. Because man's actions alter these relations, analysis of the time-dependent processes may be necessary to predict the future. Of particular importance is the need to search for possible feedback mechanisms amongst the various environmental, sociological, and economic processes [2, 10, 98].

Sometimes not only the scale of the changes to be imposed by a development project, but also the rate at which these changes will be introduced affects the final equilibrium state of the system. In some cases, the impact might be less if the rate of development is slowed down.

In other cases, changes may be set in motion leading to impacts that are perceptible only a long time after the project has been completed. If, for each of the links, the relationships which affect the changes can be defined, including delays and time-lags, then the overall changes can be estimated. In mathematical terms, the analysis would then be dynamic (time-dependent) and not static.

7.2.3

Explicit Relations

One apparent disadvantage of a model is that every element and every link must be defined explicitly. It is not enough to say, for example, that the water quality

of a lake will deteriorate. It is necessary to characterize the types of pollutants causing the change, determine their concentrations, measure various water quality parameters, estimate the size of the present contamination, and then the rate of deterioration [99–101]. In fact, this apparent disadvantage is actually a major advantage. The nature of the model process forces hidden assumptions into the open that may have little real basis. It reveals areas where information seems inadequate, and, especially, it makes the participants in the assessment, who may have very different backgrounds, aware of each other's problems.

7.2.4

Uncertainty and Gaps

When the elements and links in a model have been defined, it is likely that very few will have the exactness of simple elements. Many will have wide limits to their probable values, either through a lack of knowledge or because they do really vary in space and time [102–106]. If the average value of each element is used as a basis for the simulation, then the model will produce only a single, apparently exact, result of the consequences of an environmental change.

It is also essential that inadequacies in the data or in the assumptions are not conveniently lost within the computer simulation. Facts and values must not become confused. Because answers are usually required quickly, it is no help to start a long-term research program. In contrast to scientific research, experimental tests of the model are not normally possible in environmental impact studies.

7.3

Delimitation and Strategic Evaluation of the Problem

From the previous sections, it is clear that the problems of EIA are interdisciplinary. However, the strategy will start by imposing some specific limits to the real universe surrounding the problem. In order to reduce the problem to a manageable size, the following points should be taken into consideration [102–113]:

- *Classes of output needed to make decisions:* From the whole host of variables involved in the problem, only a fraction of them will be relevant to the final decision.
- *The geographical limits to the problems:* Although human technology has proved to be capable of producing effects at the global scale, geographical limits should be placed on the size of the problem, with only a few exceptions. This is an arbitrary limitation that usually reflects the interests involved, and helps to indicate the desired strategy. By restricting the problem to too small an area, important factors may be ignored. By trying to take in everything, the problem may become unmanageable. The preliminary analysis may indicate, however, that certain aspects can be omitted.
- *The time horizons of the impact:* The assessment of a given environmental impact has to be performed in relation to a given period of time. There is no

- simple way to define this dimension, and the decision will depend on many specific factors surrounding a given problem. Frequently, the events involved in environmental impacts are characterized by non-linear processes, or by lags between cause and effect, so that consequences that are negligible during one period of time may become important if that period is extended.
- *The sub-systems affected by the model:* The previous sections have described some of the problems of setting boundaries of time and space for the model. The result, in technical terms, will be a listing of elements and of the links between them, either as a table or a flowchart. The number of elements may be relatively small or very large. The links may also be large in number, although each link is of a relatively simple kind, or there may be complex interactions at many points. The next stage in the delimitation of the problem is to see if this mass of elements and links needs to be, or can be, considered as a group of sub-systems. This decomposition into sub-systems is useful, not only for the strategic analysis of the problem, but also for the management of the assessment.

For any major development, there is always a set of possible alternatives [111]. The initial generation of these alternatives is a crucial step, because it provides the reference frame that will largely determine the kind of information needed, as well as the type and usefulness of the model to be constructed, and the universe of more detailed alternative options needed to be assessed.

The initial generation of alternatives may be greatly helped by some rules for providing a systematic reference frame. While it would be impossible to present a complete list of alternatives for many projects, a few guidelines may be of assistance. Usually, the most obvious proposal for a development in a particular region is the one that is expected to produce the maximum benefit. However, it is important to look for alternatives that will imply a minimal cost if things do go wrong. In addition, one may look for alternatives with a high probability of being successful (i.e., low probability of failure), even if the potential benefits are not very high.

7.4

Duties

After constructing a strategic boundary and evaluating the problem, the first and obvious essential is to gather together all the available information and to identify the people who can contribute to the model (including system analysts and computer programs), as follows:

7.4.1

Initial Variable Identification and Organization

Having carefully identified the problem within the strategic framework developed above, and listed the essential variables, the following steps are necessary [45, 103, 112]:

- Organize the variables into separate classes identified according to some common properties.
- Specify hypotheses concerning the interactions between classes of variables, and illustrate these graphically. Some thought should be given to the form of the independent and dependent variables in order to facilitate interfacing with the rest of the model.
- Identify, for each interaction, all reasonable alternative hypotheses and make rough estimates of maxima, minima, and thresholds. Retain these subsequent tests of the sensitivity of the simulation model to various alternatives and extremes.

7.4.2

Assigning Degrees of Precision

When a problem can be divided into subsystems, it is important to have approximately the same degree of precision in each subsystem. The best way to do this is to make an initial estimate of the required or possible precision for each subsystem, identifying inputs, model detail, and outputs [105, 110–113]. The choice of the appropriate level of precision should be a joint effort by you and your staff, and should be based on the kind of questions you want answered, the time available for the study, and the quality of the data.

7.4.3

Construction of a Flow Diagram

A wide choice of conventions is available for drawing flow diagrams, based on control system theory, cybernetics, and information theory. The best conventions seem to be the simplest, in which one symbol designates an input or output, another an intervention, and a third a process. The same symbols are used throughout both the model and its constituent submodels.

7.4.4

Interaction Table

If separate subsystems are independently analyzed, one of the most difficult tasks is to ensure effective interfacing between sub-models. The device that seems to work best is an interaction matrix, which identifies the inputs each sub-system expects to receive from others.

Not only can the interaction table be prepared rather quickly but also it provides an immense amount of qualitative information which itself could form the basis for a preliminary assessment. Alternatively, if the resources, time, and information are not available for an extensive assessment and evaluation, the same table could be the basis for a formal evaluation.

7.5

Simple Policy Analysis

Three sets of information are necessary for the first step in the simple policy analysis, as follows [10, 105–111]:

7.5.1

Developing Impact Indicators

The strategic evaluation should have identified the major impact classes in relation to the original goal of the project. Because these classes are broad and general, they must be disaggregated into variables that are measurable and relevant. Having developed a list of indicator variables, it is then often necessary to express them in the most relevant forms.

7.5.2

Developing Policy and Management Actions

In any one development, there are several internal options for action during the construction and post-construction phases. Some relate directly to the project itself, while others are indirect actions. This process is identical to the effort made to decompose the environmental system into the system variables, and it is identical to the effort performed to decompose project goals into impact indicators.

7.5.3

Putting the Pieces Together

There are three elements necessary to develop the first rough assessment: the system variable interaction table, the list of impact indicators, and the list of policy actions. The goal is to develop a table of *actions* vs. *impacts*. This table is Box IV in Fig. 6. The interaction table of the system variables acting on one another (in Box I in Fig. 6) allows you to do this. In the complete analysis you will use the model that you are creating, but in the meantime the interaction table in Fig. 6 will provide a preliminary policy assessment and an indication of adaptations needed in the assessment activity.

Briefly, two intermediate tables are developed. The first is designed to show how each action is likely to affect each system variable (Box II, Fig. 6). The second shows how each system variable is related to each impact variable (Box III, Fig. 6). The action vs. impact table (Box IV, Fig. 6) is formed by linking Boxes II and III through Box I, as indicated in Fig. 6. With tables of this kind for each of the alternative plans, it should then be feasible to reject the most extreme proposals, leaving a smaller set for later discussion and decision.

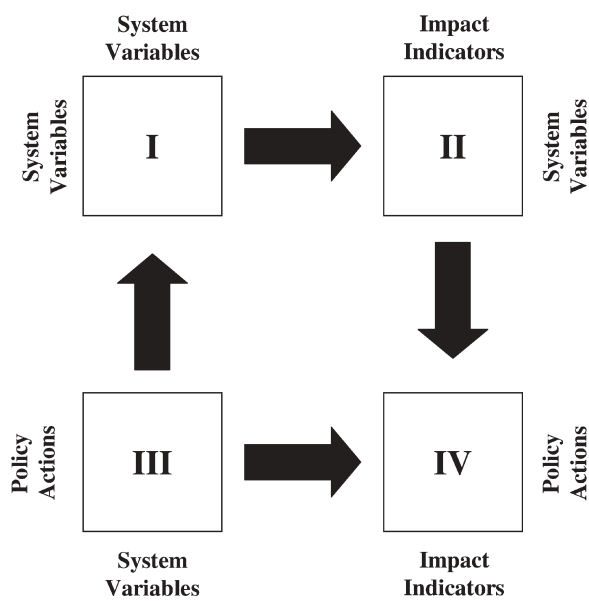


Fig. 6 Relationships between tables of system, action, and impact variables

7.6
Model Process

Now that the problem has been defined in terms of its boundaries, its sub-systems, its possible variables and their couplings, the modeling process can begin assuming that the decision to proceed beyond the stage of the simple policy analysis has been reached [10, 16, 111–113]. It is at this point that the expertise of the applied mathematician becomes paramount, and some understanding of the role is necessary to retain the necessary control of the impact assessment process.

The mathematician will first choose the kind of model to be used, who will be guided by the size of the problem, the nature of the various classes of variables, and by the degrees of uncertainty present in the relationships between them. The different models that a mathematician could use will lie between the following classes of models:

7.6.1
Deterministic versus Probabilistic

In the former, all of the relationships are constructed as if they were governed by fixed natural laws – the uncertainties and random fluctuations are not built into the model. In the latter, some or all of the relationships that are defined by statistical probabilities are included explicitly in the model, whose output then

directly represents the consequences of those probabilities. This is sometimes called the *Monte Carlo* approach.

7.6.2

Linear versus Non-Linear

Although it may be convenient to assume that relationships between variables are linear, most practical problems require the more complex assumption of non-linearity.

7.6.3

Steady-State versus Time-Dependent

Steady-state models compute a fixed final condition based on a fixed pre-action condition, whereas time-dependent models incorporate the way actions affect processes that may eventually produce impacts.

7.6.4

Predictive versus Decision-Making

Predictive models enable the consequences of particular decisions to be explored, while decision-making models indicate which of the decisions is “best” in some defined way. When a computer is used in conjunction with a mathematical model, the computer program must be unambiguous. The resulting *algorithm* must define the model in sufficient detail for its essential features to be communicated to other experts. After testing the algorithm to ensure that all of the component parts operate correctly, the next step is to validate it with respect to the real world system being studied, searching for possible inconsistencies or unrealistic results. By modifying the model at this point and subjecting the resulting version to further analysis, the process of improving the model within the limitations of the time and resource constraints of the impact assessment process should continue.

In this connection, a *sensitivity analysis* should be employed. Second, the mathematician searches for the maximum simplification of the model that is consistent with its value in a predictive or decision-making process. Frequently, it is possible to show that parts of the model that have been developed to satisfy theoretically important considerations have relatively little effect on the final outcome of the modeling process. In such cases, simplification of the model is both desirable and readily achievable.

7.7

Simulation Validation

Repetitions of analysis and refinement can, in theory, continue indefinitely, but in an EIA they will usually be brought to a halt by the need to provide results

quickly. Indeed, there may be too little time to develop the model to the degree that would be desirable in a research investigation. At some earlier stage, an attempt at validation will therefore be necessary.

Validation (i.e., the matching of the model with reality) in EIAs is not easy. Sometimes, the only apparent validation that can be achieved is the matching of future performance of the environmental system with the expectation from the model – a test which hardly meets the criteria of good science. Nor does it contribute to the decision-making process that seeks the assessment. Nevertheless, some confirmation of the appropriateness of the model can be obtained, as follows:

- First, the analysis necessary for the refinement of the model will give some confidence that the behavior of the modeled system is consistent with our expectations. Where it has been possible to divide the total system into sub-systems, the behavior of these sub-systems, singly and in aggregate, will have reinforced the knowledge of the dynamics of the system. If the behavior of an aggregated system runs counter to the intuitive expectations, there will be a need to reconsider the basis of common sense expectation. In this way, confidence in the value of the model will have been increased.
- Second, experimentation with model systems may indicate critical experiments that would enable a valid test of the model to be carried out as a direct appeal to nature, consistent with the logic of the scientific method. Such a test may seem relatively unlikely in EIAs, where the time-scale for the assessment is limited. But the model may indicate a specific, focused experiment that can contribute significantly to the validation; alternatively, existing experimental evidence that had not yet been considered may be suggested for testing the predictions of the model system.
- Third, where it has been possible to undertake surveys to obtain the necessary data for the construction and parameterization of mathematical models, it may be desirable to hold back a certain proportion of the data so that they may be used in an independent test of the hypothetical model derived from the main data set. In this way, the inconsistency of formulating and testing a hypothesis on the same set of data can be avoided.

In summary, whatever method is used in an attempt to validate the model system, one of the paramount advantages of mathematical models dominates the argument at this point. In contrast to all other forms of reasoning, the mathematical model is explicit in its statement of the relationships between the variables and of the assumptions underlying the model.

7.8

Complex Policy Analysis of Simulation Output

Once a model has been satisfactorily validated, the next step is to select from amongst the set of possible alternative policies or actions that have been generated [10, 109–112]. For example, in the case of being confronted with a set

Table 6 Hypothetical example of complex policy analysis

	Probability of		Consequences of		Probable loss	Probable benefit	Most likely net benefit
	Failure	Success	Failure	Success			
A	0.2	0.8	-80	10	-16	8	-8
B	0.8	0.2	-40	100	-32	20	-12
C	0.5	0.5	-15	10	-7.5	5	-2.5
D	0.1	0.9	-90	50	-9	45	+36
E	0.1	0.9	-20	30	-2	27	+25
F	0.1	0.9	-500	80	-50	72	+22

(such as A, B, C, D, E, F) of alternative policies or actions, generated by some kind of model, for each of the alternatives it is feasible to estimate the probability of being *right* or *wrong* on some objective basis. That is, according to the uncertainties involved in the construction of the model and the likelihood of a critical hypothesis being wrong, the degree of confidence to be placed on the *success* or *failure* of the policy might be allocated or be given.

Given this information, there are different ways of choosing, which can be best illustrated by a hypothetical example. Suppose there are six alternative policies or actions, their associated probabilities, and the relative weights to be applied to the consequences of being *right* or *wrong*, as seen in Table 6.

From these two sets of values (Table 6), it is possible to estimate in relative terms for each alternative:

- The probable loss (the probability of failing multiplied by cost of failing).
- The probable benefit (the probability of succeeding multiplied by the benefit of succeeding).
- The most likely net benefit (the probable benefit minus the probable loss).

This table may be used to make the *best* choice from amongst the six alternatives, using several different criteria for defining the word *best*, as follows:

- The first criterion is trivial, and consists of choosing the alternative that has the greatest probability of success (lowest of failure) without considering the size of benefits or costs associated with success or failure. Using this criterion, either alternatives D, E, or F would be chosen.
- The second criterion consists of choosing the alternative that provides the highest gain if successful (alternative B, with a possible benefit taken as 100 in the example). This criterion has been widely used, either explicitly or implicitly, sometimes with disastrous consequences. No account is taken of the consequences of the action being wrong, or of the probability of the action being right.
- The third criterion is to choose the alternative that produces the lowest cost in case of failure, which is in a sense the safest choice. Using this criterion,

- alternative C (with a loss of 15 if the alternative is wrong) would be selected.
- The fourth criterion is to use the alternative that provides the highest probable gain (to select the alternative which takes into account both the magnitude of the possible benefit and the probability of succeeding). In this case, alternative F (probable gain of 72) is chosen.
 - The fifth criterion is to pick alternative E, which has the lowest probable loss (−2).
 - Finally, the sixth criterion is to select the alternative with the highest value of the most likely net benefit, which takes into account both the probable benefit and the probable loss; in the case under consideration, this is alternative D (+36). Alternative A is not chosen using any of the above criteria.

The above simple example is intended to make the following points:

- There are many different criteria for choosing alternatives (in other words there are many ways of deciding what the words *best* or *worst* mean in a given context).
- Some evaluation of the likelihood of failure or success and of the respective losses and benefits is necessary for the alternatives to be evaluated.
- The six different selection criteria defined above can be grouped into two classes, according to whether the aim is to maximize the gain or to minimize the loss (ambitious versus cautious strategies). The ignorance about the behavior of complex environmental systems is so vast that it is often foolish to adopt anything but a cautious view of the outcome.

7.9

Model Presentation

To overcome the difficulties presented in Section 7.8, the:

- Environmental impact assessor should produce information that fits the interpretative capabilities of analysts (see Fig. 7). Practically, the final information is inappropriate if it exists in one form only (such as tables).
- Assessor should be able to explain the algorithms (to state clearly the ways in which raw data have been converted to finished information within the computer).

Figure 7 shows the relationships between different “Levels of Decision-Making”, the forms of displaying information in the “Information Package”, and the comparative “Depth of Explanation” versus “Ease of Interpretation” of each Form.

With a common set of data, a computer system can simultaneously produce a wide variety of specialized displays (e.g., flowcharts, tables, matrices, graphs, maps). With such a graduated series of displays, which trade off depth of explanation for simplification, almost any decision-maker can locate a display form which suits his interpretative abilities and through which an understanding and belief can be built in more or less complex forms of assessment (Fig. 7).

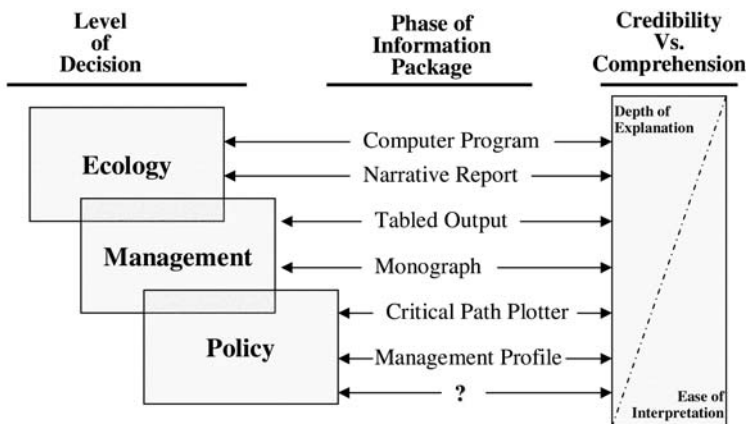


Fig. 7 Model presentation

8 Conclusions

An environmental impact assessment (EIA) is an activity designed to identify and predict the impact of an action on the biogeophysical environment and on man's health and well-being, and to interpret and communicate information about the impacts. An action is used in this chapter in the sense of any engineering project, legislative proposal, policy, program or operational procedure with environmental implications.

EIAs should be an integral part of all planning for major actions, and should be carried out at the same time as engineering, economic, and socio-political assessments. In order to provide guidelines for EIA, national goals and policies should be established which take environmental considerations into account; these goals and policies should be widely promulgated.

An EIA should contain the following: (a) a description of the proposed action and of alternatives; (b) a prediction of the nature and magnitude of environmental effects; (c) an identification of human concerns; (d) a listing of impact indicators as well as the methods used to determine their scales of magnitude and relative weights; (e) a prediction of the magnitudes of the impact indicators and of the total impact, for the project and for alternatives; (f) recommendations for acceptance, remedial action, acceptance of one or more of the alternatives, or rejection; and finally (g) recommendation for inspection procedures.

EIAs should include studies of all relevant physical, biological, economic, and social factors. At a very early stage in the EIA process, inventories should be prepared of relevant sources of data and of technical expertise. EIAs should include studies of alternatives (including that of no action), and both mid-term and long-term predictions of impacts.

Environmental impacts should be assessed as the difference between the future state of the environment if the action took place and the state if no action

occurred. Estimates of both the *magnitude* and the *importance* of environmental impacts should be obtained. Methodologies for impact assessment should be selected which are appropriate to the nature of the action, the database, and the geographic setting. Approaches that are too complicated or too simple should both be avoided. The affected parties should be clearly identified, together with the major impacts for each party.

Future EIA research should be encouraged in the following areas:

- Post-audit reviews of EIAs for accuracy and completeness in order that knowledge of assessment methods may be improved.
- Study of criteria for environmental quality.
- Study of quantifying value judgements on the relative worth of various components of environmental quality.
- Continual development of modeling techniques for impact assessments, with special emphasis on combined physical, biological, socio-economic systems.
- Study of sociological effects and impacts.
- Continual study and development of methods for communicating the results of highly technical assessments to the non-specialist.

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Recycling Solid Wastes as Road Construction Materials: An Environmentally Sustainable Approach

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Abstract Improved environmental performance in industry and society is a concept now a quarter-century old. Efforts in this regard have yielded much in the way of environmental improvement. It is easy to demonstrate that most of the activities of today's industrial society are unsustainable. Unfortunately, much of the talk about sustainability lacks a basic understanding of what truly sustainable activity would be. To set sustainability as a target or a goal for our industrial society, it is important to quantify that target or goal.

Currently, the transportation industry is under increasing pressure to use alternate or secondary materials because of its high-volume consumption of bulk materials (such as

natural fine and coarse aggregates) in road construction. Materials including industrial by-products, concrete aggregates, old asphalt pavement, scrap tires, fly ash, steel slag, and plastics are often used as alternate materials for natural aggregates. As these products are not normal construction materials, there are concerns about their environmental suitability, recyclability and sustainability in concrete and road pavement applications, as well as their environmental impact on surface and ground waters.

The present chapter (a) evaluates the general concepts of sustainability, (b) reviews and evaluates the various types of solid wastes that are currently used as road construction and repair (C&R) materials, (c) discusses both the chemical and physical properties of such wastes and their engineering uses, and finally (d) presents the general project approaches of a major research program to investigate the environmental impact of highway C&R materials on surface and ground waters.

Keywords Solid wastes · Environmental impact · Environmental analysis · Highway materials · Surface waters · Ground waters

Abbreviations

ACBFS	Air-cooled blast furnace slag
ACBFS	Formed blast furnace slag
BA	Bottom ash
BDAT	Best demonstrated available technology
BFS	Blast furnace slag
BHF	Baghouse fines
BS	Boiler slag
C&R	Construction and repair materials
CKD	Cement kiln dust
COMs	Complex organic mixtures
EAIA	Environmental analysis and impact assessment
ECBFS	Expanded blast furnace slag
EC ₅₀	Ecological concentration at which 50% growth inhibition of <i>Selenastrum capricornutum</i> occurs
LD ₅₀	Lethal dose at 50% of organisms die
EIA	Environmental impact assessment
EPA	Environmental Protection Agency
FA	Fly ash
FGD	Flue gas desulfurization
FHA	Federal Highway Administration
FS	Foundry sand
GBFS	Granulated blast furnace slag
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
IC/HPLC	Ion chromatograph/ high-pressure liquid chromatography
ICP	Inductively coupled plasma atomic emission spectrometry
KD	Kiln dust
LKD	Lime kiln dust
MPW	Mineral processing wastes
MSW	Municipal solid waste
MWC	Municipal waste combustion
NCHRP	National Cooperative Highway Research Program
NFS	Nonferrous slags
PBFS	Pelletized blast furnace slag

PCBs	Polychlorinated biphenyls
PCC	Portland cement concrete
PL	Plastics
QBP	Quarry by-products
RAP	Reclaimed asphalt pavement
RCM	Reclaimed concrete material
RCP	Recycled concrete pavement
RDF	Refuse derived-fuel
RRR	Removal, reduction and retardation
RSS	Roofing shingle scraps
SS	Steel slag
SSA	Sewage sludge ash
ST	Scrap tires
SWMs	Solid waste materials
TOC	Total organic carbon

1

Introduction

Production of synthetic and processed materials is vital for the growth of modern societies. Such production results in the creation of large quantities of solid waste materials (SWMs). Many of these SWMs remain in the environment for long periods of time and cause waste disposal problems [1–3]. Existing landfills are reaching maximum capacity and new regulations have made the establishment of new landfills difficult. Disposal cost continues to increase while the number of accepted wastes at landfills continues to decrease [1].

One answer to these problems lies in the ability to develop beneficial and sustainable uses for these wastes by recycling complex SWMs into useful products. The reuse of industrial by-products in lieu of virgin traditional materials would relieve some of the burden associated with disposal, and may provide inexpensive substitutes.

For example, use of industrial by-products in the construction of transportation networks can contribute to sustainable development. However, such uses should pose no potential environmental risk to the surrounding environments [1–7]. Currently, man-made materials including industrial by-products (such as fly ash, steel slag, plastics, and scrap tires) are used as substitutes for natural aggregates in road construction. Since these products are nontraditional construction materials, there are concerns about their environmental suitability and sustainability. Current research, which primarily focuses on the physical properties, chemical properties, engineering designs and constructability, has identified several promising uses for these wastes [7–12]. However, research projects concerning: (1) environmental impact assessment (EIA) of the leachates of various organic and inorganic SWMs on surface and ground waters, and (2) information on the wastes' chemical stability and long-term

environmental behavior are needed to insure against adverse environmental impacts [1–6, 13–15]. Without such information transportation agencies, construction material suppliers and environmental officials cannot properly assess the suitability, environmental compatibility, and sustainability of wastes used or proposed to be used in road construction.

Evaluation of environmental compatibility and sustainability of such materials is mostly limited to testing the leaching characteristics of selected materials in freshly placed road pavements [16, 17]. Thus far, no standard procedures exist to analyze the full life cycle impact of substitute materials used in road construction. Many industries, including the construction industry, are exploring the concept of sustainable development, which leads to viewing the surrounding environment as an opportunity for innovation and revenue generation as opposed to a cost center [1–6, 8, 9, 18]. The challenge for businesses, governments, and communities is to ensure that continued economic development is environmentally and socially sustainable [1, 2].

The goals of the present chapter are to: (a) review and evaluate the various types of solid wastes currently used as highway construction and repair (C&R) materials, (b) discuss the chemical and physical properties of such wastes and their engineering uses, and (c) present the general project approaches of a major study commissioned by the National Research Council (NRC), the National Cooperative Highway Research Program (NCHRP) and the Federal Highway Administration (FHA) to investigate the environmental impacts of highway C&R materials on surface and ground waters. Detailed information about the project, its different phases and models, as well as the lessons learned is presented in this and other chapters in the present book.

2 Environmental Sustainability

Waste generation is a growing problem around the world. There is a range of international legislation in place to try and deal with it, as well as voluntary targets aimed at all sectors of society.

In general, there are different types of wastes [1]. These include:

- Solid wastes: all discarded household, commercial wastes, non-hazardous institutional and industrial wastes, street sweepings, construction debris, agricultural wastes, and other non-hazardous/non-toxic solid wastes.
- Special wastes: these are household hazardous wastes such as paints, thinners, household batteries, lead-acid batteries, spray canisters, and the like. They include wastes from residential and commercial sources that comprise bulky wastes, consumer electronics, white goods, yard wastes that are collected separately, oil, and tires.
- Hazardous wastes: these are solid, liquid, contained gaseous or semisolid wastes which may cause or contribute to the increase in mortality, or to

serious or incapacitating irreversible illness, or to acute/chronic effects on the health of people and other organisms.

- Infectious wastes: mostly generated by hospitals.

Solid waste collection, transfer and disposal have become a major concern worldwide [1, 3]. In many countries, conventional systems are able to collect between 30–50% of solid wastes, and these wastes are disposed in ways detrimental to the environment. Accordingly, wastes can be diverted from disposal through a variety of means, including reuse, recycling and composting, to environmentally friendly and sustainable practices.

2.1

Sustainable Waste Management

Waste materials consist of exactly the same substances as useful raw materials and products, except that they are perceived as having no value. In fact, every kilogram of waste that we throw away represents a waste of valuable raw materials. It is now recognized that the Earth's resources are finite and there is a need to conserve them. The Earth's ability to assimilate wastes is limited, and going beyond these limits will damage natural systems and pose risks to individuals and populations.

As a consequence of these limits, it is now widely recognized and accepted that there is a need to manage all of our wastes more sustainably. Sustainability implies that something can be continued. Sustainable waste management implies the positive utilization of what has been traditionally regarded as waste, but may be no more than materials that are in the wrong place at the wrong time. Sustainable waste management means that there is a need to:

- Reduce the amount of waste produced by society.
- Make the best use of waste produced by society.
- Choose waste management practices which minimize the risk of immediate and future environmental pollution and harm to human health.

As well as reducing the quantity of waste, it is equally important to reduce its hazardous nature, since it is the nature as well as the quantity of waste that determines its potential for harming the environment.

In order to bring about sustainable waste management, one of the obstacles is that we live in a “*throughput economy*”, where materials and energy are used to make products, which are eventually discarded. To be more sustainable, there is a need to change to a “*circular economy*” by closing the materials loop – to use “waste” as the input material for other processes or products, in order to reduce waste and reduce the need for virgin raw materials. This is exactly what happens in nature. In nature, there are no wastes; all wastes are recycled by natural processes.

2.2

Environmental Impacts of Wastes

Solid waste generation represents a waste of resources and materials, which can also cause severe environmental impact on land, water and air. It is worth remembering that all pollution is a form of waste. In general, landfill, apart from representing a waste of materials, can potentially have very severe effects on the surrounding environment. These include:

- Fire and explosion: The risk of explosion is present whenever organic (biodegradable) wastes are landfilled, as they produce an explosive mixture of gases containing methane. This is known as landfill gas. In addition, certain wastes (like flammable or oxidizing substances) present a risk of fire.
- Pollution of surface and ground waters: As wastes break down in landfills, a highly polluting liquid – leachate – is produced. If not carefully controlled, this may pollute ground and surface water.
- Further impacts, such as: contamination of land, impacts on local amenities – caused by dust, odor, noise, traffic, and aesthetics.

On the other hand, landfill can be an environmental benefit. If wastes are relatively inert or are land-filled under carefully engineered conditions, previously derelict land may be reclaimed. But suitable sites near centers of waste production are becoming harder and harder to find, and this adds to the cost of transporting waste. Landfill is also becoming more expensive as regulations are tightened up.

The recently adopted landfill directive: (a) demands high standards of landfill management, and also seeks to ban certain difficult wastes from landfill, and (b) seeks a progressive reduction in the land-filling of biodegradable wastes which account for a high percentage of wastes sent to sites.

Because the Landfill Tax was placed on all wastes sent to landfills, there is evidence of a reduction of the amount of waste going to landfill. This probably partly reflects an increase in waste reduction, re-use and recycling. However, there have been reports of increases in the amounts of industrial waste being spread onto agricultural land.

3

Types of Recycled Solid Wastes

In addition to virgin materials, transportation agencies have been actively encouraging the use of waste and recycled materials for many years (Table 1). Recent legislated mandates led many agencies to expand their use of waste and by-products. The following sections discuss the various solid wastes that have been used in several highway applications.

Table 1 Waste and by-product materials used in highway construction and repair applications with annual production

#	Type	ID	Annual production (some recycled) ¹	#	Type	ID	Annual production (some recycled) ¹
1	Baghouse fines	BHF	5.4–7.2 million t; (6–8 million T)	12	Non-ferrous slag	NFS	0.45–0.9 million t; (0.5–1.0 million T)
2	Blast furnace slag	BFS	14 million t; (15.4 million T)	13	Plastics	PL	44.7 million t; (40.2 million T)
3	Carpet fiber dusts		1.2 million t; (1.32 million T)	14	Quarry by-products	QBP	3.6 billion t; (4 billion T)
4	Coal bottom ash/ boiler slag	BA/BS	53.5 million t; (59.4 million T)	15	Reclaimed asphalt pavement	RAP	NR
5	Coal fly ash	FA	45 million t; (49.6 million T)	16	Reclaimed concrete material	RCM	NR
6	Contaminated soils	CS	NR	17	Roofing shingle scrap	RSS	10 million t; (11 million T)
7	Flue gas desulfuriza- tion scrubber material	FGDSM	21.4 million t; (23.8 million T)	18	Scrap tires	ST	280 million tires discarded each year
8	Foundry sand	FS	9–13.6 million t; (10–15 million T)	19	Sewage sludge ash	SSA	0.45–0.9 million t; (0.5–1.0 million T)
9	Kiln dusts	KD	90 million t; (100 million T)	20	Steel slag	SS	6.9 million t; (7.6 million T)
10	Mineral processing wastes	MPW	Amounts since early production are 50 billion t; (55 billion T)	21	Sulfate wastes	SW	900 million t; (1 billion T)
11	Municipal solid waste incinerator ash	MSW	2.5 million t; (2.76 million T)	22	Waste glass	WG	9.2 million t; (10.2 million T)

¹ Metric ton = t = 2,205 pounds (1000 kg); a short ton = T = 2,000 pounds (907 kg); NR = not reported

3.1

Baghouse Fines

Baghouse fines (BHF) are dust particles that are captured from the exhaust gases resulting from burning coal as a source of energy. A baghouse is a large compartment fitted with several rows of filters (fabric curtains) through which gases flow to reach the exhaust stack (chimney). The fabric pores are smaller than the particles carried in the exhaust and are therefore filtered out. The filters are periodically shaken and the dust is collected from bottom hoppers. It is estimated that approximately 5.4–7.2 million metric tons (6–8 million tons) of baghouse fines are generated annually by the U.S. asphalt production industry [10, 19–34].

3.2

Blast Furnace Slag

During the production of iron, iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace along with coke for fuel. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. This molten iron product can be cast into iron products, but is most often used as a feedstock for steel production [12, 35–48].

Blast furnace slag (BFS) is a nonmetallic co-product produced in the process. It consists primarily of silicates, aluminosilicates, and calcium-alumina silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20% by mass of iron production.

Different forms of slag product are produced depending on the method used to cool the molten slag. These products (Table 2) include air-cooled blast furnace slag (ACBFS), expanded or foamed slag (EBFS or FBFS), pelletized blast furnace slag (PBFS), and granulated blast furnace slag (GBFS).

3.3

Carpet Fiber Dusts

The carpet industry in the United States produces about 1 billion square meters of carpet per year. Of this, approximately 70% is used to replace existing carpet; this translates into 1.2 million t (1.32 million T) of carpet waste produced annually [49]. Additional wastes produced by the carpet making industry increase the total amount of waste fibers to an estimated 2 million t (2.2 million T). Several research efforts are addressing ways to include these waste fibers in both asphalt pavements and Portland cement concrete.

Table 2 Types of blast furnace slag

Type	Cooling technique
Air-cooled blast slag (ACBFS)	– If the liquid slag is poured into beds and slowly cooled under ambient conditions, a crystalline structure is formed, and a hard, lump slag is produced, which can subsequently be crushed and screened
Expanded or foamed blast furnace slag (EBFS/FBFS)	– If the molten slag is cooled and solidified by adding controlled quantities of water, air, or steam, the process of cooling and solidification can be accelerated, increasing the cellular nature of the slag and producing a lightweight expanded or foamed product – Foamed slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density
Pelletized blast furnace slag (PBFS)	– If the molten slag is cooled and solidified with water and air quenched in a spinning drum, pellets, rather than a solid mass, can be produced – By controlling the process, the pellets can be made more crystalline, which is beneficial for aggregate use, or more vitrified (glassy), which is more desirable in cementitious applications – More rapid quenching results in greater vitrification and less crystallization
Granulated blast furnace slag (GBFS)	– If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs – This process results in the formation of sand size (or frit-like) fragments, usually with some friable clinker-like material – The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production – When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag (GGBFS) has cementitious properties, which make a suitable partial replacement for or additive to Portland cement

3.4
Coal Bottom Ash/Boiler Slag

Coal bottom ash (BA) and boiler slag (BS) are the coarse, granular, incombustible by-products that are collected from the bottom of furnaces that burn coal for the generation of steam, the production of electric power, or both. The majority of these coal by-products are produced at coal-fired electric utility generating stations, although considerable BA and/or BS are also produced from many smaller industrial or institutional coal-fired boilers and from coal-burning independent power production facilities [50–57]. The type of by-product (BA or BS) produced depends on the type of furnace used to burn the coal. The main differences between coal bottom ash and boiler slag are summarized in Table 3.

Table 3 Differences between bottom ash and boiler slag

Types	Description
Bottom ash (BA)	– The most common type of coal-burning furnace in the electric utility industry is the dry, bottom pulverized coal boiler – When pulverized coal is burned in a dry, bottom boiler, about 80% of the unburned material or ash is entrained in the flue gas and is captured and recovered as fly ash – The remaining 20% of the ash is dry BA, a dark gray, granular, porous, predominantly sand size minus 12.7 mm material that is collected in a water-filled hopper at the bottom of the furnace – When a sufficient amount of BA drops into the hopper, it is removed by means of high-pressure water jets and conveyed by sluiceways either to a disposal pond or to a decant basin for dewatering, crushing, and stockpiling for disposal or use – During 1996, the utility industry generated 14.5 million metric tons (16.1 million tons) of BA
Boiler slag (BS)	– <i>Wet-bottom boiler slag</i> is a term that describes the molten condition of the ash as it is drawn from the bottom of the slag-tap or cyclone furnaces. At intervals, high-pressure water jets wash the boiler slag from the hopper pit into a sluiceway which is then conveys it to a collection basin for dewatering, possible crushing or screening, and either disposal or reuse – During 1995, the utility industry in the United States generated 2.3 million metric tons (2.6 million tons) of boiler slag – There are two types of <i>wet-bottom boilers</i>: the <i>slag-tap boiler</i> and the <i>cyclone boiler</i>. The slag-tap boiler burns pulverized coal and the cyclone boiler burns crushed coal – In each type, the bottom ash is kept in a molten state and tapped off as a liquid. Both boiler types have a solid base with orifice that can be opened to permit the molten ash that has an collected at the base to flow into the ash hopper below – The ash hopper in wet-bottom furnaces contains quenching water. When the molten slag comes in contact with the quenching water, it fractures instantly, crystallizes, and forms pellets. The resulting boiler slag, often referred to as “black beauty,” is a coarse, hard, black, angular, glassy material – When pulverized coal is burned in a slag-tap furnace, as much as 50% of the ash is retained in the furnace as boiler slag. In a cyclone furnace, which burns crushed coal, some 70–80% of the ash is retained as boiler slag, with only 20–30% leaving the furnace in the form of fly ash

3.5

Coal Fly Ash

The fly ash (FA) produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones [58–60].

In general, there are three types of coal-fired boiler furnaces used in the electric utility industry. They are referred to as dry-bottom boilers, wet-bottom boilers, and cyclone furnaces. The most common type of coal burning furnace is the dry-bottom furnace [61–65].

When pulverized coal is combusted in a dry-ash, dry-bottom boiler, about 80% of all the ash leaves the furnace as fly ash, entrained in the flue gas. When pulverized coal is combusted in a wet-bottom (or slag-tap) furnace, as much as 50% of the ash is retained in the furnace, with the other 50% being entrained in the flue gas. In a cyclone furnace, where crushed coal is used as a fuel, 70–80% of the ash is retained as boiler slag and only 20–30% leaves the furnace as dry ash in the flue gas [58–63].

During 1996, the most recent year for which ash statistics are currently available, the electrical utility industry in the United States generated approximately 53.5 million metric tons (59.4 million tons) of coal fly ash. Until 1996, the amount of fly ash produced annually had remained roughly the same since 1977, ranging from 42.9–49.7 million metric tons (47.2–54.8 million tons) [61–65].

3.6

Contaminated Soils

Historically, when contaminated soils were discovered during construction, activities immediately stopped, investigations followed, regulatory reviews occurred, and major delays resulted. Typically, remediation involved excavation, treatment and disposal at an off-site facility, which not only caused a roadway construction delay but also created a large opening in the ground. Clean, structurally competent fill was shipped on site and compacted before construction resumed. Today, however, some options may exist that allow for reuse of the soil, depending on the type of contamination present and the local regulatory environment [1–4].

The types of contamination generally found fall into three classifications:

- *Petroleum and other volatile organic-impacted soils:* Petroleum-contaminated soil is the most common problem found at transportation sites. Reuse options for these soils would most likely involve incorporation with asphalt or concrete, and the final product would be subject to leachability testing to ensure it was no longer considered a hazardous material.
- *Semi- to non-volatile compound impacted soils:* Contaminants in this group include waste oils, naphthas, creosotes, coal tars, and pesticides. States may

require more stringent treatment and a larger analytical suite of petroleum compounds, metals and PCBs prior to reuse of these soils, so waste oil impacted soils are typically more expensive to recycle than gasoline-impacted soils. Naphthas, creosotes, coal tars and pesticides are considered hazardous wastes, and reuse is limited to either asphalt or concrete incorporation. These contaminants are subject to increased regulatory scrutiny due to their high degree of toxicity, so excavation and disposal would be the most cost-effective option for smaller quantities of these soils.

- *Metals-impacted soils:* Lead- and arsenic-impacted soils are the most commonly encountered metal-impacted soils. Leachability testing determines if a soil is considered hazardous under RCRA. By their nature, metals do not lend themselves to either thermal treatment or aeration, but they can be readily bound up in asphalt and concrete. Discussed below are various treatment technologies that have enabled the reuse of contaminated soils.

Each type of compound discussed before, by its nature, lends itself to either direct reuse or some degree of treatment prior to reuse. Direct reuse includes utilizing the soil as a raw material for asphalt or concrete. Treatment options range from simple and inexpensive aeration to costly complicated high temperature thermal treatment. Treatment operations discussed here include aeration, land farming, bioremediation, low-temperature thermal desorption, high temperature thermal treatment, asphalt incorporation, and concrete incorporation.

Reuse of soils impacted by volatile compounds or hydrocarbons generally involves either treatment before reuse or direct incorporation. Treatment options include the following:

- *Aeration:* an effective technique for removal of volatile organic compounds or gasoline-impacted soils, in warmer climates. The process is simple – the soils are exposed to the air through excavation and handling activities, and then further exposed by being processed through a powder screen. The volatile compounds are released from the soil into the atmosphere.
- *Land farming:* a combination of aeration and bioremediation techniques. It is also effective for removal of volatile organic compounds or gasoline- and diesel fuel-impacted soils, especially in warmer climates. The soils are spread out in thin lifts and allowed to volatilize for a period of time before being turned or disked. In southern climates, these soils can reach clean levels in a matter of days. The soils may have to be covered for protection from inclement weather, run off controlled, and possibly collected and treated. Volatile emission rates can be controlled by varying the depth of the lifts and the number of times the soils are turned. While aeration is not allowed in many states, under the right circumstances it is the most economical treatment method.
- *Bioremediation:* This has a slower treatment rate than the other options. Basically, impacted soils are mounded and then encapsulated with a plastic membrane after being blended with bacteria, nutrients, and bulking agents

to maximize the bacterial breakdown of the volatile organic or petroleum compounds. It can take several months for the heavier-ended hydrocarbon products to breakdown; however, if an area of impacted soil is known about prior to the start of construction, bioremediation can save money compared to other treatment technologies [2].

- *Low-temperature thermal desorption*: It consists of heating the soils to drive off the volatile compounds and/or hydrocarbons. The heat from the burn unit volatilizes, but may not completely destroy, the contaminants. Low-temperature desorption usually can meet clean soil criteria and the impacted soils can be transported to either a permanent facility or, if enough material is present, a mobile unit can be brought to the site. Special consideration must be given chlorinated compounds during low-temperature desorption due to their ability to break down and form hydrochloric acid in the hot air stream, causing potential air emission problems.
- *High temperature thermal treatment*: It is similar to low temperature thermal desorption, but is hot enough to thermally destroy volatile and hydrocarbon compounds. The cost of high temperature thermal treatment is, therefore, much more than low-temperature desorption, but the soil is typically completely depleted of volatile and heavy hydrocarbon compounds. PCBs are typically destroyed to 99.99% by this method. The use of the soil after high temperature thermal treatment depends on the original material's quality, as the soil can typically be used as a clean fill. In some cases, it is used as a feed stock for asphalt or concrete.

The potential uses of soils after they are treated are as varied as the treatment options themselves [10–11]. The use depends on the quality of the original material as well as the degree of treatment accomplished. Typical uses range from soil for sub-base, berms and general fill, to fill specifically for landfills, to feed stock for asphalt and concrete.

3.7

FGD Scrubber Material

The burning of pulverized coal in electric power plants produces sulfur dioxide (SO_2) gas emissions. The 1990 Clean Air Act and its subsequent amendments mandated the reduction of power plant SO_2 emissions [66–70]. The Best Demonstrated Available Technology (BDAT) for reducing SO_2 emissions is wet scrubber flue gas desulfurization (FGD) systems. These systems are designed to introduce an alkaline sorbent consisting of lime or limestone in a spray form into the exhaust gas system of a coal-fired boiler. The alkali reacts with the SO_2 gas and is collected in a liquid form as calcium sulfite or calcium sulfate slurry. The calcium sulfite or sulfate is allowed to settle out as most of the water is recycled [66–80].

FGD scrubber sludge is the wet solid residue generated from the treatment of these emissions. The wet scrubber discharge is an off-white slurry with solids

content in the range of 5–10%. Because FGD systems are usually accompanied by or combined with a fly ash removal system, fly ash is often incorporated into the FGD sludge.

The relative proportion of the sulfite and sulfate constituents is very important in determining the physical properties of FGD sludge. Depending on the type of process and sorbent material used, the calcium sulfite (CaSO_3) can contribute anywhere from 20–90% of the available sulfur, the remaining being calcium sulfate (CaSO_4). FGD sludges with high concentrations of sulfite pose a significant dewatering problem. The sulfite sludges settle and filter poorly. They are generally not suitable for land disposal or management without additional treatment. Treatment can include forced oxidation, dewatering, and/or stabilization or fixation [66–80]:

- Forced oxidation, which is a separate step after the actual desulfurization process, involves blowing air into the tank that holds calcium sulfite sludge, and results in the oxidation of the calcium sulfite (CaSO_3) to calcium sulfate (CaSO_4). The calcium sulfate formed by this reaction grows to a larger crystal size than calcium sulfite. As a result, the calcium sulfate can be filtered or dewatered to a much drier and more stable material than the calcium sulfite sludge.
- Dewatering of FGD scrubber sludge is ordinarily accomplished by centrifuges or belt filter presses.
- Stabilization of FGD scrubber material refers to the addition of a sufficient amount of dry material, such as fly ash, to the dewatered FGD filter cake so that the stabilized material can be handled and transported by construction equipment without water seepage and can also support normal compaction machinery when placed into a landfill.
- Fixation ordinarily refers to the addition of sufficient chemical reagent(s) to convert the stabilized FGD scrubber material into a solidified mass and produce a material of sufficient strength to satisfy applicable structural specifications. This can involve the addition of Portland cement, lime, and/or self-cementing fly ash to induce both physical and chemical reactions between the stabilized sludge filter cake and the added reagents. The majority of the fixation processes currently in operation involve the addition of quicklime and pozzolanic fly ash, resulting in a pozzolanic reaction (a reaction in the presence of lime – calcium oxide, CaO – and water to produce reaction products that are cementitious in nature) that provides added strength to dewatered FGD scrubber material.

As of December 1994, there were at least 157 coal-fired boiler units at 92 power plants with wet scrubbing systems operating. These plants are located in at least 32 states [66, 72–75]. Additional scrubbers are planned or under construction in order to achieve compliance with the Clean Air Act requirements. As of 1996, the operating scrubber systems at coal-fired power plants generated approximately 21.4 million metric tons (23.8 million tons) of FGD sludge annually [71–80].

3.8

Foundry Sand

Foundry sand (FS) consists primarily of clean, uniformly sized, high-quality silica sand or lake sand that is bonded to form molds for ferrous (iron and steel) and nonferrous (copper, aluminum, brass) metal castings [81–87]. Ferrous (iron and steel) industries account for approximately 95% of foundry sand used for castings. The automotive industry and its parts suppliers are the major generators of foundry sand.

The most common casting process used in the foundry industry is the sand cast system. Virtually all sand cast molds for ferrous castings are of the green sand type. Green sand consists of high-quality silica sand, about 10% bentonite clay (as the binder), 2–5% water and about 5% sea coal (a carbonaceous mold additive to improve casting finish). The type of metal being cast determines which additives and what gradation of sand is used. The green sand used in the process constitutes upwards of 90% of the molding materials used [85–87].

In addition to green sand molds, chemically bonded sand cast systems are also used. These systems involve the use of one or more organic binders in conjunction with catalysts and different hardening/setting procedures. Foundry sand makes up about 97% of this mixture. Chemically bonded systems are most often used for “cores” (used to produce cavities that are not practical to produce by normal molding operations) and for molds for nonferrous castings.

The annual generation of foundry waste (including dust and spent foundry sand) in the United States ranges from 9–13.6 million metric tons (10–15 million tons) [83–85].

3.9

Kiln Dusts

Kiln dusts (KD) are fine by-products of Portland cement and lime high-temperature rotary kiln production operations [88–98] that are captured in the air pollution control dust collection systems (cyclones, electrostatic precipitators, and baghouses). Different types of KD are discussed in Table 4.

In addition to fresh cement kiln dust (CKD) and lime kiln dust (LKD) production, it is estimated that the total amount of KD currently stockpiled throughout the country exceeds close to 90 million metric tons (100 million tons). These stockpiles are usually located relatively close to the cement and lime manufacturing plants, and vary in age and composition, with exposure to the elements reducing the chemical reactivity of the dusts.

Table 4 Different types of kiln dusts

Kiln dust	Description
Cement kiln dust (CKD)	– CKD is a fine powdery material similar in appearance to Portland cement– Fresh CKD can be classified as belonging to one of four categories, depending on the kiln process employed and the degree of separation in the dust collection system – There are two types of cement kiln processes: <i>wet-process kilns</i>, which accept feed materials in a slurry form; and <i>dry-process kilns</i>, which accept feed materials in a dry, ground form – In each type of process the dust can be collected in two ways: a portion of the dust can be separated and returned to the kiln from the dust collection system (like a cyclone) closest to the kiln, or the total quantity of dust produced can be recycled or discarded – The chemical and physical characteristics of CKD that is collected for use outside of the cement production facility will depend in great part on the method of dust collection employed at the facility – Free lime can be found in CKD, and its concentration is typically highest in the coarser particles captured closest to the kiln – Finer particles tend to exhibit higher concentrations of sulfates and alkalis. If the coarser particles are not separated out and returned to the kiln, the total dust will be higher in free lime – CKD from wet-process kilns also tends to be lower in calcium content than dust from dry-process kilns. Approximately 12.9 million metric tons (14.2 million tons) of CKD are produced annually
Lime kiln dust (LKD)	– LKD is physically similar to CKD, but chemically quite different – LKD can vary chemically depending on whether high-calcium lime (chemical lime, hydrated lime, quicklime) or dolomitic lime is being manufactured – Fresh LKD can be divided into two categories based on relative reactivity, which is directly related to free lime and free magnesia content – Free lime and magnesia content are most dependent on whether the feedstock employed is calcitic or dolomitic limestone – LKD with a high free lime content is highly reactive, producing an exothermic reaction upon addition of water – Approximately 1.8–3.6 million metric tons (2–4 million tons) of LKD are generated each year in the United States

3.10

Mineral Processing Wastes

Mineral processing wastes (MPW) are wastes that are generated during the extraction and beneficiation of ores and minerals. These wastes can be subdivided into a number of categories [99–112]: waste rock, mill tailings, coal refuse, wash slimes, and spent oil shale (Table 5). The mining and processing of mineral ores result in the production of large quantities of residual wastes that are for the most part earth- or rock-like in nature.

It is estimated that the mining and processing of mineral ores generate approximately 1.6 billion metric tons (1.8 billion tons) of mineral processing waste each year in the United States [109]. Mineral processing wastes account for nearly half of all the solid waste that is generated each year in the United States. Accumulations of mineral wastes from decades of past mining activities probably account for at least 50 billion metric tons (55 billion tons) of material [112]. Although many sources of mining activity are located in remote areas, nearly every state has significant quantities of mineral processing wastes. Table 5 describes the different kinds of MPW [102–110].

3.11

MSW Combustor Ash

Municipal solid waste (MSW) combustor ash is the by-product that is produced during the combustion of municipal solid waste in solid waste combustor facilities. In most modern mass burn solid waste combustors, several individual ash streams are produced. They include grate ash, siftings, boiler ash, scrubber ash and precipitator or baghouse ash [113–118].

At the present time in the United States, all of the ash streams are typically combined. This combined stream is referred to as combined ash. The term bottom ash is commonly used to refer to the grate ash, siftings and, in some cases, the boiler ash stream. The term fly ash is also used and refers to the ash collected in the air pollution control system, which includes the scrubber ash and precipitator or baghouse ash. In Europe, most facilities separate and separately manage the bottom ash and fly ash streams. Table 6 summarized the different types of MSW combustor ash [113–128].

There are two basic types of solid waste combustors currently in operation in the United States, mass burn facilities and refuse derived-fuel (RDF) facilities. Mass burn facilities manage over 90% of the solid waste that is combusted in the United States. Mass burn facilities are designed to handle unsorted solid waste, whereas RDF facilities are designed to handle preprocessed trash. The ash produced by RDF facilities, where the incoming municipal solid waste stream is shredded and presorted to remove ferrous metal and in certain cases nonferrous metal prior to combustion, can be expected to have different physical and chemical properties from ash generated at mass burn facilities [115–118].

Table 5 Types of mineral processing wastes

Types	Description
Waste rock	– Large amounts of waste rock are produced from surface mining operations, such as open-pit copper, phosphate, uranium, iron, and taconite mines – Small amounts are generated from underground mining – Waste rock generally consists of coarse, crushed, or blocky material covering a range of sizes, from very large boulders or blocks to fine sand-size particles and dust – Waste rock is typically removed during mining operations along with overburden and often has little or no practical mineral value – Types of rock included are igneous (granite, rhyolite, quartz), metamorphic (taconite, schist, hornblende) and sedimentary (dolomite, limestone, sandstone, oil shale) – It is estimated that approximately 0.9 billion metric tons (1 billion tons) of waste rock are generated each year in the United States
Mill tailings	– Mill tailings consist predominantly of extremely fine particles that are rejected from the grinding, screening, or processing of the raw material – They are generally uniform in character and size and usually consist of hard, angular siliceous particles with a high % of fines – Typically, mill tailings range from sand to silt-clay in particle size (40–90% passing a 0.075 mm mesh), depending on the degree of processing needed to recover the ore – The basic mineral processing techniques involved in the milling or concentrating of ore are crushing, then separation of the ore from the impurities – Separation can be accomplished by any one or more of the following methods, including: media separation, gravity separation, froth flotation, or magnetic separation – About 450 million metric tons (500 million tons) per year of mill tailings are generated vom copper, iron, taconite, lead, and zinc ore concentration processes and uranium refining, as well as other ores, such as barite, feldspar, gold, molybdenum, nickel, and silver – Mill tailings are typically slurried into large impoundments, where they gradually become partially dewatered
Coal refuse	– Coal refuse is the reject material that is produced during the preparation and washing of coal – Coal naturally occurs interbedded within sedimentary deposits, and the reject material consists of varying amounts of slate, shale, sandstone, siltstone, and clay minerals, which occur within or adjacent to the coal seam, as well as some coal that is not separated during processing

Table 5 (continued)

Types	Description
Coal refuse	– Various mineral processing techniques are used to separate the coal from the unwanted foreign matter. The equipment most frequently used in these plants is designed to separate the coal from reject materials, and incorporates methods that make use of the difference in specific gravity between the coal and host rock – Most of the coal that is cleaned is deep-mined bituminous coal – The reject material is in the form of either coarse refuse or fine refuse – Coarse coal refuse can vary in size from approximately 2–100 mm – The refuse is discharged from preparation plants by conveyor or into trucks, where it is taken and placed into large banks or stockpiles – Fine coal refuse is less than 2 mm and is usually discarded in slurry form – Approximately 75% of coal refuse is coarse and 25% is fine – Some 109 million metric tons (120 million tons) of coal refuse are generated each year in the United States: – There are more than 600 coal preparation plants located in 21 coal-producing states – The largest amounts of coal refuse can be found in Kentucky, West Virginia, Pennsylvania, Illinois, Virginia, Ohio, and Delaware – As the annual production of coal continues to increase, it is expected that the amount of coal refuse generated will also increase
Wash slimes	– Wash slimes are by-products of phosphate and aluminum production, generated from processes in which large volumes of water are used, resulting in slurries having low solids content and fines in suspension – They generally contain significant amounts of water, even after prolonged periods of drying. – In contrast, tailings and fine coal refuse, which are initially disposed of as slurries, ultimately dry out and become solid or semi-solid materials – Approximately 90 million metric tons (100 million tons) of phosphate slimes (wet) and 4.5 million metric tons (5 million tons) of alumina mud (wet) are generated every year in the United States – These reject materials are stored in large holding ponds – Because of the difficulty encountered in drying, there are no practical known uses for wash slimes

Table 5 (continued)

Types	Description
Spent oil shale	– Oil shale is mined as a source of recoverable oil, which is the waste by-product remaining after the extraction of oil – It is a black residue generated when oil shale is retorted (vaporized and distilled) to produce an organic oil-bearing substance called kerogen – Spent oil shale can range in size from very fine particles, smaller than 0.075 mm, to large chunks, up to 230 mm or more in diameter – The coarse spent oil shale resembles waste rock because of its large particle size – The material, when crushed to a maximum size of 19.0 mm, can be characterized as a relatively dense, well-graded aggregate – The oil shale industry in the United States initially developed in the early 1970s primarily in northwest Colorado with a series of pilot retorting plants that operated for a number of years (currently uneconomical and inactive)

Table 6 Types of municipal solid waste combustor ash

Types	Description
Bottom ash (BA)	– Approximately 90% of the bottom ash stream consists of grate ash, which is the ash fraction that remains on the stoker or grate at the completion of the combustion cycle – It is similar in appearance to porous, grayish, silty sand with gravel, and contains small amounts of unburnt organic material and chunks of metal – The grate ash stream consists primarily of glass, ceramics, ferrous and nonferrous metals, and minerals – It comprises approximately 75–80% of the total combined ash stream
Boiler ash and fly ash (FA)	– Boiler ash, scrubber ash, and precipitator or baghouse ash consist of particles that originate in the primary combustion zone area and are subsequently entrained in the combustion gas stream, then carried into the boiler and air pollution control system – As the combustion gas passes through the boiler, scrubber, and precipitator or baghouse, the entrained particles adhere to the boiler tubes and walls (boiler ash) or are collected in the air pollution control equipment (fly ash), which consists of the scrubber, electrostatic precipitator, or baghouse – Ash extracted from the combustion gas consists of very fine with a significant fraction measuring less than 0.1 mm in diameter

Table 6 (continued)

Types	Description
Boiler ash and fly ash	– The baghouse or precipitator ash comprises approximately 10–15% of the total combined ash stream – Approximately 29.5 million metric tons (32.5 million tons) of solid waste is combusted annually at approximately 160 municipal waste combustor plants in the United States, generating approximately 8 million metric tons (9 million tons) of residual or ash

There are also significant differences between ash generated at modern waste-to-energy facilities and that generated at older facilities. Newer facilities, with improved furnace designs, generally achieve better burnout and have reduced organic content in the ash product. Due to air pollution control requirements in newer facilities, lime or a lime-based reagent is introduced into the pollution control system to scrub out acid gases from the combustion gas stream. This produces a fly ash that contains both reacted and unreacted lime. Older facilities without acid gas scrubbing do not have lime in their fly ash. Finally, newer facilities with improved air pollution control equipment (such as baghouses) are better able to capture the finer particulate materials and trace contaminants, which many of the older facilities usually release into the air. It also is likely that, in the future, more stringent air pollution control requirements (such as mercury and NO_x control) will further alter both the physical and chemical properties of fly ash streams [117–121].

3.12
Nonferrous Slags

Nonferrous slags (NFS) are produced during the recovery and processing of nonferrous metal from natural ores. The slags are molten by-products of high temperature processes that are primarily used to separate the metal and non-metal constituents contained in the bulk ore. When cooled, the molten slag converts to a rocklike or granular material [129–135].

The processing of most ores involves a series of standardized steps. After mining, the bulk ore is processed to remove any gangue (excess waste rock and minerals). This processing typically consists of pulverizing the ore to a relatively fine state, followed by some form of gravity separation of the metals from the gangue [134–140]. The refined ore is processed thermally to separate the metal and non-metal constituents, and then further reduced to the free metal. Since most of these metals are unsuitable for use in a pure state, they are subsequently combined with other elements and compounds to form alloys with the desired properties.

In preparation for metal ion reduction, some nonoxide minerals are often converted to oxides by heating in air at temperatures below their melting point

(“roasting”). Sulfide minerals, when present (in copper and nickel ore), are converted to oxides in this process. The reduction of the metal ion to the free metal is normally accomplished in a process referred to as smelting. In this process, a reducing agent, such as coke (impure carbon), along with carbon monoxide and hydrogen, is combined with the roasted product and melted in a siliceous flux [140–145]. The metal is subsequently gravimetrically separated from the composite flux, leaving the residual slag.

There are various NFS, which include copper, nickel, phosphorus, lead, lead-zinc, and zinc. Approximately 3.6 million metric tons (4 million tons) each of copper and phosphorus slag are produced each year in the United States, while the annual production of nickel, lead and zinc slags is estimated to be in the range of 0.45–0.9 million metric tons (0.5–1.0 million tons) [143]. A summary of the different types of nonferrous slags is represented in Table 7.

Table 7 Types of nonferrous slags

Types	Description
Copper and nickel slags	– Copper and nickel slags are produced by: – <i>Roasting</i>: in which sulfur in the ore is eliminated as sulfur dioxide – <i>Smelting</i>: in which the roasted product is melted in a siliceous flux and the metal is reduced – <i>Converting</i>: where the melt is desulfurized with lime flux, iron ore, or a basic slag, and then oxygen lanced to remove other impurities – Copper slag derived by smelting of copper concentrates in a reverberatory furnace is referred to as reverberatory copper slag
Phosphorus slag	– Phosphorus slag is a by-product of the elemental phosphorus refining process – Elemental phosphorus is separated from the phosphate-bearing rock in an electric arc furnace, with silica and carbon added as flux materials to remove impurities during the slagging process – Iron, which is added to the furnace charge, combines with phosphorus to form ferrophosphorus, which can be tapped off – The slag, which remains after removal of elemental phosphorus and/or ferrophosphorus, is also tapped off
Lead, lead-zinc, and zinc slags	– Lead, lead-zinc, and zinc slags are produced during pyrometallurgical treatment of the sulfide ores – The process includes three operations similar to copper and nickel slag production: roasting, smelting, and converting – Lead and zinc are often related as co-products in both source and metallurgical treatments, and the various combinations of slags, which include lead, lead-zinc, and zinc, are similarly produced

3.13 Plastics

Plastics (PL) comprise more than 8% of the total weight of the municipal waste stream and about 12–20% of its volume [146, 147]. In 1992, approximately 30 million metric tons (33 million tons) of plastics were discarded in the United States; only 14.7 million metric tons (16.2 million tons) were recycled. Current research on the use of recycled plastics in highway construction is wide and varied.

The use of virgin polyethylene as an additive to asphalt concrete is not new; however, two new processes also use recycled plastic as an asphalt cement additive [146, 147]. These latter two processes both use recycled low-density polyethylene resin, which is generally obtained from plastic trash and sandwich bags. The recycled plastic is made into pellets and added to asphalt cement at a rate of 4–7% by weight of binder [146–148].

3.14 Quarry By-Products

Processing of crushed stone for use as construction aggregate consists of blasting, primary and secondary crushing, washing, screening, and stockpiling operations [149–152]. Quarry by-products (QBP) are produced during crushing and washing operations. There are three types of quarry by-products resulting from these operations: screenings, pond fines, and baghouse fines. Table 8 evaluates the main differences among these operations.

3.15 Reclaimed Asphalt Pavement

Reclaimed asphalt pavement (RAP) is the term given to removed and/or reprocessed pavement materials containing asphalt and aggregates [153–158]. These materials are generated when asphalt pavements are removed for reconstruction, resurfacing, or to obtain access to buried utilities. When properly crushed and screened, RAP consists of high-quality, well-graded aggregates coated by asphalt cement.

Asphalt pavement is generally removed either by milling or full-depth removal. Milling entails removal of the pavement surface using a milling machine, which can remove up to 50 mm thickness in a single pass. Full-depth removal involves ripping and breaking the pavement using a rhino horn on a bulldozer and/or pneumatic pavement breakers [155]. In most instances, the broken material is picked up and loaded into haul trucks by a front-end loader and transported to a central facility for processing. At this facility, the RAP is processed using a series of operations, including crushing, screening, conveying, and stacking.

Although the majority of old asphalt pavements are recycled at central processing plants, asphalt pavements may be pulverized in place and incorpo-

Table 8 Types of quarry by-products

Types	Description
Screenings	– Screenings is a generic term used to designate the finer fraction of crushed stone that accumulates after primary and secondary crushing and separation on a 4.75 mm mesh – The size distribution, particle shape, and other physical properties can be somewhat different from one quarry location to another, depending on the geological source of the rock quarried, the crushing equipment used, and the method used for coarse aggregate separation – Screenings generally contain freshly fractured faces, have a fairly uniform gradation, and do not usually contain large quantities of plastic fines
Settling pond fines	– Pond fines refer to the fines obtained from the washing of a crushed stone aggregate – During production, the coarser size range from washing may be recovered by means of a sand screw classifier – The remainder of the fines in the overflow are discharged to a series of sequential settling ponds or basins, where they settle by gravity, sometimes with the help of flocculating polymers – Pond clay is a term usually used to describe waste fines derived from the washing of natural sands and gravels
Baghouse fines	– Some quarries operate as dry plants because of dry climatic conditions or a lack of market for washed aggregate products – Dry plant operation requires the use of dust collection systems, such as cyclones and baghouses, to capture dusts generated during crushing operations. These dusts are referred to as baghouse fines – It is estimated that at least 159 million metric tons (175 million tons) of quarry by-products are being generated each year, mostly from crushed stone production operations – As much as 3.6 billion metric tons (4 billion tons) of QBP have probably accumulated

rated into granular or stabilized base courses using a self-propelled pulverizing machine. Hot in-place and cold in-place recycling processes have evolved into continuous train operations that include partial depth removal of the pavement surface, mixing the reclaimed material with beneficiating additives (such as virgin aggregate, binder, and/or softening or rejuvenating agents to improve binder properties), and placing and compacting the resultant mix in a single pass.

Reliable figures for the generation of RAP are not readily available from all state highway agencies or local jurisdictions. Based on incomplete data, it is estimated that as much as 41 million metric tons (45 million tons) of RAP may be produced each year in the United States [153–158].

3.16

Reclaimed Concrete Material

Reclaimed concrete material (RCM) is sometimes referred to as recycled concrete pavement (RCP), or crushed concrete [159–162]. It consists of high-quality, well-graded aggregates, bonded by a hardened cementitious paste. The aggregates comprise approximately 60–75% of the total volume of concrete. RCM is generated through the demolition of Portland cement concrete elements of roads, runways, and structures during road reconstruction, utility excavations, or demolition operations.

In many metropolitan areas, the RCM source is from existing Portland cement concrete curb, sidewalk and driveway sections that may or may not be lightly reinforced. The RCM is usually removed with a backhoe or pay loader and is loaded into dump trucks for removal from the site. The RCM excavation may include 10–30% sub-base soil material and asphalt pavement. Therefore, the RCM is not pure Portland cement concrete, but a mixture of concrete, soil, and small quantities of bituminous concrete [159–161].

The excavated concrete that will be recycled is typically hauled to a central facility for stockpiling and processing, or processed on site using a mobile plant. At the central processing facility, crushing, screening, and ferrous metal recovery operations occur. Present crushing systems, with magnetic separators, are capable of removing reinforcing steel without much difficulty. Welded wire mesh reinforcement, however, may be difficult or impossible to remove effectively [160].

3.17

Roofing Shingle Scrap

There are two types of roofing shingle scraps (RSS). They are referred to as tear-off roofing shingles, and roofing shingle tabs, also called prompt roofing shingle scrap [1–4]. Tear-off roofing shingles are generated during the demolition or replacement of existing roofs. Roofing shingle tabs are generated when new asphalt shingles are trimmed during production to the required physical dimensions. The quality of tear-off roofing shingles can be quite variable [163–167].

Approximately 10 million metric tons (11 million tons) of asphalt RSS is generated each year in the United States [1]. It is estimated that 90–95% of this material is from residential roof replacement (“tear-offs”), with the remainder being leftover material from shingle production (“roofing shingle tabs”).

Roofing shingles are produced by impregnating either organic felt produced from cellulose fibers or glass felt produced from glass fibers with hot saturated asphalt, which is subsequently coated on both sides with more asphalt and finally surfaced with mineral granules. Most roofing shingles produced are of the organic felt type. The saturant and coating asphalt need not be the same. Both saturant and coating asphalts are produced by “blowing”, a process in which air is bubbled through molten asphalt flux. The heat and oxygen act to change the

characteristics of the asphalt. The process is monitored, and the “blowing” is stopped when the desired characteristics have been produced [163–167].

The largest component of roofing shingles (60–70% by mass) is the mineral material. There are several different types in each shingle [2]. They can include ceramic granules (comprising crushed rock particles, typically trap rock, coated with colored, ceramic oxides), lap granules (coal slag ground to roughly the same size as the ceramic granules), back-surfacer sand (washed, natural sand used in small quantities to keep packaged shingles from sticking together), and asphalt stabilizer (powdered limestone that is mixed into the asphalt).

3.18

Scrap Tires

Approximately 280 million tires are discarded each year by American motorists – approximately one tire for every person in the United States [168–178]. Around 30 million of these tires are reused, leaving roughly 250 million scrap tires to be managed annually. About 85% of these scrap tires (ST) are automobile tires, the remainder being truck tires [169–171]. Besides the need to manage these scrap tires, it has been estimated that there may be as many as 2–3 billion tires that have accumulated over the years and are contained in numerous stockpiles [1, 167–171]. Scrap tires can be managed as a whole tire, a slit tire, a shredded or chipped tire, as ground rubber, or as a crumb rubber product (Table 9).

3.19

Sewage Sludge Ash

Sewage sludge ash (SSA) is the by-product produced during the combustion of dewatered sewage sludge in an incinerator. Sewage sludge ash is primarily a silty material with some sand-size particles [179–191]. The specific size range and properties of the sludge ash depend to a great extent on the type of incineration system and the chemical additives introduced in the wastewater treatment process.

At present, two major incineration systems, multiple hearth and fluidized bed, are employed in the United States. Approximately 80% of the incinerators used in the United States are multiple hearth incinerators [179–191]:

- A multiple hearth incinerator is a circular steel furnace that contains a number of solid refractory hearths and a central rotating shaft. Rabble arms that are designed to slowly rake the sludge on the hearth are attached to the rotating shaft. Dewatered sludge (approximately 20% solids) enters at the top and proceeds downward through the furnace from hearth to hearth, pushed along by the rabble arms. Cooling air is blown through the central column and hollow rabble arms to prevent overheating. The spent cooling air with its elevated temperature is usually recirculated and used as combustion air

to save energy. Flue gases are typically routed to a wet scrubber for air pollution control. The particulates collected in the wet scrubber are usually diverted back into the sewage plant.

- Fluidized bed incinerators consist of a vertical cylindrical vessel with a grid in the lower sections to support a bed of sand. Dewatered sludge is injected into the lower section of the vessel above the sand bed and combustion air flows upward and fluidizes the mixture of hot sand and sludge. Supplemental fuel can be supplied by burning above and below the grid if the heating value of the sludge and its moisture content are insufficient to support combustion.

Incineration of sewage sludge (dewatered to approximately 20% solids) reduces the weight of feed sludge requiring disposal by approximately 85%. There are approximately 170 municipal sewage treatment plant incinerators in the United

Table 9 Types of scrap tires (ST)

Types	Description
Whole tires	- A typical scrapped automobile tire weighs 9.1 kg - Roughly 5.4–5.9 kg consists of recoverable rubber, composed of 35% natural rubber (latex) and 65% synthetic rubber - Steel-belted radial tires are the predominant type of tire currently produced in the United States - A typical truck tire weighs 18.2 kg and also contains from 60–70% recoverable rubber - Truck tires typically contain 65% natural rubber and 35% synthetic rubber - Although the majority of truck tires are steel-belted radials, there are still a number of bias ply truck tires, which contain either nylon or polyester belt material
Slit tires	- Slit tires are produced in tire cutting machines - These cutting machines can slit the tire into two halves or can separate the sidewalls from the tread of the tire
Shredded or chipped tires	- The production of tire shreds or tire chips involves primary and secondary shredding - A tire shredder is a machine with a series of oscillating or reciprocating cutting edges, moving back and forth in opposite directions to create a shearing motion, that effectively cuts or shreds tires as they are fed into the machine - The size of the tire shreds produced in the primary shredding process can vary from as large as 300–460 mm long by 100–230 mm wide, down to as small as 100–150 mm in length, depending on the manufacturer, model, and condition of the cutting edges

Table 9 (continued)

Types	Description
Shredded or shreds	– The shredding process results in exposure of steel belt fragments along the edges of the tire shreds – Production of tire chips, which are normally sized from 76 mm down chipped tires to 13 mm, requires two-stage processing of the tire (primary and secondary shredding) to achieve adequate size reduction – Secondary shredding results in the production of chips that are more equidimensional than the larger size shreds that are generated by the primary shredder, but exposed steel fragments will still occur along the edges of the chips
Ground rubber	– Ground rubber may be sized from particles as large as 19 mm to as fine as 0.15 mm depending on the type of size reduction equipment and the intended application – The production of ground rubber is achieved by granulators, hammer mills, or fine grinding machines – Granulators typically produce particles that are regularly shaped and cubical with a comparatively low-surface area – The steel belt fragments are removed by a magnetic separator – Fiberglass belts or fibers are separated from the finer rubber particles, usually by an air separator – Ground rubber particles are subjected to a dual cycle of magnetic separation, then screened and recovered in various size fractions
Crumb rubber	– Crumb rubber usually consists of particles ranging in size from 4.75 to <0.075 mm – Most processes that incorporate crumb rubber as an asphalt modifier use particles ranging in size from 0.6–0.15 mm – Three methods are currently used to convert scrap tires to crumb rubber: – <i>The cracker mill process</i>: the most commonly used method tears apart or reduces the size of tire rubber by passing the material between rotating corrugated steel drums. This process creates an irregularly shaped torn particle with a large surface area. These particles range in size from approximately 5–0.5 mm and are commonly referred to as ground crumb rubber – <i>The granulator process</i>: which shears apart the rubber with revolving steel plates that pass at close tolerance, producing granulated crumb rubber particles, ranging in size from 9.5–0.5 mm – <i>The micro-mill process</i>: which produces a very fine ground crumb rubber in the size range from 0.5 mm to as small as 0.075 mm – In some cases, cryogenic techniques are also used for size reduction. Essentially, this involves using liquid nitrogen to reduce the temperature of the rubber particles to minus 87 °C (–125°F), making the particles quite brittle and easy to shatter into smaller particles

States, processing approximately 20% of the nation's sludge, and producing between 0.45–0.9 million metric tons (0.5–1.0 million tons) of sludge ash on an annual basis [182–190].

3.20

Steel Slag

Steel slag (SS), a by-product of steel making, is produced during the separation of the molten steel from impurities in steel-making furnaces. The slag occurs as a liquid melt and is a complex solution of silicates and oxides that solidifies upon cooling. Virtually all steel is now made in integrated steel plants using a version of the basic oxygen process or in speciality steel plants (mini-mills) using the electric arc furnace process. The open-hearth furnace process is no longer used [192–195].

In the basic oxygen process, hot liquid blast furnace metal, scrap, and fluxes, which consist of lime (CaO) and dolomitic lime (CaO.MgO , “dolime”), are charged to a converter (furnace). A lance is lowered into the converter and high-pressure oxygen is injected. The oxygen combines with and removes the impurities in the charge. These impurities consist of carbon as gaseous carbon monoxide, and silicon, manganese, phosphorus and some iron as liquid oxides, which combine with lime and dolime to form the steel slag. At the end of the refining operation, the liquid steel is tapped (poured) into a ladle while the steel slag is retained in the vessel and subsequently tapped into a separate slag pot.

There are many grades of steel that can be produced, and the properties of the steel slag can change significantly with each grade. Grades of steel can be classified as high, medium, and low, depending on the carbon content of the steel. High-grade steels have high carbon content. To reduce the amount of carbon in the steel, greater oxygen levels are required in the steel-making process. This also requires the addition of increased levels of lime and dolime (flux) for the removal of impurities from the steel and increased slag formation.

There are several different types of steel slag produced during the steel-making process. These different types [192–195] are referred to as furnace or tap slag, raker slag, synthetic or ladle slags, and pit or cleanout slag:

- The steel slag produced during the primary stage of steel production is referred to as *furnace slag* or *tap slag*. This is the major source of steel slag aggregate. After being tapped from the furnace, the molten steel is transferred in a ladle for further refining to remove additional impurities still contained within the steel. This operation is called ladle refining because it is completed within the transfer ladle. During ladle refining, additional steel slags are generated by again adding fluxes to the ladle to melt. These slags are combined with any carryover of furnace slag and assist in absorbing deoxidation products (inclusions), heat insulation, and protection of ladle refractories. The steel slags produced at this stage of steel making are generally referred to as raker and ladle slags.

- Pit slag and cleanout slag are other types of slag commonly found in steel-making operations. They usually consist of the steel slag that falls onto the floor of the plant at various stages of operation, or slag that is removed from the ladle after tapping.

Because the ladle refining stage usually involves comparatively high flux additions, the properties of these synthetic slags are quite different from those of the furnace slag and are generally unsuitable for processing as steel slag aggregates. These different slags must be segregated from furnace slag to avoid contamination of the slag aggregate produced.

3.21

Sulfate Wastes

Fluorogypsum and phosphogypsum are sulfate-rich by-products generated during the production of hydrofluoric and phosphoric acid, respectively. Full descriptions of these wastes [196–206] are given in Table 10.

3.22

Waste Glass

Glass is a product of the super-cooling of a melted liquid mixture consisting primarily of sand (silicon dioxide) and soda ash (sodium carbonate) to a rigid condition, in which the super cooled material does not crystallize and retains the organization and internal structure of the melted liquid. When waste glass is crushed to sand size particles, similar to those of natural sand, it exhibits properties of an aggregate material [207–214].

In 1994 approximately 9.2 million metric tons (10.2 million tons) of post-consumer glass was discarded in the municipal solid waste stream in the United States. Approximately 8.1 million metric tons (8.9 million tons) or 80% of this waste glass was container glass [210–213].

4

Properties of Solid Wastes

In order to successfully study the environmental impact assessment and chemodynamics (fate and transport) of leachates from solid waste materials that are used as in highway construction and repair applications, it is very important to comprehensively study the different physical and chemical properties specific for each waste material. The following is a summary of these properties.

Table 10 Types of sulfate wastes

Types	Description
Fluorogypsum	– Fluorogypsum is generated during the production of hydrofluoric acid from fluorspar (a mineral composed of calcium fluoride) and sulfuric acid – Fluorogypsum is discharged in slurry form and gradually solidifies into a dry residue after the liquid has been allowed to evaporate in holding ponds – When removed from the holding ponds, the dried material must be crushed and screened – This produces a sulfate-rich, well-graded sandy silt material with some gravel-size particles – Approximately 90,000 metric tons (100,000 tons) of fluorogypsum are generated annually in the United States
Phosphogypsum	– Phosphogypsum is a solid by-product of phosphoric acid production – The most frequently used process for the production of phosphoric acid is the “wet process,” in which finely ground phosphate rock is dissolved in phosphoric acid to form a mono- calcium phosphate slurry – Sulfuric acid is added to the slurry to produce phosphoric acid (H_3PO_4) and a phosphogypsum (hydrated calcium sulfate) by-product – Phosphogypsum is generated as a filter cake in the “wet process” and is typically pumped in slurry form to large holding ponds, where the phosphogypsum particles are allowed to settle – The resulting product is a moist gray, powdery material that is predominantly silt sized and has little or no plasticity – Approximately 32 million metric tons (35 million tons) of phosphogypsum are produced annually – Total accumulations of phosphogypsum are well in excess of 720 million metric tons (800 million tons) – As a general rule, 4–5 metric tons (4.5–5.5 tons) of phosphogypsum are generated for every ton of phosphoric acid produced.

4.1

Baghouse Fines

The physical properties of baghouse fines are varied. The size distribution of baghouse fines (BHF) consists of a coarse fraction and a fine fraction, with the dividing size being the 0.075 mm mesh sieve. There can be a considerable range in the % of dust particles passing through 0.075 mm mesh. Plants without a primary collection system often collect dust with less than 50% of the material collected passing the 0.075 mm mesh sieve. On the other hand, more than

half of the plants with a primary collection system collect dust with 90–100% of the particles finer than 0.075 mm mesh [19–34]. Other relevant physical properties of BHF are specific gravity, specific surface area, and hygroscopic moisture. With few exceptions, baghouse fines normally absorb less than 2% moisture at 50% relative humidity. BHF contain little or no clay and will generally have little or no trouble meeting the plasticity requirement for mineral filler, which limits the plasticity index value to 4.0.

With few exceptions, the pH of baghouse fines is alkaline, with values ordinarily ranging from 7.2–10.8 for dusts from gravel, granite, or trap rock aggregates, and values ranging from 11.0–12.4 for dusts from limestone and dolomite aggregates. The chemical properties of BHF can be expected to reflect the properties of the feed aggregate [19–34].

4.2

Blast Furnace Slag

The typical physical properties of blast furnace slags (BFS) are summarized in Table 11. These properties are listed and discussed for the following slag types [35–38]: air-cooled blast furnace slag (ACBFS), expanded blast furnace slag (EBFS), pelletized blast furnace slag (PBFS), and granulated blast furnace slag (GBFS).

Figure 1 illustrates the typical chemical composition of blast furnace slag. The chemical composition shown is in general applicable to all types of slag (ACBFS, EBFS, PBFS, GBFS). Figure 1 suggests that the chemical composition of BFS produced in North America has remained relatively consistent over the years.

When ground to the proper fineness, the chemical composition and glassy (non-crystalline) nature of vitrified slags are such that upon combination with water, they react to form cement-like hydration products. The magnitudes of

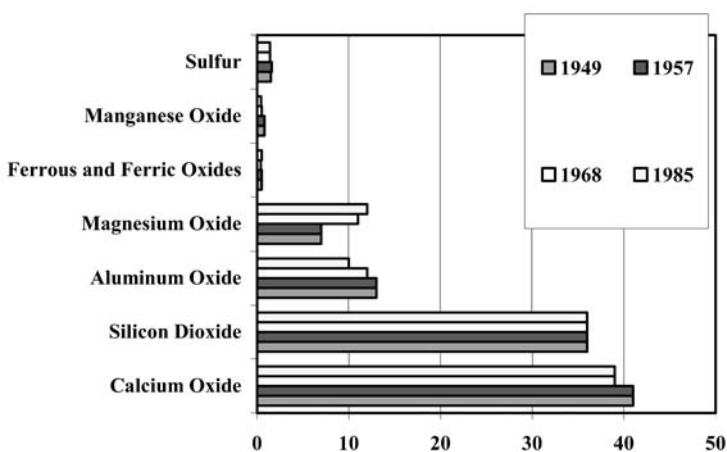


Fig. 1 Chemical composition of blast furnace slag

Table 11 Typical physical properties of blast furnace slag

Types	Physical properties
Air-cooled blast furnace slag (ACBFS)	– Crushed ACBFS is angular, roughly cubical, and has textures ranging from rough, vesicular (porous) surfaces to glassy (smooth) surfaces with conchoidal fractures – Considerable variability in the physical properties of blast furnace slag depends on the iron production process. For example, some recently produced ACBFS was reported to have a compacted unit weight as high as 1940 kg/m³ – The water absorption of ACBFS can be as high as 6%. Although ACBFS can exhibit these high absorption values, ACBFS can be readily dried since little water actually enters the pores of the slag and most is held in the shallow pits on the surface
Expanded blast furnace slag (EBFS)	– Crushed EBFS is angular, roughly cubical in shape, and has texture that is rougher than that of air-cooled slag – The porosity of EBFS aggregates is higher than ACBFS aggregates – The bulk relative density of EBFS is difficult to determine accurately, but it is approximately 70% of that of air-cooled slag – Typical compacted unit weights for EBFS aggregates range from 800–1040 kg/m³
Pelletized blast furnace slag (PBFS)	– Unlike ACBFS and EBFS, PBFS has a smooth texture and rounded shape – Consequently, the porosity and water absorption are much lower than those of ACBFS or expanded blast furnace slag – Pellet sizes range from 13–0.1 mm, with the bulk of the product in the –9.5 mm to +1.0 mm range – PBFS has a unit weight of about 840 kg/m³
Granulated blast furnace slag (GBFS)	– GBFS is a glassy granular material that varies, depending on the chemical composition and method of production, from a coarse, popcorn like friable structure greater than 4.75 mm in diameter to dense, sand-size grains less than 4.75 mm – Grinding reduces the particle size to cement fineness, allowing its use as a supplementary cementitious material in Portland cement concrete.

these cementation reactions depend on the chemical composition, glass content, and fineness of the slag. The chemical reaction between GBFS and water is slow, but it is greatly enhanced by the presence of calcium hydroxide, alkalis and gypsum (CaSO₄).

4.3

Carpet Fiber Dusts

There is no published information on the physical and chemical properties of carpet fiber dusts in the literature.

4.4

Coal Bottom Ash/Boiler Slag

Physically, bottom ashes (BA) have angular particles with a very porous surface texture. Bottom ash particles range in size from a fine gravel to a fine sand with a low percent of silt-clay sized particles. The ash is usually a well-graded material, although variations in particle size distributions may be encountered in ash samples taken from the same power plant at different times [50–57]. Bottom ash is predominantly sand-sized, usually with 50–90% passing a 4.75 mm mesh sieve, 10–60% passing 0.42 mm mesh, 0–10% passing 0.075 mm mesh, and a coarse size usually ranging from 19–38.1 mm.

Boiler slags (BS) are predominantly single-sized, and within a diameter range of 5.0–0.5 mm. Ordinarily, boiler slags have a smooth surface texture, but if gases are trapped in the slag as it is tapped from the furnace, the quenched slag will become somewhat vesicular or porous. BS from the burning of lignite or sub-bituminous coal tends to be more porous than that from burning the eastern bituminous coals [56]. BS is essentially a coarse to medium sand with 90–100% passing a 4.75 mm mesh sieve, 40–60% passing 2.0 mm mesh, 10% or less passing 0.42 mm mesh, and 5% or less passing 0.075 mm mesh [54]. The specific gravity of dry bottom ash is a function of chemical composition, with a higher carbon content resulting in a lower specific gravity. Bottom ash with a low specific gravity has a porous or vesicular texture, a characteristic of popcorn particles that readily degrade under loading or compaction [57].

Chemically, BA and BS are composed principally of silica, alumina, and iron, with smaller percentages of calcium, magnesium, sulfates, and other compounds. The composition of the BA or BS particles is controlled primarily by the source of the coal and not by the type of furnace. BA or BS derived from lignite or sub-bituminous coals have higher amounts of calcium than the BA or BS from anthracite or bituminous coals. Sulfate is usually very low (less than 1.0%), unless pyrites have not been removed from the coal fuels.

Due to the salt content and, in some cases, the low pH of BA and BS, these materials could exhibit corrosive properties. When using BA or BS in an embankment, backfill, sub-base, or even possibly in a base course, the potential for corrosion of metal structures that may come in contact with the material is of concern and should be investigated prior to use.

Corrosivity indicator tests normally used to evaluate BA or BS are pH, electrical resistivity, soluble chloride content, and soluble sulfate content. Materials are judged to be noncorrosive if the pH exceeds 5.5, the electrical resistivity is

greater than 1,500 Ωcm , the soluble chloride content is less than 200 ppm, or the soluble sulfate content is less than 1,000 ppm [57].

4.5

Coal Fly Ash

Fly ash (FA) consists of fine, powdery particles that are predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ashes is generally similar to that of a silt (less than 0.075 mm). Although sub-bituminous coal fly ashes are also silt-sized, they are generally slightly coarser than bituminous coal fly ashes [58–65]. The specific gravity of fly ash usually ranges from 2.1–3.0, while its specific surface area may range from 170–1000 m^2/kg .

The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter the color, the lower the carbon content. Lignite or sub-bituminous coal fly ashes are usually light tan to buff in color, indicating relatively low amounts of carbon as well as the presence of some lime or calcium. Bituminous coal fly ashes are usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash.

The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. There are basically four types, or ranks, of coal, each of which varies in terms of its heating value, its chemical composition, ash content, and geological origin. The four types of coal are: anthracite, bituminous, sub-bituminous, and lignite. In addition to being handled in a dry, conditioned, or wet form, fly ash is also sometimes classified according to the type of coal from which the ash was derived.

The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium oxide, with varying amounts of carbon. Lignite and sub-bituminous coal fly ashes are characterized by higher concentrations of calcium and magnesium oxides and a reduced amount of silica and iron oxide, as well as a lower carbon content, compared to bituminous coal fly ash [58–62]. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash.

Figure 2 shows the normal range of chemical composition for fly ash produced from different coal types (expressed as % by weight). It compares the normal range of the chemical constituents of bituminous (# 1) coal fly ash with those of lignite (# 3) coal fly ash and sub-bituminous (# 2) coal fly ash. From the figure, it is evident that lignite and sub-bituminous coal fly ashes have a higher calcium oxide content and lower organic carbon than fly ashes from bituminous coals. Lignite and sub-bituminous coal fly ashes may have a higher concentration of sulfate compounds than bituminous coal fly ashes.

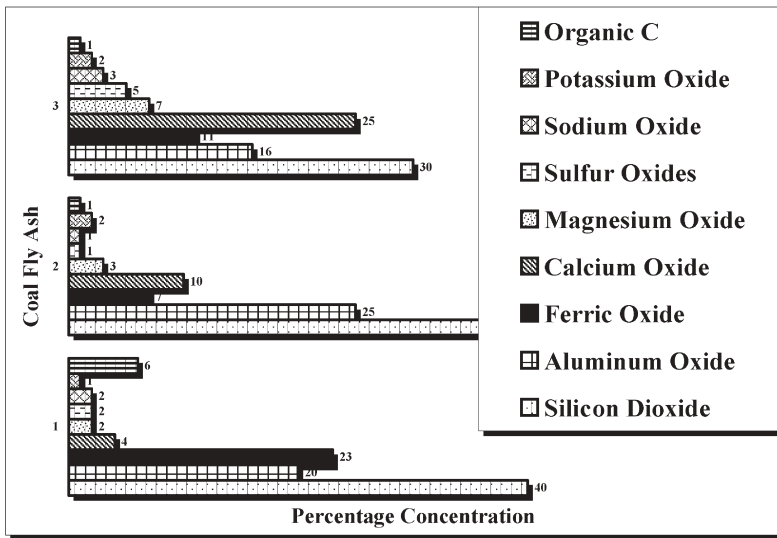


Fig. 2 Chemical composition of coal fly ash

4.6

Contaminated Soils

Physical characteristics of soil particles depend mainly on particle size, moisture content, and organic carbon content [1–4]. On the other hand, the chemical characteristics depend on the kind of contamination (organic or inorganic) of soils.

4.7

FGD Scrubber Material

Dewatered flue gas desulfurization (FGD) scrubber material is most frequently generated as calcium sulfite, although some power plant scrubbing systems have the forced oxidation design, resulting in a calcium sulfate (or by-product gypsum) material. Calcium sulfite FGD scrubber material is oxidized to sulfate and used for road base, while the calcium sulfate FGD scrubber material is frequently used for wallboard or as a cement additive [66–80].

The degree to which FGD scrubber material is treated influences its physical properties. Basic physical properties include solids content, moisture content, specific gravity, and wet and dry density [67]. When dewatered, the calcium sulfite FGD sludges become a soft filter cake with a solids content typically in the 40–65% range. Calcium sulfate FGD sludges can be dewatered much more easily and may achieve solid contents as high as 70–75% after dewatering [67].

Dewatered and unstabilized calcium sulfite FGD scrubber sludge consists of fine silt-clay sized particles with approximately 50% finer than 0.045 mm. It has

a dry density in the range of 960–1,280 kg/m³ (60–80 lbs/ft³), with a specific gravity of solids in the 2.4 range [63–80].

The solid contents of fixated FGD scrubber material ordinarily range from 60–80%. The specific gravity of fixated FGD sulfite scrubber material can range from 2.25–2.60, with an average of 2.38. Between 88–98% of the particles are in the silt size range. Depending on the amount of fly ash in the blend, maximum dry density values of fixated FGD scrubber material can range from 1,280–1,600 kg/m³ at optimum moisture contents ranging from 20–30% when tested using the standard Proctor (ASTM D698) test method [64, 65].

The chemical composition of FGD scrubber material varies according to the scrubbing process, type of coal, sulfur content, and presence or absence of fly ash. Lime is the most commonly used reagent in the scrubbing process. Except for those subjected to forced oxidation, sludges from the scrubbing of bituminous coals are generally sulfite-rich, whereas forced oxidation sludges and sludges generated from scrubbing of sub-bituminous and lignite coals are sulfate-rich. Fly ash is a principal constituent of FGD scrubber material only if the scrubber serves as a particulate control device in addition to SO₂ removal, or if separately collected fly ash is mixed with the sludge [71].

Dewatered unstabilized calcium sulfite FGD scrubber sludges have a paste like consistency with low shear strength and little bearing capacity. They are thixotropic, meaning that, when agitated, they revert to a liquid or slurry form. They have no unconfined compressive strength, an angle of internal friction around 20°, and a permeability in the range of 10⁻⁴ to 10⁻⁵ cm/s [69].

Stabilized or fixated calcium sulfite FGD scrubber material has unconfined compressive strength values in the range of 170 kPa (25 lb/in²) to 1380 kPa (200 lb/in²), an angle of internal friction of 35–45°, and coefficient of permeability values in the range of 10⁻⁶ to 10⁻⁷ cm/s [75].

If stabilized or fixated FGD scrubber sludge is to be used for road base construction, then the unconfined compressive strength is more likely to be in the range of 1720 kPa (250 lb/in²) to as high as 6900 kPa (1,000 lb/in²), depending on specification requirements and reagent addition rates. The flexural strength of stabilized FGD sludge road base materials is normally in the 690–, 720 kPa (100–250 lb/in²) range [66]. To achieve these strength ranges, additional fixation reagents (Portland cement, lime, fly ash, and so on) will usually be required.

4.8

Foundry Sand

The grain size distribution of spent foundry sand is very uniform, with approximately 85–95% of the material between 0.6–0.15 mm mesh (sieve) sizes. 5–12% of foundry sand can be expected to be smaller than 0.075 mm. The particle shape is typically sub-angular to rounded. Waste foundry sand gradations have been found to be too fine to satisfy some specifications for fine aggregate [81–87].

Spent foundry sand has low absorption and is non-plastic. Reported values of absorption were found to vary widely, which can also be attributed to the presence of binders and additives [83]. The content of organic impurities (particularly from sea coal binder systems) can vary widely and can be quite high. This may preclude its use in applications where organic impurities could be important (such as Portland cement concrete aggregate) [84]. The specific gravity of foundry sand has been found to vary from 2.39–2.55. This variability has been attributed to the variability in fines and additive contents in different samples [83]. In general, foundry sands are dry, with moisture contents less than 2%. A large fraction of clay lumps and friable particles has been reported, which is attributed to the lumps associated with the molded sand, which are easily disintegrated in the test procedure [86].

Spent foundry sand consists chemically of silica sand coated with a thin film of burnt carbon, residual binder (bentonite, sea coral, resins), and dust. Figure 3 shows the chemical composition of a typical sample of spent foundry sand as determined by x-ray fluorescence.

Silica sand is hydrophilic and consequently attracts water to its surface. This property could lead to moisture-accelerated damage and associated stripping problems in an asphalt pavement. Antistripping additives may be required to counteract such problems. Depending on the binder and type of metal cast, the pH of spent foundry sand can vary from approximately 4–8 [87]. It has been reported that some spent foundry sands can be corrosive to metals [85].

Because of the presence of phenols in foundry sand, there is some concern that precipitation percolating through stockpiles could mobilize leachable fractions, resulting in phenol discharges into surface or ground water supplies. Foundry sand sources and stockpiles must be monitored to assess the need to establish controls for potential phenol discharges [84–87].

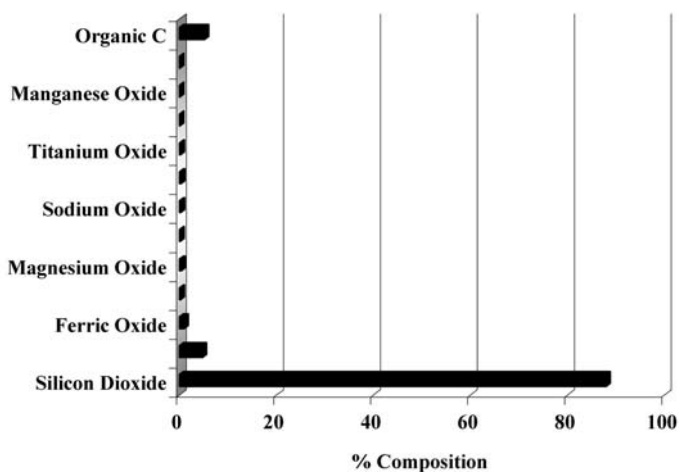


Fig. 3 Chemical composition of foundry sand

4.9

Kiln Dusts

Physically, cement kiln dust (CKD) and lime kiln dust (LKD) are fine, powdery materials of relatively uniform size. Approximately 75% of the kiln dust particles are finer than 0.030 mm. The fineness of kiln dust, as Portland cement, can be determined using the Blaine air permeability apparatus in accordance with ASTM method C204 [88–98].

The maximum particle size of most CKD is about 0.30 mm, with the Blaine fineness ranging from about 4600 (coarser) to 14,000 (finer) cm^2/g [91]. LKD is generally somewhat more coarse than CKD, having a top size of about 2 mm and Blaine fineness ranging between about 1300–10000 cm^2/g . In comparison, the Blaine fineness of type Portland cement is about 3500–3800 cm^2/g [94]. The specific gravity of CKD is typically in the range of 2.6–2.8, less than that of Portland cement (specific gravity of 3.15). LKD exhibits specific gravities ranging from 2.6–3.0 [91].

Chemically, CKD has a composition similar to conventional Portland cement [88–98]. The principal constituents are compounds of lime, iron, silica and alumina. The free lime content of LKD can be significantly higher than that of CKD (up to about 40%), with calcium and magnesium carbonates as the principal mineral constituents. There is very little, if any, free lime or free magnesia content in stockpiled CKD and LKD that has been exposed to the environment for long periods.

The pH of CKD and LKD water mixtures is typically about 12. Both materials contain significant alkalis, and are consequently considered to be caustic. Due to the caustic nature of CKD and LKD, some corrosion of metals (like aluminum) that come in direct contact with CKD and LKD may occur.

Trace metal constituents in CKD are generally found in concentrations <0.05% by weight. Because some of these constituents are potentially toxic at low concentrations, it is important to assess their levels (and mobility or leachability) in CKD before considering its use.

4.10

Mineral Processing Wastes

The material properties of the various categories of mineral processing wastes are influenced by the characteristics of the parent rock, the mining and processing methods used, and the methods of handling and/or disposing of the mineral by-product [99–112]. The physical and chemical properties of waste rock, mill tailings, and coarse coal refuse are summarized and discussed in Table 12.

4.11

MSW Combustor Ash

During the 1970s and 1980s a number of comprehensive investigations were undertaken to characterize the properties of municipal waste combustor ash.

Table 12 Physical and chemical properties of mineral processing wastes

Types	Physical properties	Chemical properties
Waste rock	- It results from blasting or ripping and usually consists of a range of sizes, from large blocks down to cobbles and pebbles - It can be processed to a desired gradation by crushing and sizing, like any other source of aggregate - The hardness of the waste rock is determined by the rock type: - Iron ores are often found in hard igneous or metamorphic rock formations, so waste rock from iron is usually hard and dense - Lead and zinc ores are found in limestone and dolomite rock, so the waste rock from processing these ores will have characteristics much like other carbonate aggregates - The specific gravity of waste rock ranges from 2.4–3.0 for most rock types and from 3.2–3.6 for waste rock from iron ore and taconite mining	- There are little to no chemical data on waste rock
Mill tailings	- The grain size distribution can vary considerably, depending on the ore processing methods used, the method of handling, and the location of the sample relative to the discharge point in the tailing pond. - In general, the lower the concentration of ore in the parent rock, the greater the amount of processing needed to recover the ore and the finer the particle size of the resultant tailings	- Mill tailings are virtually cohesionless materials with internal friction angles that can range from 28–45° - Maximum dry density values may range from 1600–2300 kg/m³, with optimum moisture content values that may be between 10–18% - Permeability values ranging from 10⁻² to 10⁻⁴ cm/s have been reported, with most values in the 10⁻³ cm/s range

Table 12 (continued)

Types	Physical properties	Chemical properties
Mill tailings	- Some ores, such as iron ore, are found in relatively high % and are fairly easy to separate. Therefore, the resultant tailings are coarser than those from other ores, such as copper, which is found in very low %, and requires very fine grinding for separation. Hence, copper tailings are usually quite fine-grained - There is a scarcity of published information on specific gravity, unit weight, and moisture content for most types of mill tailings - The specific gravity ranges between 2.60–3.35 - The dry rodded weight of most mill tailings is likely to range from 1450–2200 kg/m³. - The moisture content is highly variable, depending on the particle sizing of the tailings and the % solids of the tailing slurry - Mill tailings are almost always non-plastic	- Most tailings are siliceous materials. Besides iron ore and taconite tailings, gold and lead-zinc tailings samples also contain a fairly substantial % of iron - Although pH readings are not reported, some sources of mill tailings, especially those with low calcium and magnesium contents, could be acidic Coal refuse
Coal refuse	- Coarse coal refuse is a well-graded material with nearly all particles smaller than 100 mm - Differences in the range of particle sizes can be attributed to variations in the processing methods used at different coal preparation plants - The predominant portion of coarse coal refuse is from a fine gravel to a coarse to medium sand, with from 0–30% passing a 0.075 mm mesh	The optimum moisture content may range from 6–15%, the maximum dry density can range from while 1300 kg/m³ to 2000 kg/m³. A wide variety of moisture-density curves have been developed for coarse coal refuse because of the variability of the material, although most moisture-density curves are relatively flat. Permeability values of compacted coarse coal refuse can vary over a fairly wide range from 10⁻⁴ to 10⁻⁷ cm/s, depending on the gradation of the refuse before and after compaction

Table 12 (continued)

Types	Physical properties	Chemical properties
Coal refuse	- The shear strength of coarse coal refuse is derived primarily from internal friction with comparatively low cohesion. Friction angles have been found to range from 25–42°, with anthracite refuse normally having lower friction angles than bituminous refuse - The specific gravity of coarse coal refuse normally ranges from 2.0–2.8 for bituminous coal refuse and from 1.8–2.5 for anthracite coal refuse - The specific gravity is directly proportional to the plasticity index of the refuse. As the plasticity index increases, the specific gravity also increases. The plasticity index for coarse coal refuse can range from non-plastic up to a value of 16 - The natural moisture content of coarse coal refuse has been found to range from 3% to as high as 24%, but is usually less than 10%	- Like mill tailings, coarse coal refuse is a siliceous material, but it has considerably more alumina than tailings. Coarse coal refuse is almost always acidic

Most of the data from these early investigations reflect the characteristics of ash from batch-fed or older continuous flow grate designs that are unlike the modern, high-efficiency energy recovery combustors in operation today. During the past few years there have been a number of comprehensive investigations that have characterized the properties of combined and bottom ash residues generated from these newer facilities [113–118].

Physical properties of MSW combustor ash [113–118] indicate that:

- MSW combustor ash is a relatively lightweight material compared to natural sands and aggregate. The bulk specific gravities that were reported range from 1.5–2.2 for sand-size or fine particles and 1.9–2.4 for coarse particles, compared to approximately 2.6–2.8 for conventional aggregate materials.
- Combustor ash is highly absorptive with absorption values ranging from 5–17% for fine particles and from about 4–10% for coarse particles. Conventional aggregates typically exhibit absorption values of less than 2%.
- Prior to exiting a municipal solid waste combustor, the ash is quenched, resulting in the high moisture content values. This high moisture content is due the quenching and relatively high porosity and absorptive nature of combustor ash.
- The relatively low unit weights further underscore the lightweight nature of combustor ash, and the loss on ignition values suggest that the ash can contain relatively high levels of organics compared with conventional aggregates. Combustor ash is primarily a sandy material, with the major fraction passing a 4.75 mm mesh sieve. Ash also contains a relatively high <0.075 mm diameter silt fraction.

Figure 4 shows the major elemental chemical constituents present in MSW combustor ash. The most abundant elements in municipal waste combustor ash

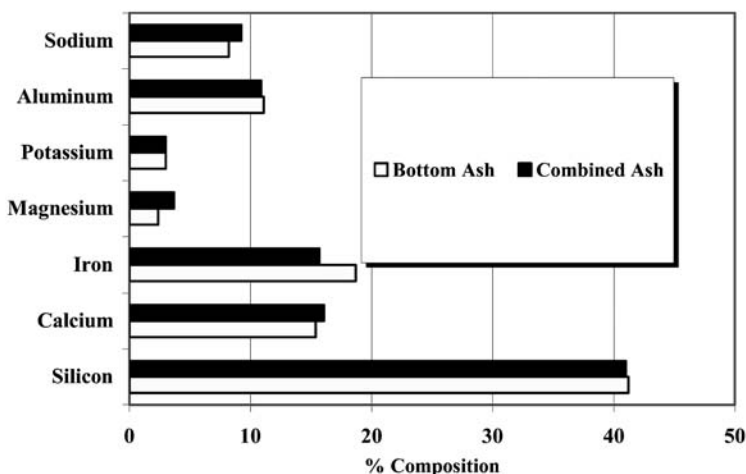


Fig. 4 Elemental composition of MSW combustor ash

are silicon, calcium, and iron. Although ash compositions can be expected to vary from facility to facility, these elements are present within relatively predictable ranges.

The presence of a relatively high salt content and trace metal concentrations, including such elements as lead, cadmium, and zinc, in municipal waste combustor ash have raised concerns in recent years regarding the environmental acceptability of using ash as an aggregate substitute material.

The presence of calcium as the oxide, as well as other oxides, in relatively high concentrations in MSW combustor ash makes the ash susceptible to hydration and/or cementation reactions with subsequent swelling. The presence of elemental aluminum in the ash when combined with water can also result in the formation of hydrogen gas. In addition, the high oxide (salt) content also suggests that ash could be corrosive if placed in contact with metal structures, and that it would likely interfere with curing and strength development if used in Portland cement concrete.

4.12

Nonferrous Slags

Table 13 lists some typical physical properties for nonferrous slags (NFS). Because they have similar properties, lead, lead-zinc, and zinc slags are grouped together. Chemically, copper, lead, lead-zinc, and zinc slags are essentially ferrous silicates, while phosphorus slag and nickel slag are primarily calcium/magnesium silicates. Table 14 lists the typical chemical compositions of these slags [129–135].

During slag production, the sudden cooling that results in the vitrification of NFS prevents the molecules from being locked up in crystals. In the presence of an activator (such as calcium hydroxide from hydrating Portland cement), vitrified nonferrous slags react with water to form stable, cemented, hydrated calcium silicates. The reactivity depends on the fineness to which the slag is ground. These vitrified slags can be of such compositions that when ground to proper fineness, they may also react directly with water to form hydration products that provide the slag with cement-like properties. High iron contents (essentially ferrous silicate slags) in these slags appear to limit hydraulicity and make grinding difficult.

Hydratable oxides may also be present in NFS from some sources, which could potentially contribute to volumetric instability. Depending on the ore and metallurgical process, nonferrous slags produced from sulfide ores can contain leachable elemental sulfur and heavy metals, which should be investigated prior to use. Sulfurous leachate is primarily of aesthetic concern, resulting in sulfur odor and possible discoloration of water in poor drainage conditions. In addition, phosphate rocks can contain between 30–200 ppm uranium. Most of this uranium is incorporated in the phosphorus slag and results in the release of some radiation (in the form of radon gas).

Table 13 Physical properties of nonferrous slags

Types	Description
Nickel slag	– Air-cooled nickel slag is brownish-black in color – It crushes to angular particles but has a smooth, glassy texture – The specific gravity of may be as high as 3.5, while the absorption is quite low (0.37%) – The unit weight of nickel slag is somewhat higher than that of conventional aggregate – Granulated nickel slag is essentially an angular, black, glassy slag “sand” with most particles in the size range of –2 mm to 0.150 mm – It is more porous, with lower specific gravity and higher absorption, than air-cooled nickel slag
Copper slag	– Air-cooled copper slag has a black color and glassy appearance – the specific gravity will vary with iron content, from a low of 2.8 to as high as 3.8 – The unit weight of copper slag is somewhat higher than that of conventional aggregate – The absorption of the material is typically very low – Granulated copper slag is more porous and therefore has lower specific gravity and higher absorption than air-cooled copper slag – The granulated copper slag is made up of regularly shaped, angular particles, mostly between 4.75–0.075 mm in size.
Phosphorus slag	– Air-cooled phosphorus slag tends to be black to dark gray, vitreous (glassy), and of irregular shape. Individual particles are generally flat and elongated, with sharp fracture faces similar to broken glass – The crushed material has a unit weight of 1360–1440 kg/m³ which is less than that of conventional aggregate, with absorption values of about 1.0–1.5% – Expanded phosphorus slag has a unit weight of 880–1000 kg/m³ and higher absorption than air-cooled slag due to its more has a vesicular nature – Granulated phosphorus slag is made up of regularly shaped, angular particles, mostly between 4.75–0.075 mm in size – It is more porous than air-cooled slag and consequently has lower specific gravity and higher absorption
Lead, lead-zinc, and zinc slag	– Slags of this group are often black to red in color and glassy – They have sharp, angular particles that are cubic in shape – The unit weights of lead, lead-zinc, and zinc slags are somewhat higher than conventional aggregate materials – Granulated lead, lead-zinc, and zinc slags tend to be porous, with up to 5% absorption – The specific gravity can vary from less than 2.5 to as high as 3.6 – These slags are made up of regularly shaped, angular particles, mostly between 4.75–0.075 mm in size

Table 14 Typical chemical compositions of nonferrous slag

Element	Copper slag	Nickel slag	Phosphorus slag	Lead slag	Lead-zinc slag
SiO ₂	36.6	29.0	41.3	35.0	17.6
Al ₂ O ₃	8.1	Trace	8.8	—	6.1
Fe ₂ O ₃	—	53.06	—	—	—
CaO	2.0	3.96	44.1	22.2	19.5
MgO	—	1.56	—	—	1.3
FeO	35.3	—	—	28.7	—
K ₂ O	—	—	1.2	—	—
F	—	—	2.8	—	—
MnO	—	Trace	—	—	2.0–3.0
P ₂ O ₅	—	—	1.3	—	—
Cu	0.37	—	—	—	—
BaO	—	—	—	—	2.0
SO ₃	—	0.36	—	—	—
S	0.7	—	—	1.1	2.8
PbO	—	—	—	—	0.8

4.13

Plastics

Plastics (PL) in the United States comprise more than 8% of the total weight of the municipal waste stream and about 12–20% of the volume [146, 147]. Both physical and chemical properties depend mainly on the characteristics of polyethylene or other polymer materials.

4.14

Quarry By-Products

Screenings are uniformly sized, fine, sandy materials with some silt particles. Screenings commonly range in particle size from 3.2 mm down to finer than 0.075 mm. Normally, the amount of particle sizes finer than 0.075 mm is 10% or less by weight. Stockpiles of screenings may contain some particles up to 4.75 mm in size, which is usually the screen mesh size used for separation. Some weathered rock or overburden material may be present in the screenings from certain processing operations.

Pond fines, when initially recovered from the pond, consist of a fine-grained slurry with a low solids content, usually with 90–95% of the particles finer than 0.15 mm and 80% or more of the particles finer than 0.075 mm. Although particle sizing may vary somewhat with fines from different types of stone, the range in particle size of baghouse fines is from 0.075 mm down to 0.001 mm or even finer.

There is very little difference in the chemistry or mineralogy of screenings and pond fines from the same quarry or rock source, and also very little difference in the chemistry within the size fractions of the pond fines [149–151].

4.15

Reclaimed Asphalt Pavement

The physical properties of RAP are largely dependent on the properties of the constituent materials and the type of asphalt concrete mix (wearing surface, binder course, and so on). There can be substantial differences between asphalt concrete mixes in aggregate quality, size, and consistency. Since the aggregates in surface course (wearing course) asphalt concrete must have high resistance to wear/abrasion (polishing) to contribute to acceptable friction resistance properties, these aggregates may be of higher quality than the aggregates in binder course applications, where polishing resistance is not of concern [153–158].

Both milling and crushing can cause some aggregate degradation. The gradation of milled RAP is generally finer and denser than that of the virgin aggregates. Crushing does not cause as much degradation as milling. Consequently, the gradation of crushed RAP is generally not as fine as milled RAP; however, it is finer than virgin aggregates crushed with the same type of equipment.

The particle size distribution of milled or crushed RAP may vary to some extent depending on the type of equipment used to produce the RAP, the type of aggregate in the pavement, and whether any underlying base or sub-base aggregate has been mixed in with the reclaimed asphalt pavement material during the pavement removal.

The unit weight of milled or processed RAP depends on the type of aggregate in the reclaimed pavement and the moisture content of the stockpiled material. Although available literature on RAP contains limited data pertaining to unit weight, the unit weight of milled or processed RAP has been found to range from 1940–2300 kg/m³, which is slightly lower than that of natural aggregates.

Information on the moisture content of RAP stockpiles is sparse, but indications are that the moisture content of the RAP will increase while in storage. Crushed or milled RAP can pick up a considerable amount of water if exposed to rain. Moisture contents up to 5% or higher have been measured for stored crushed RAP [155].

The asphalt cement content of RAP typically ranges from 3–7% by weight. The asphalt cement adhering to the aggregate is somewhat harder than new asphalt cement. This is due primarily to exposure of the pavement to atmospheric oxygen (oxidation) during use and weathering. The degree of hardening depends on several factors, including the intrinsic properties of the asphalt cement, the mixing temperature/time (it increases with increasing high temperature exposure), the degree of asphalt concrete compaction (it in-

creases if not well compacted), asphalt cement/air voids content (it increases with lower asphalt/higher air voids content), and age in service (it increases with age).

Mineral aggregates constitute the overwhelming majority (93–97% by weight) of RAP. Only a minor % (3–7%) of RAP consists of hardened asphalt cement. Consequently, the overall chemical composition of RAP is essentially similar to that of the naturally occurring aggregate that is its principal constituent. Asphalt cement is made up of mainly high molecular weight aliphatic hydrocarbon compounds, but also small concentrations of other materials such as sulfur, nitrogen, and polycyclic hydrocarbons (aromatic and/or naphthenic) of very low chemical reactivity. Asphalt cement is a combination of asphaltenes and maltenes (resins and oils). Asphaltenes are more viscous than either resins or oils and play a major role in determining asphalt viscosity. Oxidation of aged asphalt causes the oils to convert to resins and the resins to convert to asphaltenes, resulting in age hardening and a higher viscosity binder [157].

4.16

Reclaimed Concrete Material

Processed reclaimed concrete material (RCM), which is 100% crushed material, is physically characterized by being highly angular in shape. Due to the adhesion of mortar to the aggregates incorporated in the concrete, processed RCM has a rougher surface texture, lower specific gravity, and higher water absorption than comparably sized virgin aggregates. As processed RCM particle size decreases, there is a corresponding decrease in specific gravity and increase in absorption, due to the higher mortar proportion adhering to finer aggregates. High absorption is particularly noticeable in crushed fine material, which is less than 4.75 mm in size, and particularly in material from air-entrained concrete. The <0.075 mm fraction is usually minimal in the RCM product. Processed RCM is generally more permeable than natural sand, gravel, and crushed limestone products [159–162].

On the other hand, the cement paste component of RCM has a substantial influence on RCM alkalinity. Cement paste consists chemically of a series of calcium-aluminum-silicate compounds, including calcium hydroxide, which is highly alkaline. The pH of RCM-water mixtures often exceeds 11. RCM may be contaminated with chloride ions from the application of deicing salts to roadway surfaces or with sulfates from contact with sulfate-rich soils. Chloride ions are associated with corrosion of steel, while sulfate reactions lead to expansive disintegration of cement paste. RCM may also contain aggregate susceptible to alkali-silica reactions. When incorporated in concrete, ASR-susceptible aggregates may cause expansion and cracking. The high alkalinity of RCM (pH>11) can result in corrosion of aluminum or galvanized steel pipes in direct contact with RCM and in the presence of moisture. Similarly, RCM that is highly contaminated with chloride ions can lead to corrosion of steel.

4.17

Roofing Shingle Scrap

Roofing shingle scraps (RSS) are unlike other by-product or secondary materials in that they contain components of fine aggregate, mineral filler, and asphalt cement. There are also differences between the types of shingles (organic and glass felt) produced [1–4]. Generally, organic felt shingles exhibit higher moisture content and lower specific gravity than glass felt shingles. Shredded organic felt shingle scrap also exhibits much higher absorption than shredded fiberglass shingle scrap.

Asphalt cement in old roofing shingles undergoes oxidative age hardening and stearic hardening (a hardening process in which solid compounds separate from volatile oils in the asphalt cement). Consequently, the asphalt cement in old tear-off roofing shingles is somewhat harder than new asphalt. Although the stearic hardening process has been demonstrated to be reversible by reheating and/or solubilizing, oxidative age hardening is not reversible [163–167].

4.18

Scrap Tires

The following physical properties are considered [168–178] for various kinds of scrap tires (ST) scrap tires:

- Tire shreds are basically flat, irregularly shaped tire chunks with jagged edges that may or may not contain protruding, sharp pieces of metal, which are parts of steel belts or beads. The size of tire shreds may range from as large as 460 mm to as small as 25 mm, with most particles within the 100–200 mm range. The average loose density of tire shreds varies according to the size of the shreds, but can be expected to be between 390–535 kg/m³. The average compacted density ranges from 650–840 kg/m³.
- Tire chips are more finely and uniformly sized than tire shreds, ranging from 76 mm down to approximately 13 mm in size. Although the size of tire chips, like tire shreds, varies with the make and condition of the processing equipment, nearly all tire chip particles can be gravel sized. The loose density of tire chips can be expected to range from 320 kg/m³ to 490 kg/m³, and their compacted density from 570–730 kg/m³. Tire chips have absorption values that range from 2.0–3.8%.
- Ground rubber particles are intermediate in size between tire chips and crumb rubber. The particle size of ground rubber ranges from 0.85–9.5 mm.
- Crumb rubber used in hot mix asphalt normally has 100% of the particles finer than 4.75 mm. Although the majority of the particles used in the wet process are sized within the 0.42–1.2 to mm range, some crumb rubber particles may be as fine as 0.075 mm. The specific gravity of crumb rubber is approximately 1.15, and the product must be free of fabric, wire, or other contaminants.

The main chemical characteristic of tire chips and tire shreds is their non-reactivity under normal environmental conditions. The principal chemical component of tires is a blend of natural and synthetic rubber, but additional components include carbon black, sulfur, polymers, oil, paraffins, pigments, fabrics, and bead or belt materials.

4.19

Sewage Sludge Ash

Sewage sludge ash (SSA) is characterized, physically, by its silty-sandy material. A relatively large fraction of the particles (up to 90% in some ashes) are less than 0.075 mm in size. Sludge ash has relatively low organic and moisture content. Permeability and bulk specific gravity properties are not unlike those of natural inorganic silt. Sludge ash is a non-plastic material [180–191].

Sludge ash consists primarily of silica, iron and calcium oxide. The composition of the ash can vary significantly, as previously noted, and depends in great part on the additives introduced in the sludge conditioning operation. There are no specific data available relative to the pozzolanic or cementation properties of sludge ash, but sludge ash is not expected to exhibit any measurable pozzolanic or cementation activity. Figure 5 presents the typical chemical composition of sludge ash.

Trace metal concentrations (such as lead, cadmium, zinc, copper) found in sludge ash are typically higher than concentrations found in natural fillers or aggregate. This has resulted in some reluctance to use this material; however, recent investigations (leaching tests) suggest that these trace metal concentrations are not excessive and do not pose any measurable leaching problem. [179–191].

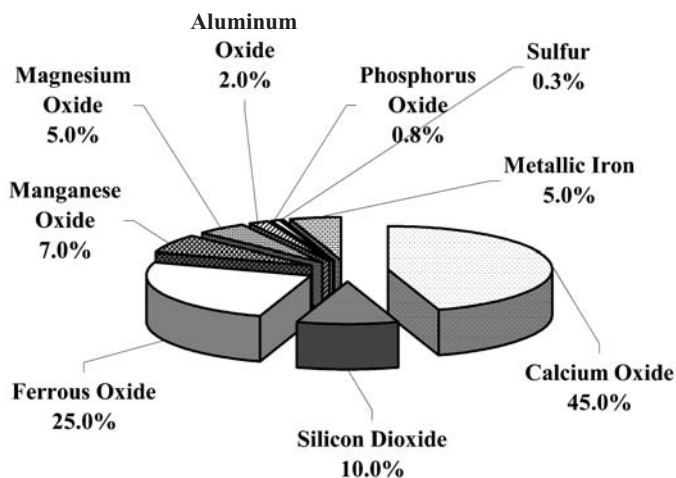


Fig. 5 Typical chemical composition of sewage sludge ash

4.20

Steel Slag

Physically, steel slag (SS) aggregates are highly angular in shape and have rough surface textures. They have a high bulk specific gravity and moderate water absorption (less than 3%).

The chemical composition of slag is usually expressed in terms of simple oxides calculated from elemental analysis determined by x-ray fluorescence. Figure 6 shows the characteristic oxide compounds present in steel slag from a typical base oxygen furnace. Virtually all steel slags fall within these chemical ranges, but not all steel slags are suitable as aggregates. Of more importance is the mineralogical form of the slag, which is highly dependent on the rate of slag cooling in the steel-making process [192–195].

Free calcium and magnesium oxides are not completely consumed in the steel slag, and there is general agreement in the technical literature that the hydration of unslaked lime and magnesia in contact with moisture is largely responsible for the expansive nature of most steel slags [192–195]. The free lime hydrates rapidly and can cause large volume changes over a relatively short period of time (weeks), while magnesia hydrates much more slowly and contributes to long-term expansion that may take years to develop.

Steel slag is mildly alkaline, with a solution pH generally in the range of 8–10. However, the pH of leachate from steel slag can exceed 11, a level that can be corrosive to aluminum or galvanized steel pipes placed in direct contact with the slag.

4.21

Sulfate Wastes

Table 15 gives the different physical and chemical properties of both fluorogypsum and phosphogypsum [196–206]. These properties can affect the engineering uses and application of sulfate wastes on roadways and highways.

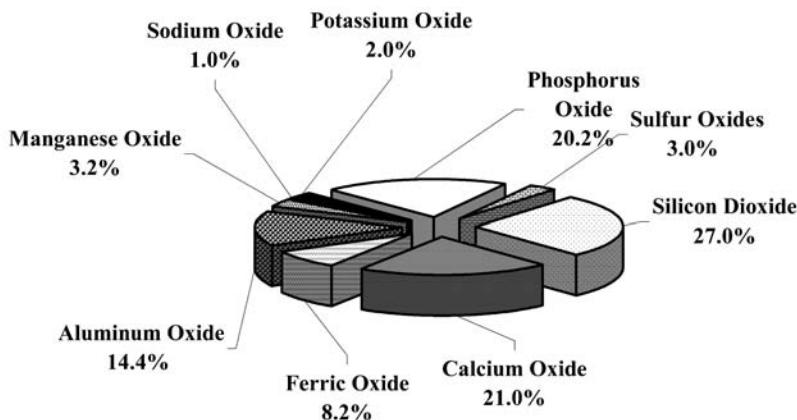


Fig. 6 Typical chemical composition of steel slag

Table 15 Physical and chemical properties of fluorogypsum and phosphogypsum

	Fluorogypsum	Phosphogypsum
Physical properties	- Fluorogypsum solidifies in holding ponds and must be removed, crushed, and graded, when used as an aggregate substitute material - In the process of size reduction, coarse 38 mm top size material and fine, -2.0 mm, sulfate-rich material is produced - The coarse sulfate is a well-graded sand and gravel size material, while the fine sulfate is a silty-clay type material - The average moisture content of the coarse sulfate material reportedly ranges from 6–9%, while the average moisture content of the fine sulfate material ranges from 6–20% - The average specific gravity of the coarse and fine sulfate is 2.5, indicating that fluorogypsum is slightly lighter in weight than naturally occurring aggregates, such as crushed limestone or sand and gravel	- Phosphogypsum is a damp, powdery, silt or silty-sand material with a maximum size range between 0.5–1.0 mm and between 50–75% passing a 0.075 mm mesh size - The majority of the particles are finer than 0.075 mm, and the moisture content usually ranges from 8–20% - There are two predominant forms of phosphogypsum: - Dihydrate phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and - Hemihydrate phosphogypsum ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) - Dihydrate phosphogypsum is generally more finely graded than hemihydrate phosphogypsum - The specific gravity of phosphogypsum ranges from 2.3–2.6 - The optimum moisture content of either type of phosphogypsum can be expected to fall within the range of 15–20% - The maximum dry density is likely to range from 1470–1670 kg/m^3 - The addition of fly ash or Portland cement to phosphogypsum yields slightly higher maximum dry density and optimum moisture content values for stabilized phosphogypsum mixtures, in comparison with unstabilized phosphogypsum blends
Chemical composition	- Fluorogypsum is primarily calcium sulfate with approximately 1–3% fluoride present, exhibiting slightly acidic properties	- The major constituent in phosphogypsum is calcium sulfate and, as a result, phosphogypsum exhibits acidic properties - Phosphogypsum contains small residual amounts of phosphoric acid and sulfuric acid, and also some trace concentrations of uranium and radium, which result in low levels of radiation

4.22

Waste Glass

The physical properties of waste glass are very characteristic. For example, crushed glass (cullet) particles are generally angular in shape and can contain some flat and elongated particles. The degree of angularity and the quantity of flat and elongated particles depend on the degree of processing (the crushing). Smaller particles, resulting from extra crushing, will exhibit somewhat less angularity and reduced quantities of flat and elongated particles. Proper crushing can virtually eliminate sharp edges and the corresponding safety hazards associated with manual handling of the product [207–210].

Uncontaminated or clean glass itself exhibits consistent properties; however, the properties of waste glass from MRFs are much more variable due to the presence of non-glass debris present in the waste stream [210]. Glass collected from MRF facilities can be expected to exhibit a specific gravity of approximately 2.5. The degree of variability in this value depends on the degree of sample contamination.

Crushed glass, which exhibits coefficients of permeability ranging from 10^{-1} to 10^{-2} cm/sec, is a highly permeable material, similar to a coarse sand. The actual coefficient of permeability depends on the gradation of the glass, which, in turn, depends on the degree of processing (crushing and screening) to which the glass is subjected. The particle size distribution of glass received from MRF facilities can vary greatly.

Chemically, glass-formers are those elements that can be converted into glass when combined with oxygen. Silicon dioxide (SiO_2), used in the form of sand, is by far the most common glass-former. Common glass contains about 70% SiO_2 . Soda ash (anhydrous sodium carbonate, Na_2CO_3) acts as a fluxing agent in the melt. It lowers the melting point and the viscosity of the formed glass, releases carbon dioxide, and helps stir the melt. Other additives are also introduced into glass to achieve specific properties. For example, either limestone or dolomite is sometimes used instead of soda ash. Alumina, lead oxide, and cadmium oxide are used to increase the strength of the glass and increase resistance to chemical attack. Various iron compounds, chromium compounds, carbon, and sulfur are used as coloring agents.

Most glass bottles and window glass are made from soda-lime glass, which accounts for approximately 90% of the glass produced in the United States. Lead-alkali-silicate glasses are used in the manufacture of light bulbs, neon signs, and crystal and optical glassware. Borosilicate glasses, which have extraordinary chemical resistance and high temperature softening points, are used in the manufacture of cooking and laboratory ware [212].

Glass is generally considered to be an inert material; however, it is not chemically resistant to hydrofluoric acid and alkali. Expansive reactions between amorphous silica (glass) and alkalis (such as sodium and potassium found in high concentrations in high alkali Portland cement) could have deleterious effects if glass is used in Portland cement concrete structures [208, 209].

Generally, any proposal to incorporate a nonconventional material, and particularly a waste or by-product material, into a pavement structure requires, in addition to an engineering evaluation, an investigation of its physical (size distribution, specific gravity, specific surface area, hygroscopic moisture, plasticity index) and chemical properties (pH, composition, absorption capacity). These properties need be addressed prior to determining the acceptability of the material in order to determine the environmental, occupational health and safety, recyclability, economic and implementation issues. Such an evaluation is complicated by the number of technical disciplines as well as institutional considerations that must be included in the process.

5 Uses of Solid Wastes

The Resource Conservation and Recovery Act of 1976 (RCRA) and its subsequent amendments and regulations provide an environmental regulatory framework for the testing, reporting, storage, treatment, recycling and disposal of waste and by-product materials in the United States. There is, however, no analogous regulatory framework for selecting, characterizing, recovering, and recycling of waste and by-product materials.

The absence of such a regulatory framework is, in most cases, an obstacle to recycling, since the prospective recycler is uncertain what target environmental criteria must be achieved in terms of material or product quality. At the same time, the absence of such formal regulatory testing, reporting, and management safeguards can result in the use of waste and by-product materials in applications that may be environmentally unsuitable.

Several engineering research projects have indicated that a useful recycling option of waste and by-product materials is in road construction. In general, the U.S. public road system consists of 6.3 million centerline kilometers of paved and unpaved surface [215, 216]. If two-lane roads with minimal shoulders are assumed as the norm, then the total surface area exceeds 50,000 square kilometers. Roughly 40% of the total is unpaved, consisting of earth, stone, or gravel, often stabilized, graded and aligned to encourage surface runoff. The remaining 60% is paved, most surfaced with asphalt bound aggregates. Portland cement concrete (PCC) is used as a surfacing in only six percent of all paved public roads. Yet even at this relatively low level of use, more than 2,000 square kilometers are covered by PCC. In road construction, aggregates make up the majority of the material, whether the pavement surface is unpaved, asphalt or Portland cement concrete. Aggregates constitute roughly two-thirds of a typical PCC mix, 95% of an asphalt mix and nominally 100% of most unpaved roads. Table 16 summarizes the highway and pavement applications (asphalt concrete, Portland cement concrete, granular base, embankment or fill, stabilized base, flowable fill) and material uses in such practices. Table 17 lists the types of solid waste materials used for each application.

Table 16 Highway and pavement applications and material uses

Application	Usage
Asphalt concrete	Aggregate – Hot mix asphalt – Cold mix asphalt – Seal coat or surface treatment Asphalt cement modifier Mineral filler
Portland cement concrete	Aggregate Supplementary cementitious materials
Granular base	–
Embankment or fill	–
Stabilized base	Aggregate Cementitious materials – Pozzolan – Pozzolan activator Self-cementing material
Flowable fill	Aggregate Cementitious materials – Pozzolan – Pozzolan activator Self-cementing material

Table 17 Application – material matrix

Application/use	Waste material
Asphalt concrete – aggregate (hot mix asphalt)	Blast furnace slag Coal bottom ash Coal boiler slag Foundry sand Mineral processing wastes Municipal solid waste combustor ash Nonferrous slags Reclaimed asphalt pavement
Asphalt concrete – aggregate (cold mix asphalt)	Coal bottom ash Reclaimed asphalt pavement
Asphalt concrete – aggregate (seal coat or surface treatment)	Blast furnace slag Coal boiler slag Steel slag
Asphalt Concrete – mineral filler	Baghouse dust Sludge ash Cement kiln dust

Table 17 (continued)

Application/use	Waste material
Asphalt Concrete – mineral filler	Lime kiln dust Coal fly ash
Asphalt concrete – asphalt cement modifier	Roofing shingle scrap Scrap tires Contaminated soils
Portland cement concrete – aggregate	Reclaimed concrete
Portland cement concrete – supplementary Cementitious materials	Coal fly ash Blast furnace slag Carpet fiber dusts
Granular base	Blast furnace slag Coal boiler slag Mineral processing wastes Municipal solid waste combustor ash Nonferrous slags Reclaimed asphalt pavement Contaminated soils Reclaimed concrete Steel slag Waste glass
Embankment or fill	Coal fly ash Mineral processing wastes Nonferrous slags Reclaimed asphalt pavement Reclaimed concrete Scrap tires
Stabilized base – aggregate	Coal bottom ash Coal boiler slag
Stabilized base – cementitious materials (pozzolan, pozzolan activator, or self-cementing material)	Coal fly Ash Cement kiln dust Lime kiln dust Sulfate wastes
Flowable fill – aggregate	Coal fly ash Foundry sand Quarry fines
Flowable fill – cementitious material (pozzolan, pozzolan activator, or self-cementing material)	Coal fly ash Cement kiln dust Lime kiln dust

A comprehensive listing of the various applications/uses (Table 18) and recycle/disposal (Table 19) options of solid wastes are also discussed in the present chapter.

Table 18 Highway applications and uses of solid waste materials

Waste type	Application	Highway uses	Reference
Baghouse fines (BHF)	Asphalt concrete mineral filler	– Baghouse fines or dust is used in asphalt paving mixture or the mineral filler – Mineral fillers can constitute up to 5% of some asphalt pavements	19–34
Blast furnace slag (BFS)	Aggregate substitute	– ACBFS is used as a conventional aggregate in granular base, hot mix asphalt, Portland cement concrete, and embankments or fill applications – The material can be crushed and screened to meet specified gradation requirements using conventional aggregate processing equipment – Special quality control procedures are required to address the lack of consistency in some properties such as gradation, specific gravity, and absorption – GBFS is used as a mineral admixture for Portland cement concrete – GBFS and vitrified pelletized blast furnace slag are also used in the manufacture of blended hydraulic cements (AASHTO M240) – When used in blended cements, they are milled to a fine particle size in accordance with AASHTO M302 requirements – The ground slag can be introduced and milled with the cement feedstock or blended separately after the cement is ground to its required fineness	35–48
Carpet fiber dusts (CFD)	Supplementary cementitious materials	– Several research efforts are addressing ways to include these waste fibers in both asphalt pavements and Portland cement concrete – To determine the effectiveness of using recycled fibers from old carpet for concrete reinforcement: – Fibers were mixed with concrete in a standard drum mixer at a rate of 2% by volume – Compressive and flexural strengths were compared with concrete free of fibers and concrete containing 0.5% virgin polypropylene fibers	23–25

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Carpet fiber dusts (CFD)	Asphalt pavements and Portland cement concrete	- The results indicated that using 2% carpet waste in the mix had no appreciable effect on flexural strengths but did markedly decrease 28-day compressive strengths. However, toughness indices (calculated as recommended in ASTM C1018) show that the addition of carpet wastes can be effective in increasing the concrete's energy absorption abilities. - Another research effort in this area focused on the use of waste nylon fibers to reduce plastic shrinkage cracking: - The fibers were packed in water-soluble bags and added to fresh concrete during the mixing process at a rate of 0.6 kilograms per cubic meter (1.0 pounds per cubic yard) - Laboratory tests on a limited number of samples indicated no significant difference from conventional concrete in terms of compressive or flexural strength. Results from field testing, which involved the construction and heating of panels to increase the rate of hydration, indicated that the addition of waste nylon fibers into Portland cement concrete panels can reduce plastic and shrinkage cracking by approximately 90% - Research has also been conducted on the use of waste or recycled fibers in a dense-graded asphalt mix	23-25
Coal bottom ash (BA)/boiler slag (BS)	Asphalt concrete aggregate bottom ash and boiler slag	- BA and BS have been used as fine aggregate substitute in hot mix asphalt wearing surfaces and base courses, and emulsified asphalt cold mix wearing surfaces and base courses - Because of the "popcorn," clinker-like low durability nature of some BA particles, BA has been used more frequently in base courses than wearing surfaces. Boiler slag has been used in wearing surfaces, base courses and asphalt surface treatment or seal coat applications	50-57

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Coal bottom ash (BA)/boiler slag (BS)	Asphalt concrete aggregate bottom ash and boiler slag	- There are no known uses of BA in asphalt surface treatment or seal coat applications - Screening of oversized particles and blending with other aggregates will typically be required to use BA and BS in paving applications - Pyrites that may be present in the BA should also be removed prior to use - Pyrites (iron sulfide) are volumetrically unstable, expansive, and produce a reddish stain when exposed to water over an extended time period - Both BA and BS have occasionally been used as unbound aggregate or granular base material for pavement construction. BA and BS are considered fine base aggregates in this use. To meet required specifications, they need be blended with other natural aggregates prior to its use as a base or subbase material - Screening or grinding may also be necessary prior to use, particularly for the bottom ash, where large particle sizes, typically greater than 19 mm, are present in the ash - BA or BS have been used in stabilized base applications - Stabilized base or subbase mixtures contain a blend of an aggregate and cementitious materials that bind the aggregates, providing the mixture with greater bearing strength - Types of cementitious materials typically used include Portland cement, cement kiln dust, or pozzolans with activators, such as lime, cement kiln dusts, and lime kiln dusts - When constructing a stabilized base using either bottom ash or boiler slag, both moisture control and proper sizing are required - Deleterious materials such as pyrites should also be removed	50-57
	Granular base; ash and boiler		
	Stabilized base aggregate ash and boiler slag		

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Coal bottom ash (BA)/boiler slag (BS)	Embankment or backfill material	- Bottom ash and ponded ash have been used as structural fill materials for the construction of highway embankments and/or the backfilling of abutments, retaining walls, or trenches - These materials may also be used as pipe bedding in lieu of sand or pea gravel - To be suitable for these applications, the bottom ash or ponded ash must be at or reasonably close to its optimum moisture content, free of pyrites and/or “popcorn” like particles, and must be non-corrosive - Reclaimed ponded ash must be stockpiled and adequately dewatered prior to use - Bottom ash may require screening or grinding to remove or reduce oversize materials (greater than 19 mm in size)	50–57
	Flowable fill aggregate (bottom ash)	- Bottom ash has been used as an aggregate material in flowable fill mixes - Ponded ash also has the potential for being reclaimed and used in flowable fill - Since most flowable fill mixes involve the development of comparatively low compressive strength, no advance processing of bottom ash or ponded ash is needed - Neither bottom ash nor ponded ash needs to be at any particular moisture content to be used in flowable fill mixes, because the amount of water in the mix can be adjusted in order to provide the desired flow ability	
Coal fly ash (FA)	Portland cement concrete–supplementary cementitious material	- Fly ash has been successfully used as a mineral admixture in PCC for nearly 60 years. It can also be used as a feed material for producing Portland cement and as a component of a Portland–pozzolan blended cement - Fly ash must be in a dry form when used as a mineral admixture - Fineness, loss on ignition, and chemical content are the most important characteristics of fly ash affecting its use in concrete - Fly ash used in concrete must also have sufficient pozzolanic reactivity and must be of consistent quality	58–65

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Coal fly ash (FA)	Asphalt concrete – mineral filler	– Fly ash has been used as a substitute mineral filler in asphalt paving mixtures for many years – Mineral filler in asphalt paving mixtures consists of particles less than 0.075 mm in size that fill the voids in a paving mix and serve to improve the cohesion of the binder (asphalt cement) and the stability of the mixture – Fly ash must be in a dry form for use as a mineral filler – It is possible that some sources of fly ash that have a high lime (CaO) content may also be useful as an antistripping agent in asphalt paving mixes – Stabilized bases or subbases are mixtures of aggregates and binders, such as Portland cement, which increase the strength, bearing capacity, and durability of a pavement substructure – Because fly ash may exhibit pozzolanic properties, or self-cementing properties, or both, it can and has been successfully used as part of the binder in stabilized base construction applications – When pozzolanic-type fly ash is used, an activator must be added to initiate the pozzolanic reaction – The most commonly used activators or chemical binders in pozzolan-stabilized base (PSB) mixtures are lime and Portland cement, although cement kiln dusts and lime kiln dusts have also been used with varying degrees of success – Flowable fill is a slurry mixture consisting of sand or other fine aggregate material and a cementitious binder that is normally used as substitute for a compacted earth backfill – Fly ash has been used in flowable fill applications as a fine aggregate and as a supplement to or replacement for the cement – Either pozzolanic or self-cementing fly ash can be used in flowable fill – When large quantities of pozzolanic fly ash are added, the fly ash can act as both fine aggregate and part of the cementitious matrix	58–65
	Stabilized base – supplementary cementitious material		
	Flowable fill – aggregate or supplementary cementitious material		

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Coal fly ash (FA)	Embankment and fill material	– Fly ash has been used for several decades as an embankment or structural fill material, particularly in Europe – There has been relatively limited use of fly ash as an embankment material in this country, although its use in this application is becoming more widely accepted – As an embankment or fill material, fly ash is used as a substitute for natural soils – Fly ash in this application must be stockpiled and conditioned to its optimum moisture content to ensure that the material is not too dry and dusty or too wet and unmanageable	58–65
Contaminated soils	Subbase, berms, fill for landfills, feed stock for asphalt and concrete	– The potential uses of soils after they are treated are as varied as the treatment options themselves – Use is ultimately a function of the quality of the original material as well as the degree of treatment accomplished – Typical uses range from soil for subbase, berms and general fill, to fill specifically for landfills, to feed stock for asphalt and concrete	1–4
FGD scrubber material	Stabilized base	– Stabilized or fixated FGD scrubber material has been used successfully for road base construction, at a number of different sites in Florida, Pennsylvania, Ohio, and Texas – Stabilization or fixation of FGD scrubber material can be accomplished by the addition of quicklime and pozzolanic fly ash, Portland cement, or self-cementing fly ash – The FGD scrubber sludge is dewatered before the addition of stabilization or fixation reagents – Additional fixation reagents may need to be added for stabilized base construction in order to meet compressive strength or durability requirements	66–80

Table 18 (continued)

Waste type	Application	Highway uses	Reference
FGD scrubber material	Embankments	- Small amounts of fixated FGD scrubber material have been used for embankment construction in western Pennsylvania - The material was reclaimed from a landfill and used in conjunction with a fly ash embankment project - No additional reagents were needed for embankment construction	66–80
Foundry sand (FS)	Asphalt concrete and flowable fill aggregate	- FS has been used as a substitute for fine aggregate in asphalt paving mixes - It has also been used as a fine aggregate substitute in flowable fill applications - Prior to use, spent foundry sand requires crushing or screening to reduce or separate oversized materials that may be present - Stockpiles of sufficient size typically need to be accumulated so that a consistent and uniform product can be produced - Since only small quantities of spent foundry sand are generated at small foundries, it will generally be necessary for these operators to transport their spent sand to a central storage area that receives sand from a group of plants before transferring it to an end user	81–87
Kiln dusts (KD)	Asphalt concrete mineral filler	- CKD and LKD have been used as mineral filler in asphalt concrete mixes - The blending of CKD into the asphalt cement binder prior to incorporation with the hot mix aggregate results in a binder that can significantly reduce asphalt cement requirements (between 15–25% by volume) - Further, the lime components of the CKD and LKD can assist in promoting stripping resistance. In this application, these dusts can be used to replace hydrated lime or liquid antistripping agents - CKD can also be used as a replacement for Portland cement or hydrated lime in slurry seals - Slurry seal mixes with 2% kiln dust prepared in the laboratory, using a stripping fine aggregate gave excellent results in abrasion resistance testing	88–98

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Kiln dusts (KD)	Asphalt concrete aggregate	- CKD and LKD can also be agglomerated or pelletized to produce an artificial aggregate for special applications - In Japan an oil-absorbing artificial aggregate is reportedly manufactured using CKD that is used to improve the rutting resistance of asphalt concrete pavements by absorbing the lighter fractions of excess asphalt cement binder during hot weather - CKD can be added to asphalt binder to produce a low ductile mastic asphalt - Mastic asphalt is a mixture of asphalt binder and fine mineral material - When mastic asphalt is produced using CKD mixed 50/50 with an asphalt cement binder, a potential exists for a relatively large volume replacement of asphalt cement - The European use of mastic asphalts, with low ductility, for bridge deck waterproofing and protection is well documented, and this could represent a potential application for kiln dusts in the United States - CKD can be used as a cementitious material or a pozzolan activator in stabilized base or flowable fill applications - LKD has potential for use as a pozzolan activator in each respective application - As a cementitious material, CKD can replace or be used in combination with Portland cement - As a pozzolan activator, both CKD and LKD can replace or be used in combination with Portland cement or hydrated lime	88-98
	Asphalt cement modifier		
	Stabilized base or flowable fill cementitious materials		
Mineral processing wastes (MPW)	Asphalt concrete aggregate, granular base, and embankment or fill	- Some waste rock has successfully been used as aggregate in construction applications, especially in asphalt paving and in granular base courses - Waste rock has also been used as riprap for banks and channel protection, and as rock fill for embankment construction - Where additional sizing of waste rock is necessary, in order to meet specification requirements, most, if not all, sources can be crushed and/or screened in the same way that a conventional rock source is crushed and screened	99-112

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Mineral processing wastes (MPW)	Mill tailings	- Coarse tailings, which are generally considered those tailings that are larger than a 2.0 mm mesh, have been used as aggregate in granular base course, asphalt pavements, chip seals, and, in some cases, concrete structures - Fine tailings have been used as fine aggregate in asphalt paving mixes, particularly overlays, and as an embankment fill material - There are numerous examples of the use of mill tailings in local and state highway construction projects throughout the United States - Conventional crushing and screening techniques can be used for sizing mill tailings	99–112
	Coal refuse	- Coal refuse has been used as embankment fill, with some coarse coal refuse also used in stabilized base applications - Most older coal refuse embankments/stockpiles contain a fairly high % of carbonaceous material, which because of poor disposal practices in the past, can ignite spontaneously - Coal refuse banks are cleaned prior to use in order to remove the carbonaceous material. In addition, modern coal refuse disposal practices mitigate this problem by placing the refuse in thin, well-compacted layers and covering all exposed surfaces with several feet of earth fill in order to reduce or eliminate the presence of oxygen needed to initiate or support combustion - Spent oil shale has some potential for use as fine aggregate or mineral filler in asphalt paving - Coarse spent oil shale requires crushing and sizing prior to use	113–121
Municipal solid waste (MSW) combustor ash	Asphalt paving	- MSW combustor ash has been tested for use as an aggregate substitute in asphalt paving mixes, where it has performed in a satisfactory manner, particularly in base or binder course applications - Processed ash that is screened to less than 19 mm with ferrous and nonferrous metal removal can be introduced to replace anywhere from 10–25% of the natural aggregate normally present in the mix for surface course applications and up to 50% for base course applications	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Municipal solid waste (MSW) combustor ash	Granular base, fill, and embankments	- MSW waste combustor ash (grate ash) has been used as a granular base in road construction, as a fill material, and as an embankment material in Europe for almost two decades - The use of ash in granular base and fill applications in the USA has been limited primarily to demonstrations - In granular base or embankment applications, properly processed ash (screened to less than 25–38 mm and metal removed) can be either blended or used alone in these applications - Ash can also be stabilized with Portland cement or lime to produce a stabilized base material	113–121
Nonferrous slags (NFS)	Asphalt concrete aggregate	- Because they are produced in remote geographic locations, NFS are not commonly used in highway construction applications - Nonetheless, there have been reported uses of nonferrous slag as an aggregate substitute in hot mix asphalt and granular base applications - Phosphorus, copper, and nickel slags have been used as aggregate substitutes in hot mix paving - Air-cooled slags can be used as coarse or fine aggregate, while granulated slags can be used as fine aggregate	129–145
	Granular base, embankment, and fill	- There has been limited use of copper, nickel, and phosphorus NFS as a granular base material - NFS have the potential for use as an aggregate in embankments, although there is little documentation of use in this application - Processing of nonferrous air-cooled slags for use as aggregate involves conventional crushing and screening to meet the specified gradation requirements	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Nonferrous slags (NFS)	Granular base, embankment, and fill	- Granulated slag particles are generally of fine aggregate size and may require blending with other suitable material to satisfy specified gradation requirements - Granulated copper/nickel slags can be expected to exhibit some cementitious properties similar to granulated phosphorus slags; however, there is no documented use of these slags in this capacity	129–145
Plastics (PL)	Guardrail posts and block-outs, delineator posts, fence posts, noise barriers, signposts, and snow poles	- Many agencies and private companies have been experimenting with the use of recycled plastic for items such as guardrail posts and block-outs, delineator posts, fence posts, noise barriers, signposts, and snow poles: - The Federal Highway Administration has approved the use of a guardrail-offset block made of 100% recycled wood and plastic. Although the product's initial cost is currently higher than for conventional block material, it is believed that the post will resist damage and deterioration better than conventional materials, thereby resulting in reduced overall lifecycle cost - A Carson City, Nevada, company is marketing a noise wall that contains recycled rubber tires and recycled plastics. The wall's shell is made of a pultruded thermosetting composite of polyester and glass, and the fill section is made of ground, recycled plastics and rubber tires - In May 1992, Alberta Transportation and Utilities initiated a research project on the use of recycled plastic fence and guardrail posts. These posts were purchased and distributed to districts throughout the province as alternatives to wood posts. The cost of these plastic fences and guardrail posts was somewhat higher than for corresponding wood posts	13–15

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Plastics (PL)	Guardrail posts and block-outs, delineator posts, fence posts, noise barriers, signposts, and snow poles	- Two of the most common reported uses of recycled plastic were highway appurtenances and noise barriers, in which Florida and New York have led the way: - Florida has developed standard specifications for at least 15 different applications ranging from sign and fence posts to A-frame barricades - Early published reports indicated many failures, ranging from poor consistency of material resulting in poor post performance, to posts warping and swaying from truck traffic - As improved recycled materials have entered the market, these problems have been resolved - Florida reports that plastic posts are expected to be less expensive than treated wood posts based on life cycle analysis - North Carolina reports that recycled plastic guardrail blockouts actually work much better than wood and can often be reused after a crash. One of the applications is that of recycled plastic marine pilings. The plastic pilings eliminate the concern of wood-treated post releasing chemicals to the water body, and are not susceptible to the marine-borer worm	13–15
Quarry by-products (QBP)	Portland cement concrete, asphalt concrete, and flowable fill Granular base Mineral filler	- Screenings have properties that are suitable for use as an aggregate substitute in Portland cement concrete, flowable fill, and asphalt paving applications - Baghouse fines and/or pond fines could potentially replace much of the fines in flowable fill mixes, depending on strength requirements, which are usually fairly low - If properly blended, screenings can potentially be used in granular base courses - Quarry baghouse fines have been successfully used as a mineral filler in asphalt paving - Dewatered pond fines have the potential for use as a mineral filler in hot mix asphalt paving, depending on the clay content of the pond fines	149–150

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Quarry by-products (QBP)	Mineral filler	- The only quarry fines by-product that would require significant processing for any of the foregoing applications are the pond fines, which would have to be adequately dewatered before use - Pond fines would require a greater degree of dewatering for use as mineral filler in asphalt than for use in flowable fill	149–150
Reclaimed asphalt pavement (RAP)	Asphalt concrete aggregate and asphalt cement supplement	- RAP can be used as an aggregate substitute material, but in this application it also provides additional asphalt cement binder, thereby reducing the demand for asphalt cement in new or recycled asphalt mixes containing RAP - When used in asphalt paving applications (hot mix or cold mix), RAP can be processed at either a central processing facility or on the job site (in-place processing). Introduction of RAP into asphalt paving mixtures is accomplished by either hot or cold recycling	153–185
	Hot mix asphalt (central processing facility)	- Recycled hot mix is normally produced at a central RAP processing facility, which usually contains crushers, screening units, conveyors, and stackers designed to produce and stockpile a finished granular RAP product processed to the desired gradation - This product is subsequently incorporated into hot mix asphalt paving mixtures as an aggregate substitute	
	Hot mix asphalt (in-place recycling)	- Both batch plants and drum-mix plants can incorporate RAP into hot mix asphalt - Hot in-place recycling is a process of repaving that is performed as either a single or multiple pass operation using specialized heating, scarifying, rejuvenating, lay down, and compaction equipment- There is no processing required prior to the actual recycling operation	
	Cold mix asphalt (central processing facility)	- The RAP processing requirements for cold mix recycling are similar to those for recycled hot mix, except that the graded RAP product is incorporated into cold mix asphalt paving mixtures as an aggregate substitute	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Reclaimed asphalt pavement (RAP)	Cold mix asphalt (in-place recycling)	- The cold in-place recycling process involves specialized plants or processing trains, whereby the existing pavement surface is milled to a depth of up to 150 mm, processed, mixed with asphalt emulsion (or foamed asphalt), and placed and compacted in a single pass. There is no processing required prior to the actual recycling operation	153-185
	Granular base aggregate	- To produce a granular base or subbase aggregate, RAP must be crushed, screened, and blended with conventional granular aggregate, or sometimes-reclaimed concrete material - Blending granular RAP with suitable materials is necessary to attain the bearing strengths needed for most load-bearing unbound granular applications - RAP by itself may exhibit a somewhat lower bearing capacity than conventional granular aggregate bases	
	Stabilized base aggregate	- To produce a stabilized base or subbase aggregate, RAP must also be crushed and screened, then blended with one or more stabilization reagents so that the blended material, when compacted, will gain strength	
	Embankment or fill	- Stockpiled RAP material may also be used as a granular fill or base for embankment or backfill construction, although such an application is not widely used and does not represent the highest or most suitable use for the RAP - The use of RAP as an embankment base may be a practical alternative for material that has been stockpiled for a considerable time period, or may be commingled from several different project sources - Use as an embankment base or fill material within the same right of way may also be a suitable alternative to the disposal of excess asphalt concrete that is generated on a particular highway project	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Reclaimed concrete material (RCM)	Aggregate substitute	- The use of RCM as an aggregate substitute in pavement construction is well established, and includes its use in granular and stabilized base, engineered fill, and Portland cement concrete pavement applications - Other potential applications include its use as an aggregate in flowable fill, hot mix asphalt concrete, and surface treatments - To be used as an aggregate: - RCM must be processed to remove as much foreign debris and reinforcing steel as possible - Reinforcing steel is sometimes removed before loading and hauling to a central processing plant - Most processing plants have a primary and secondary crusher - The primary crusher (for instance a jaw crusher) breaks the reinforcing steel from the concrete and reduces the concrete rubble to a maximum size of 75–100 mm - As the material is conveyed to the secondary crusher, steel is typically removed by an electromagnetic separator – Secondary crushing further breaks down the RCM, which is then screened to the desired gradation - To avoid inadvertent segregation of particle sizes, coarse and fine RCM aggregates are typically stockpiled separately	159–162
Roofing shingle (RS) scrap	Asphalt cement modifier	- Recent tests strongly suggest that RS scrap or tabs can be used as an asphalt cement modifier - The incorporation of roofing shingles into asphalt mixes results in reduced asphalt cement requirements and tends to result in stiffer mixes, with improved temperature susceptibility and rut resistance - Prompt RS scrap is mainly produced in tabs approximately 285 mm long by 9.5 mm wide by 3 mm thickness, which must then be processed to suitable size for introduction into the hot mix asphalt	163–167

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Roofing shingle (RS) scrap	Asphalt cement modifier	- The asphalt tabs are processed in various stages: - The tabs are first shredded using a rotary shredder consisting of two slow-speed blades turning at approximately 50 revolutions per minute - This reduces the chips into smaller, but still quite coarse pieces - The smaller pieces are then reduced to a nominal size of about 9.5 mm or finer using a high-speed hammer mill operating at about 800–900 revolutions per minute - To keep the RS material from agglomerating during processing, it is usually passed through the shredding equipment only once, or the material is kept cool by watering at the hammer mill, then stockpiled - The application of water is not very desirable since the processed material becomes quite wet and must be dried prior to introduction into hot mix asphalt - Tear-off RS could potentially be used as an asphalt modifier, but tear-off shingle scrap is much more difficult to process because of the presence of contaminants and debris (such as nails, wood, and insulation), which must be removed to prevent equipment damage during size reduction	163–167
	Aggregate substitute and mineral filler	- RS incorporated into asphalt paving mixes not only modify the binder, but also, depending on the size of the shredded material, function like an aggregate or mineral filler - Organic felt and glass felt particles in particular tend to function like a mineral filler substitute	
Scrap tires (ST)	Embankment construction—shredded or chipped tires	- Shredded or chipped tires have been used as a lightweight fill material for construction of embankments; however, recent combustion problems at three locations have prompted a reevaluation of design techniques when shredded or chipped tires are used in embankment construction	168–178

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Scrap tires (ST)	Aggregate substitute-ground rubber	- Ground rubber has been used as a fine aggregate substitute in asphalt pavements - In this process, ground rubber particles are added into the hot mix as a fine aggregate in a gap-graded friction course type of mixture - This process, commonly referred to as the dry process, typically uses ground rubber particles ranging from approximately 6.4 mm down to 0.85 mm - Asphalt mixes in which ground rubber particles are added as a portion of the fine aggregate are referred to as rubberized asphalt	168–178
	Asphalt modifier-crumb rubber	- Crumb rubber can be used to modify the asphalt binder (for instance, to increase its viscosity) in a process in which the rubber is blended with asphalt binder (usually in the range of 18–25% rubber) - This process, commonly referred to as the wet process, blends and partially reacts crumb rubber with asphalt cement at high temperatures to produce a rubberized asphalt binder - Most of the wet processes require crumb rubber particles between 0.6 mm and 0.15 mm in size - The modified binder is commonly referred to as asphalt-rubber - Asphalt-rubber binders are used primarily in hot mix asphalt paving, but are also used in seal coat applications as a stress absorbing membrane (SAM), a stress absorbing membrane interlayer (SAMI), or as a membrane sealant without any aggregate	
	Retaining walls-whole and slit tires	Although not a direct highway application, whole tires have been used to construct retaining walls to stabilize roadside shoulder areas and provide channel slope protection	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Scrap tires (ST)	Retaining walls—whole and slit tires	– For each application, whole tires are stacked vertically on top of each other. Adjacent tires are then clipped together horizontally and metal posts are driven vertically through the tire openings and anchored into the underlying earth as necessary to provide lateral support and prevent later displacement. Each layer of tires is filled with compacted earth backfill – Slit scrap tires can be used as reinforcement in embankments and tied-back anchor retaining walls. By placing tire sidewalls in interconnected strips or mats, and taking advantage of the extremely high tensile strength of the sidewalls, embankments can be stabilized in accordance with the reinforced earth principles. Sidewalls are held together by means of metal clips when reinforcing embankments, or by a cross-arm anchor bar assembly when used to anchor retaining walls	168–178
Sewage sludge ash (SSA)	Asphalt concrete aggregate and mineral filler	– SSA has been used in asphalt paving mixes to replace both fine aggregate and mineral filler size fractions in the mix – SSA can also be vitrified to produce a frit for use as an aggregate substitute material. A plant operated in New York State for approximately 3 years, but closed in 1995. It produced a vitrified frit-like product that was approved by the New York State Department of Transportation for use as fine aggregate substitute in paving mixes	179–191
	Flowable fill aggregate	– SSA has reportedly been used as a fine aggregate substitute in flowable fill applications, although there is no documented use of sludge ash in this application	

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Steel slag (SS)	Asphalt concrete aggregate, granular base, and embankment or fill	- The use of SS as an aggregate is considered a standard practice in many jurisdictions, with applications that include its use in granular base, embankments, engineered fill, highway shoulders, and hot mix asphalt pavement - Prior to its use as a construction aggregate material, SS must be crushed and screened to meet the specified gradation requirements for the particular application - The slag processor may also be required to satisfy moisture content criteria practices similar to those used in the conventional aggregates industry to avoid potential segregation - In addition, as previously noted, expansion due to hydration reactions should be addressed prior to use	192–195
Sulfate wastes (SW)	Embankment, fill, and road base material	- Limited local use has thus far been made of reclaimed dried fluorogypsum - This material has been previously used in West Virginia as a fill material, as a subbase material, and as aggregate in a lime-fly ash stabilized base - The solidified fluorogypsum was blasted, removed, crushed and screened prior to being used as a coarse and fine aggregate material in base course applications - To date, phosphogypsum has been successfully demonstrated as a road base material in stabilized and unbound base course installations and in roller-compacted concrete mixes - The only processing required for the phosphogypsum is the use of a vibrating power screen to break up lumps prior to mixing with a binder	196–206
Waste glass (WG)	Stabilized base filler		
Waste glass (WG)	Asphalt concrete aggregate	- Waste glass has been used in highway construction as an aggregate substitute in asphalt paving - Many communities have recently incorporated glass into their roadway specifications, which could help to encourage greater use of the material	207–214

Table 18 (continued)

Waste type	Application	Highway uses	Reference
Waste glass (WG)	Granular base or fill	- Crushed glass or cullet, if properly sized and processed, can exhibit characteristics similar to that of a gravel or sand. As a result, it should also be suitable for use as a road base or fill material - When used in construction applications, glass must be crushed and screened to produce an appropriate design gradation. Glass crushing equipment normally used to produce a cullet is similar to rock crushing equipment (like hammer mills, rotating breaker bars, rotating drum and breaker plate, impact crushers) - Because MRF glass crushing equipment has been primarily designed to reduce the size or densify the cullet for transportation purposes and for use as a glass production feedstock material, the crushing equipment used in MRFs is typically smaller and uses less energy than conventional aggregate or rock crushing equipment - Successful production of glass aggregate using recycled asphalt pavement (RAP) processing equipment (crushers and screens) has been reported - Magnetic separation and air classification may also be required to remove any residual ferrous materials or paper still mixed in with the cullet - Due to the relatively low glass-generation rates from small communities, stockpiles of sufficient size need to be accumulated to provide a consistent supply of material in order for glass use to be practical in pavement construction applications	207-214

Table 19 Recycling and disposal options for solid waste materials

Type	Recycling	Disposal	Reference
Baghouse fines (BHF)	- Most asphalt producers whose plants are equipped with baghouses try to recycle as much of the dust back into their own paving mixes as possible - 80–90% of BHF are currently being recycled into hot mix asphalt	- Although most of the BHF are returned to the asphalt mixing plant, some producers (<10%) with excess dust dispose of the dust by sluicing it to a settling pond or returning it to the quarry - Where wet scrubbers are employed for dust control instead of baghouses, the washed fines are generally discarded	19–34
Blast furnace slag (BFS)	- Almost all of the BFS produced in the USA is utilized, and about 90% of this slag is ACBFS - The proportion of ACBFS currently being produced, however, is decreasing relative to granulated and pelletized BFS production. - ACBFS has been used as an aggregate in Portland cement concrete, asphalt concrete, concrete, asphalt and road bases - Pelletized BFS has been used as lightweight aggregate and for cement manufacture - Foamed slag has been used as a lightweight aggregate for Portland cement concrete - Granulated blast furnace slag (GBFS) has been used as a raw material for cement production; as an aggregate, insulating and sandblasting shot materials. GBFS is used commercially as a supplementary cementitious material in Portland cement concrete	- Less than 10% of the blast furnace slag generated is disposed of in landfills	35–48

Table 19 (continued)

Type	Recycling	Disposal	Reference
Coal bottom ash (BA) / boiler slag (BS)	- 30% of all BA and 93% of all BS produced in 1996 were utilized - Leading BA applications are snow and ice control, as aggregate in lightweight concrete masonry units, and raw feed material for production of Portland cement - BA has also been used as a road base and subbase aggregate, structural fill material, and as fine aggregate in asphalt paving and flowable fill - Leading BS applications are blasting grit, roofing shingle granules, and snow and ice control - BS has also been used as an aggregate in asphalt paving, as a structural fill and in road base and subbase applications	- Discarded BA and BS are either landfilled or sluiced to storage lagoons. When sluiced to storage lagoons, the BA or BS is usually combined with fly ash (FA). This blended FA and BA or BS is referred to as <i>ponded ash</i> - 30% of all coal ash is handled wet and disposed of as ponded ash. Ponded ash is potentially useable, but variable in its characteristics because of its manner of disposal - Ponded ash can be reclaimed and stockpiled, during which time it can be dewatered. The higher the % of BA or BS there is in ponded ash, the easier it is to dewater and the greater its potential for reuse - Reclaimed ponded ash has been used in stabilized base or subbase mixes and in embankment construction, and can also be used as fine aggregate or filler material in flowable fill	50-57
Coal fly ash (FA)	- In 1996, approximately 14.6 million metric tons (16.2 million tons) of FA were used. Approximately 22% of the total quantity of FA produced was used in construction-related applications - Between 1985 and 1995, FA usage has fluctuated between 8.0 and 11.9 million metric tons (8.8 and 13.6 million tons) per year	- Approximately 70-75% of FA generated is still disposed of in landfills or storage lagoons - Much of this ash, however, is capable of being recovered and used	58-65

Table 19 (continued)

Type	Recycling	Disposal	Reference
Coal fly ash (FA)	- FA is useful in many applications because it is a pozzolan, meaning it is a siliceous or aluminosiliceous material that, when in a finely divided form and in the presence of water, will combine with calcium hydroxide (from lime, Portland cement, or kiln dust) to form cementitious compounds		58-65
Contaminated soils	- In general, impacted soils can be recycled in asphalt incorporation and concrete incorporation - Metals cannot be effectively treated by aeration, bioremediation, or thermal treatment to be recycled, but can be handled by asphalt or concrete incorporation - Because petroleum is exempted by RCRA and regulated by the states, many states, including most of the petroleum-producing states, allow petroleum-impacted soils to be used in asphalt - Research conducted by the New Jersey Department of Transportation concluded that 20% of the petroleum-contaminated soils could be used and may be added to bituminous-stabilized base course or used as a soil aggregate, as long as the soil complies with the aggregate quality and gradation requirements	- A large portion of contaminated soils is still disposed in landfills	1-4

Table 19 (continued)

Type	Recycling	Disposal	Reference
Contaminated soils	- Other research indicated that fixation of low hydrocarbon levels within concrete is technically feasible because the effective diffusivity of the contaminants within the concrete was reduced by three to five orders of magnitude over the molecular diffusivities in unfixed soils, and the presence of fly ash in the concrete helped reduce diffusivities even one more order of magnitude		1-4
Flue gas desulfurization (FGD) scrubber material	- Fixated or stabilized calcium sulfate FGD scrubber material has been used as an embankment and road base material - Oxidized FGD scrubber material (calcium sulfate), once it has been dewatered, has been sold to wall-board manufacturers as by-product gypsum. This material has also been used as feed material, in place of gypsum, for the production of Portland cement. Wallboard production represents the largest single market for FGD scrubber material - Although there is significant interest in using calcium sulfate FGD scrubber material in wall-board construction and in Portland cement production (as a gypsum source), relatively small amounts of calcium sulfate FGD scrubber material are presently being recycled	- Almost all FGD scrubber sludge generated at the present time is disposed of in holding ponds or in landfills - Stabilization or fixation and placement in landfills is the most common method of disposal	66-80

Table 19 (continued)

Type	Recycling	Disposal	Reference
Flue gas desulfurization (FGD) scrubber material	- In 1996, 0.8 million metric tons (0.9 million tons) of calcium sulfate FGD scrubber material were used to produce wallboard and approximately 0.06 million metric tons (0.07 million tons) of this material were used as feed material for cement production - In 1996, 0.04 million metric tons (0.05 million tons) of primarily fixated calcium sulfite FGD scrubber material were used for structural fill. Also, approximately 0.11 million metric tons (0.12 million tons) were used for road base construction		66-80
Foundry sand (FS)	- In typical foundry processes, sand from collapsed molds or cores can be reclaimed and reused - Little information is available regarding the amount of FS that is used for purposes other than in-plant reclamation, but spent FS has been used as a fine aggregate substitute in construction applications and as kiln feed in the manufacture of Portland cement	- Most of the spent FS from green sand operations is land filled, sometimes being used as a supplemental cover material at landfill sites	81-87
Kiln dusts (KD)	- 64% of the cement kiln dusts (CKD) produced is reused within the cement plant - CKD is used as a stabilizing agent for wastes, where its absorptive capacity and alkaline properties can reduce the moisture content, increase the bearing capacity, and provide an alkaline environment for waste materials	- At the present time, approximately 80% of the surplus CKD remaining after reuse in cement manufacturing is stockpiled or land filled - Most of the LKD generated in the United States is currently disposed of in stockpiles or landfills	88-98

Table 19 (continued)

Type	Recycling	Disposal	Reference
Kiln dusts (KD)	- CKD and lime kiln dusts (LKD) have been used as stabilizing and solidifying agents in the treatment of soft or wet soils for engineering purposes and for environmental remediation - Both dusts have also been used as pozzolan initiators, as a pelletized lightweight aggregate material, as a mineral filler in asphalt pavements, and as a fill material in earth embankments - A significant potential market for CKD and LKD exists for its use as a soil conditioner for agricultural purposes and as an acid-neutralizing agent in agricultural and water treatment applications		88-98
Mineral processing wastes (MPW)	- Large quantities of MPW have historically been used as highway construction materials whenever it has been economical and appropriate to do so - The mining industry has traditionally made use of its own waste materials, either by reprocessing to recover additional minerals as economic conditions become more favorable, or by using them for internal construction purposes - MPW are used in the construction of dikes, impoundments, and haul roads on the mining property, and in mine rehabilitation such as cemented mine backfill	- The processing of ores typically involves grinding and the addition of water and chemicals in the ore treatment refining plant, with a large portion of the resulting waste leaving the plant in the form of a slurry. Usually this slurry is impounded to permit settling of the solids, with any free water accumulated in the pond pumped back to the plant or allowed to discharge from the pond to an adjacent water course	99-112

Table 19 (continued)

Type	Recycling	Disposal	Reference
Mineral processing wastes (MPW)	- Many MPW have limited potential for use as aggregates because of their fineness, high impurity content, trace metal leachability, propensity for acid generation, and/or remote location - some sources of waste rock or coarse mill tailings may be suitable for use as granular base/subbase, railroad ballast, Portland cement concrete aggregate, asphalt aggregate, flowable fill aggregate or fill, and engineered fill or embankment. - Coarse coal refuse has been successfully used for the construction of highway embankments in both the United States and Great Britain. Coarse coal refuse has also been blended with fly ash and used in a number of stabilized road base installations. Burnt coarse refuse has also been used as an unbound aggregate for shoulders and secondary roads. Fine coal refuse has been recovered for reuse as fuel and is being burned in many cogeneration facilities now operating in the United States	- Other waste rock (gangue) excavated from the ore body, and any coarse wastes separated during processing are stored in waste piles or in the base of tailings dam embankments. By far, the largest fraction of mining waste, such as waste rock, is disposed of in heaps (or piles) at the source - Coarse coal refuse is typically removed from the preparation plant and disposed of in large piles or banks. Such deposits of refuse are sometimes referred to as carbon banks (anthracite) or gob piles (bituminous). Sometimes, refuse in these banks or piles can ignite and burn because of spontaneous combustion	99–112
Municipal solid waste (MSW) combustor ash	Most operating facilities in the USA recover the ferrous metal fraction present in MSW combustor ash, which can comprise up to 15% of the total ash fraction	At the present time in the United States almost all of the annual 8 million metric tons (9 million tons) of ash produced is landfilled. This is in sharp contrast to the aforementioned European practice	113–121

Table 19 (continued)

Type	Recycling	Disposal	Reference
Municipal solid waste (MSW) combustor ash	- Only a very small fraction (<5%) of the nonferrous fraction of the ash generated in the USA is recovered and utilized, most of the ash is used as a landfill cover material - In some European nations, more than one-half of the bottom ash generated by MSW combustors is used in construction applications. In Europe, the most common application is the use of ash as a granular road base material - In the USA and Japan, numerous studies in recent years have focused on the potential for using processed bottom ash and combined ash as an aggregate substitute in asphalt concrete, Portland cement concrete, and as an aggregate in stabilized base applications - Although neither federal nor most state regulations categorically restrict the use of MSW combustor ash, the presence of trace metals, such as lead and cadmium, in MSW combustor ash, and concern over leaching of these metals, as well as the presence of dioxins and furans in selected ash fractions (fly ash), has led many regulatory agencies to take a cautious approach in approving the use of MSW combustor ash as a substitute aggregate material		113-121

Table 19 (continued)

Type	Recycling	Disposal	Reference
Nonferrous slags (NFS)	- <i>Copper and nickel slags</i> have been used as granular base and embankment materials, aggregate substitutes in hot mix asphalt, mine backfill materials, railway ballast materials, grit blast abrasives, roofing granule material, and in the manufacture of blended cements (granulated copper and nickel slags) - <i>Phosphorus slag</i> has been used as an aggregate substitute in hot mix asphalt, as a lightweight masonry aggregate, and as cement kiln feed - Granulated phosphorus slag has also been used experimentally in the production of a blended cement product - Some <i>lead, lead-zinc and zinc slags</i> have reportedly been used in the manufacture of ceramic tiles and as an aggregate substitute in hot mix asphalt	- Nonferrous slags are produced in a few locations, often remote from potential markets. As a result, nonferrous slags are not well utilized and most of the nonferrous slag produced is disposed of in slag dumps or stockpiles	129–145
Quarry by-products (QBP)	- The exact quantity of QBP that are being recycled is not known - Very little of the 159 million metric tons (175 million tons) produced annually is thought to be used; mainly the pond fines as an embankment material and in base or subbase applications - Some use has been made of limestone screenings as agricultural limestone, and baghouse fines from quarry sources have been used as mineral filler in asphalt paving	- Virtually all of the QBP generated are disposed at of the quarry source - Screenings are stockpiled in a dry or damp form. Pond fines are conveyed in slurry form to settling ponds. Baghouse fines are usually sluiced into settling ponds	149–150

Table 19 (continued)

Type	Recycling	Disposal	Reference
Reclaimed asphalt pavement (RAP)	- The majority of the RAP that is produced is recycled and reused - Recycled RAP is almost always returned back into the roadway structure in some form, usually incorporated into asphalt paving by means of hot or cold recycling, but it is also sometimes used as an aggregate in base or subbase construction - Approximately 33 million metric tons (36 million tons), or 80–85% of the excess asphalt concrete presently generated, is reportedly being used either as a portion of recycled hot mix asphalt, in cold mixes, or as aggregate in granular or stabilized base materials - Some of the RAP that is not recycled or used during the same construction season that it is generated is stockpiled and is eventually reused	- Excess asphalt concrete is disposed of in landfills or sometimes in the right of way. In most situations, this occurs where small quantities are involved, or where the material is commingled with other materials, or facilities are not readily available for collecting and processing the RAP - It is estimated that the amount of excess asphalt concrete that must be disposed is less than 20% of the annual amount of RAP that is generated	153–185
Reclaimed concrete material (RCM)	- RCM can be used as an aggregate for cement-treated or lean concrete bases, a concrete aggregate, an aggregate for flowable fill, or an asphalt concrete aggregate - RCM can also be used as a bulk fill material on land or water, as a shore line protection material (rip rap), a gabion basket fill, or a granular aggregate for base and trench backfill	- Disposal in landfills, near the right-of-way, and in borrow pits or depleted quarries has historically been the most common method of managing RCM. However, recycling has become a more attractive option, particularly in aggregate-scarce areas and in large urban areas where gathering and distribution networks for RCM have been developed	159–162

Table 19 (continued)

Type	Recycling	Disposal	Reference
Roofing shingle scrap (RSS)	Small quantities of prompt shingle scrap, shredded to 38 mm and smaller, have been used as a gravel substitute for the wearing surface for rural roads and farm lanes. Increasing use of processed tabs or prompt roofing shingle scrap and, to a much lesser extent, tear-off roofing material is being made as a modifier to hot mix asphalt pavements, stone mastic asphalt pavements, and cold mix asphalt patching material	Most roofing shingle scrap is presently disposed of by land filling	163–167
Scrap tires (ST)	- About 7% of the 250 million scrap tires generated annually are exported to foreign countries, 8% are recycled into new products, and roughly 40% are used as tire-derived fuel, either in whole or chipped form - Currently, the largest single use for scrap tires is as a fuel in power plants, cement plants, pulp and paper mill boilers, utility boilers, and other industrial boilers. At least 100 million scrap tires were used in 1994 as an alternative fuel either in whole or chipped form - At least 9 million scrap tires are processed into ground rubber annually. Ground tire rubber is used in rubber products (such as floor mats, carpet padding, and vehicle mud guards), plastic products, and as a fine aggregate addition (dry process) in asphalt friction courses. Crumb rubber has been used as an asphalt binder modifier (wet process) in hot mix asphalt pavements	- Approximately 45% of the 250 million tires generated annually are disposed of in landfills, stockpiles, or illegal dumps. - As of 1994, at least 48 states have some type of legislation related to land filling of tires, including 9 states that ban all tires from landfills. There are 16 states in which whole tires are banned from landfills. Thirteen other states require that tires be cut in order to be accepted at landfills	168–178

Table 19 (continued)

Type	Recycling	Disposal	Reference
Scrap tires (ST)	- Of the ~30 million tires that are not discarded each year, most go to retreaders, who retread about one-third of the tires received - Automobile and truck tires that are retreaded are sold and returned to the marketplace - Currently there are roughly 1,500 retreaders operating in the United States, but the number is shrinking because there is a decline in the market for passenger car retreads - The truck tire retread business is increasing and truck tires can be retreaded three to seven times before they have to be discarded - Sludge ash has been previously used as a raw material in Portland cement concrete production, as aggregate in flowable fill, as mineral filler in asphalt paving mixes, and as a soil conditioner mixed with lime and sewage sludge - Some California sludge ash with high copper content has reportedly been sent to an Arizona smelter for copper recovery - Sludge ash has also been proposed as a substitute lightweight aggregate product, produced by firing sludge ash or a mixture of sludge ash and clay at elevated or sintering temperatures - Other potential uses that have been reported include the use of ash in brick manufacturing and as a sludge dewatering aid in wastewater treatment systems		168-178s
Sewage sludge ash (SSA)		- Most of the sludge ash generated in the United States is presently landfilled	179-191

Table 19 (continued)

Type	Recycling	Disposal	Reference
Sewage sludge ash (SSA)	- Applications that could potentially make use of SSA in highway construction include the use of ash as part of a flowable fill for backfilling trenches, or as a substitute aggregate material or mineral filler additive in hot mix asphalt		179–191
Steel Slag (SS)	- It is estimated that between 7.0–7.5 million metric tons (7.7–8.3 million tons) of steel slag is used each year in the United States - The primary applications for steel slag in the United States are its use as a granular base or as an aggregate material in construction applications	- While most of the furnace slag is recycled for use as an aggregate, excess steel slag from other operations is usually sent to landfills for disposal	192–195
Sulfate wastes (SW)	- <i>Fluorogypsum</i> is not being used in any commercial applications; however, it has been evaluated for use as a road base material, and in the production of impure plasterboard - <i>Phosphogypsum</i> is a calcium sulfate hydrate that is pumped into ponds, eventually dewatered, and ultimately disposed of in large stockpiles called stacks. It has been recovered and reused with some success in stabilized road bases, unbound road bases, and roller-compacted concrete. It can be used for agricultural purposes, if the radium-226 concentration of the source material is less than 10 pCi/g	- All <i>fluorogypsum</i> is currently landfilled or disposed of in holding ponds - At the present time all <i>phosphogypsum</i> is stockpiled in large stacks, some of which may occupy several hundred hectares of land	196–206

Table 19 (continued)

Type	Recycling	Disposal	Reference
Waste glass (WG)	- There are widespread efforts to recover and recycle post-consumer glass through the collection of WG at Material Recovery Facilities (MRFs) - At most MRFs, waste glass is hand-sorted by color, and crushed for size reduction - Crushed glass (referred to as cullet), is reused as a raw material for use in the manufacture of new glass containers - Traditionally, glass recycling has involved the collection and sorting of glass by color for use in the manufacture of new glass containers - Recycling post-consumer glass from the municipal solid waste stream for use as a raw material in new glass products is limited, however, by the high cost of collection and processing of waste glass, and specifications that limit impurities in the glass production process - In addition, during collection and handling of glass, the high % of glass breakage (30–60%) limits the quantity of glass that can actually be recovered using hand-sorting practices	- The EPA has estimated that in 1994 approximately 9.1 million metric tons (10.1 million tons) or 77% of the waste glass generated in the United States was landfilled	207–214

6
NCHRP Project: a Case Study

The viability and integrity of the USA highway systems depend mainly upon the continual rehabilitation and maintenance of the existing network. In such activities, a wide variety of materials are used, including Portland cement concrete, asphalt cement concrete, petroleum-base sealants, various solid wastes, wood preservatives, and additives [1–4, 217–220]. During the wet seasons, there is a potential for leaching some of the chemical constituents in these materials and the possibility of transport to adjacent surface and subsurface water bodies. Toxic chemicals, organic and/or inorganic, from these materials could result in adverse environmental effects on the ecological health of streams, ponds, wetlands, and groundwater systems [2, 3, 221]. If such water bodies are used as a source of potable water, adverse human health effects could occur as well.

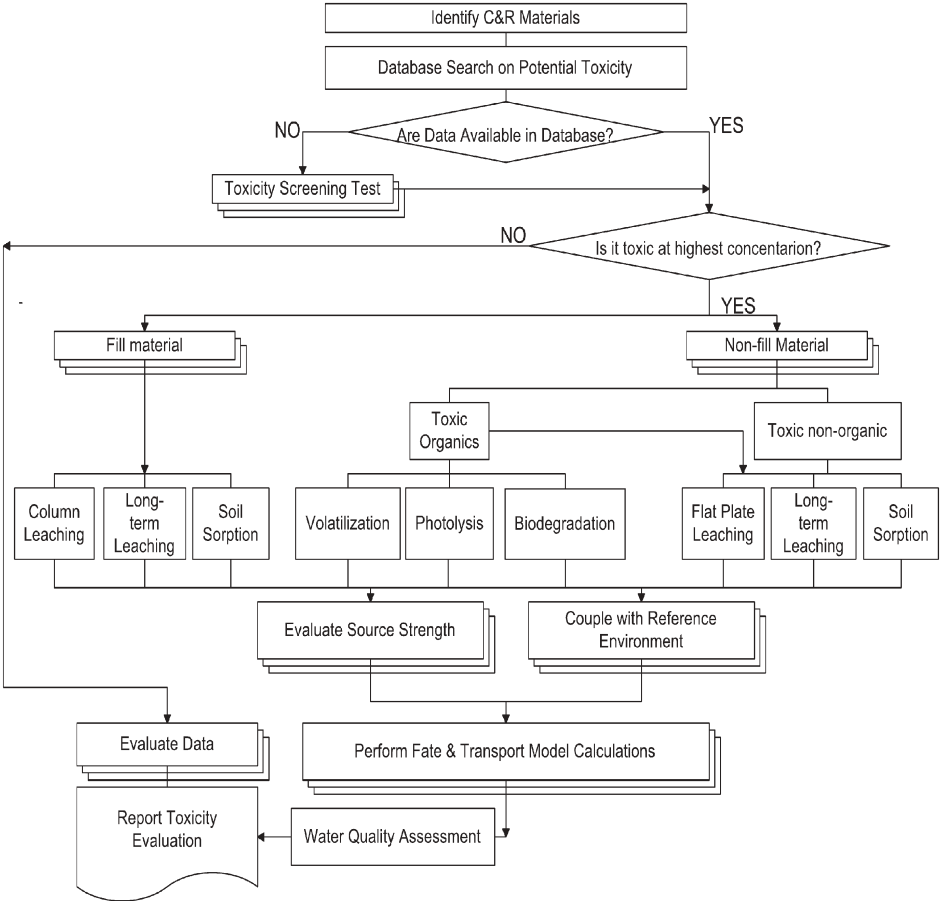


Fig. 7 Evaluation methodology

Accordingly, the Department of Civil, Construction and Environmental Engineering at Oregon State University has conducted a study commissioned by the US-National Academy of Sciences, Transportation Research Board, National Cooperative Highway Research Program (NCHRP) in order to identify the possible impact of highway C&R materials on the quality of surface and ground waters [215, 216, 222–224]. The scope of the study includes the development of a validated toxicity-based methodology to assess such impacts and to apply the methodology to a spectrum of materials in representative highway environments (Fig. 7). The research program was conducted in three fundamental phases (see other chapters in the present book, [3, 215, 216]):

- *Phase I:* Focused on a broad screening of common C&R material to identify the extent of the problem and to guide the succeeding phases. The products of Phase I were a comprehensive list of the most commonly used C&R materials with their toxicity assessment, a protocol for toxicity measurement and assessment, a preliminary description of a conceptual analytical model to predict the fate and transport of soluble toxicants in the soil-water matrix, and the description of an overall evaluation methodology to be used for additional/future C&R materials.
- *Phase II:* Focused on analysis of leaching characteristics of C&R materials, full development of a fate and transport model, and the validation of the overall evaluation methodology. Validation of the methodology was achieved by evaluating a number of C&R materials and by broadening the evaluation criteria to include leaching kinetics, highway reference environments, and impact interpretation.
- *Phase III:* Focused on additional laboratory testing to validate modeling assumptions, expand the current database, and compare laboratory testing and leaching methodologies with conventional EPA procedures.

6.1

Methodology

The evaluation methodology (Fig. 7) was developed as a practical procedure that provides government agencies and private industry with a systematic process for assessing the potential toxicity resulting from the use of C&R materials in road construction and repair [215, 216, 222–224]. To achieve potential benefits, the methodology is simple enough for users not extensively trained in all of its facets, and does not necessarily rely upon new experimental activities for routine application. The methodology involves fairly simple, standard toxicity screening tests leading to more detailed toxicity and chemistry tests, and a computer model that uses the test results in computing the concentrations and loads of mobile toxicants at the highway site boundary [215, 216]. A knowledge base containing the results of toxicity and chemistry tests is a part of this methodology in order to compile relevant data and avoid unnecessary duplicate lab testing.

6.1.1

Laboratory Testing

The process starts with a database search to determine whether human health information, ecological toxicity data, or chemical data exist on the C&R material of interest (Fig. 7). If data are unavailable, the user requests toxicity screening tests (algae and daphnia were the primary aquatic indicators used in this study). If the test results show no toxicity, no further investigation is required. If the screening tests results show toxicity, the user requests tests for evaluating the source strength and effects of reference environments on toxicity response, and chemistry.

The evaluation tests that are conducted depend on whether the subject C&R material is used as a fill material or a non-fill (such as pavement or piling) material. Leaching tests that are conducted for fill materials include column leaching and long-term batch leaching, while those conducted for non-fill materials include flat plate leaching and long-term batch leaching (Fig. 7). For evaluation of removal, reduction and retardation (RRR) processes, soil sorption tests are conducted for both fill and non-fill materials, while volatilization, photolysis, and biodegradation tests are conducted only on non-fill materials that have organics in their leachates.

For all leaching and RRR process tests (Fig. 7, [225–228]), samples are taken as a function of time to assess changes in chemical characteristics (presence and concentration of toxicants) and in biological toxicity (algal chronic toxicity bioassay and daphnia acute toxicity bioassay). Chemical and toxicity data are then fit to leaching and RRR process model equations by regression methods. Leaching and RRR process model parameters are then coupled with a highway reference environment and evaluated using the fate and transport model. The model computes the likely concentrations and loads of mobile toxicants at the highway boundary.

6.1.2

Fate-Transport-Toxicity Model

The mathematical model consists of estimates of contaminant leaching, followed by fate, transport and toxicity analyses related to removal, reduction, and retardation (RRR) processes [214, 215, 229–231]. More specifically, the transport processes of advection and dispersion (in the soil only) are coupled to the RRR processes of sorption, biodegradation, photolysis and volatilization [232]. The main purpose of the model is to predict constituent concentrations and toxicity at the edge of surface and subsurface receiving waters at the boundary of a highway C&R site (at distances on the order of a few meters from the point of generation of the loadings). According to Hesse et al [229], the model has been formulated for six reference environments (permeable highway surface, impermeable highway surface, piling, borehole, culvert, and fill). In addition, off-site transport due to lateral flow in an underlying surficial aquifer

is included as an option. The model might be used in the following modes [215, 216]:

- Laboratory and related information about a given C&R material may be retrieved. If the material has been evaluated as part of this project, its data will be included for evaluation by the user. Fundamental information includes whether or not a material was found to be toxic under any circumstances. If so, RRR parameters (coefficients related to its fate and transport) will also be provided where determined from the laboratory tests.
- Anticipated flows, concentrations and loads in the runoff from a C&R site may be computed, whether via a surface or subsurface pathway. Concentrations will indicate the relative magnitude of constituents in situations where the highway runoff is the source of the receiving water (in other words the upstream or "headwaters" of a small drainage channel). Likewise, the associated toxicity may be categorized from "low" or non-toxic to "extremely high," based on criteria adopted during the research project. Loads (milligrams for instance) of a chemical surrogate will serve as the basis for receiving water quality modeling, should such be necessary, and also for relative computations about the impact of the quantity of a constituent in a specified volume or flow rate of receiving water.

6.1.3

Solid Wastes Tested

Portland and asphalt cement concrete and constituents used in their production represent the largest volume of construction material. In addition, Table 1 shows that many agencies are routinely using industrial by-products in construction materials. This search identified hundreds of different materials broadly grouped into three major categories: asphalt concrete (AC), Portland cement concrete (PCC), and other materials [215, 216]. The following is a summary:

- Asphalt concrete is the most widely used road surfacing material in the world, constituting more than 90% of the surfaced roads in the U.S. The wide application of asphalt has also invited the use of a large number of asphalt additives. These additives are used to improve the asphalt properties with respect to durability, strength, aging, temperature stability, adhesion, electrical conductivity, and rheological properties. A list of common additives includes liquid and fibrous polymers, rejuvenating agents (light-molecular weight petroleum products), carbon black, sulfur, and crumb rubber (ground scrap-tires).
- Portland cement is also associated with transportation infrastructure construction. In addition to its use in pavements, Portland cement concrete is a common construction material for bridges, tunnels and viaducts in our transportation systems. Portland cement is also used in grouting, pipe bedding, and soil stabilization. As with asphalt concrete, the wide range of uses has led to a proliferation of admixtures. These admixtures are used to improve

the concrete properties with respect to workability, durability, and strength. A list of common additives includes air entraining agents (like organic salts, organic acids, fatty acids, detergents), water reducers (like lignosulfates, lignosulfonic acids, sulfonated melamine, sulfonated naphthalene, zinc salts), strength accelerating agents (like calcium chloride, calcium acetate, carbonates, aluminates, nitrates, calcium butyrate, oxalic acids, lactic acids, formaldehyde), and other, less common admixtures (like coloring agents – iron oxides and titanium dioxide; corrosion inhibitors – sodium benzoate; fillers – fly ash, bottom ash, furnace slags; pumping acids – acrylic polymers, polyethylene oxides, polyvinyl alcohol).

- Other materials include treated timber, reinforcement steel, reinforcement fibers, epoxy-based materials, cathodic protective coatings, pipes, and bridge deck sealers. Use of such materials brings additional chemicals (like creosote, ammoniacal-copper-zinc-arsenate or ACZA, and copper-chromated-arsenate, or CCA).

The leachability, chemodynamics and impact of these materials and their mobile constituents on surface and ground water is of primary concern [1–4]. There is an ongoing concern that waste materials are increasingly being used as construction materials. This concern, coupled with the implicit need to demonstrate the ability of the protocol to discriminate toxic from non-toxic materials, led to the development of the list of candidate materials shown in Table 20.

The literature search and testing conducted in Phase I helped identify C&R materials suitable for further testing. The list of materials screened for toxicity in Phase II is shown in Table 21. After initial screening for toxicity, detailed leaching

Table 20 Waste materials selected for use in the NCHRP project

Waste or by-product material	Intended use
Crushed reclaimed concrete	Aggregate base – aggregate replacement
Recycled asphalt pavement	Asphalt mix – aggregate replacement/binder modification
MSW – Bottom ash	Asphalt mix – aggregate replacement
Fly ash	Aggregate base – stabilizer/aggregate replacement
Bottom ash	Asphalt mix – aggregate replacement
Foundry sand	Asphalt mix – aggregate replacement
Shingles	Asphalt mix – binder modification
Ground tire rubber (CRM)	Asphalt mix – binder modification
Phosphogypsum	Aggregate base – stabilizer/aggregate replacement
Mine tailings – Coarse	Asphalt mix – aggregate replacement
Mine tailings – Fine	Asphalt mix – aggregate replacement

and RRR process testing were also performed for selected materials in Phase II (Table 21). In addition, materials such as PCC-with- and -without-plasticizer, and a “standard asphalt cement concrete” (SACC) received detailed testing as part of Phase III. For all materials, short-term (24-hr) leaching and definitive algal toxicity testing were performed to determine the EC_{50} (the ecological concentration at which 50% growth inhibition of *Selenastrum capricornutum* occurs).

Table 21 List of construction and repair (C&R) materials that were tested in detail during the NCHRP project

Full description	Tests performed
Bottom ash modified asphalt mix	Short- and long-term batch leaching, flat plate
Foundry sand modified asphalt mix	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation
Steel slag (EAF) modified asphalt mix	Short- and long-term batch leaching, flat plate
Steel slag (BOF) modified asphalt mix	Short- and long-term batch leaching, flat plate
Hot mix asphalt control	Short- and long-term batch leaching, flat plate
Methacrylate sealer (MMA)	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation, column leaching
Ammoniacal copper zinc arsenate (ACZA)	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation column leaching
Phosphogypsum modified base aggregates	Short- and long-term batch leaching, soil sorption, column leaching
Portland cement concrete with/without plasticizer	Short- and long-term batch leaching, soil sorption, photolysis
Fly ash modified base aggregates	Short- and long-term batch leaching, soil sorption
Crumb rubber modified asphalt mix	Short- and long-term batch leaching, flat plate, Soil sorption, volatilization, photolysis, biodegradation
5% Shingles + 25% recycled asphalt pavement (shingles with asphalt)	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation
30% Recycled asphalt pavement (shingles control)	Short-term, long-term batch leaching
MSW incinerator bottom ash modified asphalt mix	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation
Standard asphalt cement concrete (SACC)	Short- and long-term batch leaching, flat plate, soil sorption, volatilization, photolysis, biodegradation

6.1.4

Soils and Soil Preparation

From the eleven soil orders found in the US, three soils were selected to determine the effect of soil adsorptive capacity on the reduction of toxicity in leachates prepared from C&R materials [1–4, 215, 216, 233–237]. The selected soils are:

- *Mollisol*: the order *Mollisol* is distributed throughout the Ohio and Upper Mississippi Valleys. The *Mollisol* for this study is of the Woodburn Series and was collected from Benton County, Oregon. The soil is typically described as montmorillonitic, containing moderate quantities of organic matter. It may be slightly acid to moderately alkaline.
- *Ultisol*: the order *Ultisol* is distributed widely across the plains, Virginia, North Carolina, South Carolina, and Georgia as well as other areas such as the Sierra Nevada Mountain Province and Western Oregon. The *Ultisol* for this study was of the Olyic series and was collected from Washington County, Oregon. The soil is typically acid, low in organic matter and high in kaolin and oxide minerals.
- *Aridisol*: the order *Aridisol* is, as its name suggests, typical of arid climate conditions and found in the southwest deserts. The *Aridisol* for this project is of the Sagehill series and was collected from Gilliam County, Oregon. The soil is an alkaline coarse-grained soil with free CaCO_3 . It has high infiltration rates and capacities.

6.1.5

Leachate Preparation for Toxicity Screening Test

Only material that passed a 1/4-inch meshed screen was used for preparing leachates. The short-term batch leaching procedure was followed, in which deionized water and C&R material were mixed end-over-end, in the dark, for 24 h at 24 ± 2 °C. At the end of the 24 h the mixtures were placed into 500 mL tubes and centrifuged to separate the solid materials. The supernatant fluid was filtered through a 0.45 μm filter. A C&R material leachate that was processed as described above is referred to as “100% leachate” in this study [227, 228, 238, 239].

It is obvious that the laboratory leachate preparation, which involves grinding and extensively shaking the test samples for 24 h, does not represent leaching of materials found in actual highway sites. The laboratory-prepared leachates have extremely high concentrations of water-born substances/toxicants compared to those expected under actual field conditions. However, the rationale behind this sample preparation was to check toxicity under the worst-case scenario. If a material does not show measurable toxicity under such extreme conditions, no more testing should be required. Materials that show measurable toxicity need to be examined under more representative field conditions for final evaluation of possible toxicity.

6.2

Leaching and RRR Process Test Methods

In Phase II, important processes that affect the chemical composition, toxicity, and fate of leachates from highway C&R materials and assemblages were evaluated in laboratory tests [1–4, 215, 216, 222–224]. The tests provided information on the leachability of constituents in C&R materials under a range of conditions thought to provide reasonable estimates of expected leachate chemical concentrations. The tests provided information on the removal, reduction, and retardation of leachate constituents by natural processes. Algae and daphnia toxicity tests assessed the toxicity of the samples at the leachate source or after modification by RRR processes, and chemical analyses enabled quantification of leachate chemical components at all stages of the laboratory tests. Each laboratory test resulted in the measurement of mass transfer rates of leachate chemical components under controlled conditions, the results of which were applied to specific mathematical models of the process.

Six reference environments were chosen to cover a wide range of highway construction material use [229]. Specifically, these environments included permeable highway surface, impermeable highway surface, piling, borehole, fill and culvert. The mathematics of leaching and RRR processes was included in the overall mathematical model for each reference environment. The linkage of the model to each reference environment is made through the fitting coefficients for the model components derived from the laboratory tests, which results in a battery of tests for each reference environment.

To describe fully the leaching of C&R materials under field conditions present in the selected reference environments, a battery of leaching tests is employed that are specifically designed to simulate various physical and chemical release mechanisms. Both equilibrium (batch leaching under controlled pH) and non-equilibrium tests (column leaching under various flow rates and flat-plate surface leaching) have been developed to describe the full range of leaching processes. The batch leaching tests simulate equilibrium-leaching behavior (the concentration of a chemical that will leach under a defined pH), whereas column tests provide cumulative release data that describe leaching rates (concentration versus time) under conditions of constant surface renewal. To describe the fate and transport of leachate constituents after leachate generation, a series of RRR process tests is employed to simulate the physical, chemical, and biological mechanisms operating in field conditions.

6.2.1

Leaching Methods

Batch leaching tests are designed to determine rates of desorption and equilibrium sorption relationships under conditions of high mixing, high surface areas of the construction material, and continuous surface renewal [1–4, 240–

Table 22 Leaching tests in the NCHRP project

Test	Description
Batch leaching	– The short-term (24-hour) leaching test also is conducted to provide leachate for RRR tests (like volatilization, photolysis, biodegradation, and soil sorption). The leachate is analyzed during the screening process and is utilized to determine the RRR model coefficients – Analysis of the leachate during the toxicological and chemical screening process provides the chemical composition and toxicity data needed for initial evaluation of the test material. This evaluation aids in the scheduling of experiments for each test material. – For example, if a material is found to be composed of mostly inorganic matter, then the biodegradation, volatilization, and photolysis experiments are not required, as these RRR processes will not affect inorganic chemical concentrations
Flat plate leaching	– The flat plate tests determine the leaching rates from a defined surface where mass transfer across a solid/liquid boundary controls the leaching or flux rate (expressed in $\text{mg}/\text{cm}^2 \text{ h}$). It focuses on release by diffusion from the granular construction materials in a simulated on-site experiment – The test material is formed into a flat plate and immersed in the bottom of a glass container of distilled water. The material is leached into the water phase, which is mixed above the flat plate with a paddle stirrer – Increasing concentrations of the contaminant are measured chemically with time. The flux rate of the compound of interest across the diffusion-controlled surface can then be determined. This flux will represent the transport of chemicals from an in-place, flat and compacted material surface, such as a highway surface
Column leaching	– The column experiment is used to simulate the reference environment where the crushed test material (by itself or mixed with an aggregate) is used as a fill material (1–4, 215, 216) – The laboratory column is filled with the test material and distilled water is pumped through the column. The contaminants are leached from the test material into the flowing water – The concentration of the contaminant of concern is at a peak at the beginning of the test and decreases with time. Hence, sampling should occur more frequently at the beginning of the experiment – The faster the flow rate, the more quickly the contaminants will be leached from the fill material. Therefore, the frequency of sampling also depends on the flow rate

256]. Column leaching tests are designed to determine the rates of desorption under conditions of low mixing, high surface areas, and continuous surface renewal. The flat plate tests are designed to determine desorption under conditions of low mixing, low surface areas, and diffusion-limited surface transport. Table 22 summarizes information about each test.

6.2.2

RRR Process Methods

A complete summary of the different removal, reduction, and retardation (RRR) processes that affect the constituents in the leachate experiments is given in Table 23.

Table 23 RRR process techniques in the NCHRP project

Test	Description
Soil sorption	– Batch tests (tests on individual samples) are conducted with soil-plus-leachate suspensions using the three standard soils (Woodburn, Sagehill and Olyic) – The soils are prepared from air-dried samples, and sieved through 1/4" screen for mixing with the leachate from the 24-h batch leaching test – The concentrations of leachate in the solution are designed to evaluate the capability of environmental soils to adsorb available contaminants – The soil particles must be fully dispersed within the aqueous phase to achieve complete adsorption
Photolysis	– Photolysis is pollutant oxidation induced by sunlight energy resulting in irreversible alterations of the molecules. Through photolysis, light can affect the chemical composition and toxicity of organic compounds that comprise the TOC leached from C&R materials – The rate at which a pollutant photochemically degrades depends on numerous chemical and environmental factors, such as the light absorption properties and reactivity of a compound, the light transmission characteristics, and the intensity of solar radiation. For example, polycyclic aromatic hydrocarbons (PAHs) containing three or more rings are able to absorb radiation strongly in the UV-A (320–400 nm) and UV-B (290–320 nm) regions of the solar spectrum – To study the photochemical changes of the leachate from materials in a controlled manner, the use of artificial lighting is required
Volatilization	– Volatilization is the process whereby chemical components in liquid and solid phases volatilize and escape to the atmosphere as gases (1–4).

Table 23 (continued)

Test	Description
Volatilization	– Most formulations for the volatilization process are based on: (a) theoretical considerations of energy exchange, (b) empirical correlation, and (c) various combinations of the two – In considering the volatilization of contaminants, the factors that must be considered are: (a) escape from the interface, (b) diffusion through the surface boundary layer, and (c) turbulent diffusion in the atmosphere. – The escape from the surface depends mainly on the vapor pressure of the contaminant at a given temperature, the molecular weight, and Henry's coefficient. After the contaminant has escaped from the surface, it must diffuse outward in the stagnant boundary layer that is normally present. Then, the contaminant will be transported away from the stagnant layer by advection and turbulent diffusion
Biodegradation	– Biodegradation is a process by which organic compounds can be degraded aerobically and/or anaerobically by microorganisms – In general, microorganisms are ubiquitous in the subsurface environment and actively catalyze reactions through enzymatic activity – The rate at which a compound biodegrades in the subsurface environment depends mainly upon the availability of a suitable electron acceptor and the presence of appropriate microbial consortia

6.2.3

Toxicity Analyses

Toxicity testing represents a more direct measurement of the possible ecological hazard of individual highway C&R materials. This methodology involves the use of standard test organisms in laboratory or field exposures to samples or solutions eluted or leached from highway C&R materials [1–4, 215, 216]. The advantage of laboratory tests using standard test organisms is that the procedures are well defined and accepted by most toxicologists [257–299]. Bioassays are not limited by the variability found within sampling indigenous biota. Moreover, biological field studies are time consuming, expensive, and provide only a retrospective observation of biological effects. Alternatively, bioassays can be conducted rapidly under controlled laboratory conditions. They can also be used prospectively to help evaluate environmental risks under alternative environmental conditions.

The objective of this testing protocol was to develop a methodology for assessing the toxicity of C&R materials that produces reliable, reproducible results [222–224]. The methodology is based on performing both biological and chemical assessment, followed by performing computer simulations to put

the laboratory test results into a more realistic environmental framework. The methods used are cost-effective tests that generate data useful for identifying materials that might allow leaching of toxic constituents into surface and ground waters. Two aquatic test organisms were selected: (a) a freshwater green algae, *Selenastrum capricornutum*; and (b) a freshwater macroinvertebrate, *Daphnia magna*. These species are ecologically sensitive and form the bottom of the food web. It was considered of critical importance that both a plant and an animal species be selected for testing of the highway C&R materials. Plants and animals have biological differences that would cause them to react differently (or not at all) to different chemicals. A microbial toxicity test is included in Phase II. The Microtox test was added to allow for preparation of smaller volumes of leachate for the many additional tests required for elution and leaching kinetics. The Microtox test is also very short in duration (5 and 15 minutes). Concerns about the test sensitivity and applicability limit its wide use for C&R materials toxicity testing.

Three levels of toxicity tests are part of biological assessment: screening, range finding and definitive tests. The screening test is a short-term test to evaluate the potential of a material to produce some selected adverse effect on selected organisms (like daphnia and algae in this study). Usually it is performed at maximum concentration possible (for instance, 24 h shaking of material at a ratio of solid:water of 1:4, by weight). The range finding test is conducted to estimate the concentrations appropriate for performing a definitive test. A range finding test is a repeat of the screening test, but performed using a range of concentration (such as 0.01, 0.1, 1, 10, 100%). A definitive test is conducted to determine the concentration producing an EC_{50} or LC_{50} . The EC_{50} is the concentration that inhibits algal growth to 50% relative to a control. LC_{50} is the concentration that causes 50% mortality of daphnia. Note that a lower EC_{50} or LC_{50} implies greater toxicity, because the same effect is observed at a lower concentration of full-strength leachate. The following is a summary:

- *Algae (Selenastrum capricornutum) Chronic Toxicity Test*: An algal chronic toxicity test [261, 264] is performed by placing 50 mL of leachate into each of the three replicate 125 mL Erlenmeyer flasks to obtain a leachate series of five concentrations, from 0–80%. The test flasks are inoculated with algae at a final concentration of 10,000 cells/mL and are incubated in an environmental growth chamber for 96 h. Algae cultured in algal assay medium served as the controls. One mL samples are transferred from each of the flasks to counting beakers and transported to where they are counted with an electronic particle counter to define the concentration of leachate that inhibits 50% (EC_{50}) of the algal population growth relative to the algal population in the control cultures. The concentration is expressed as percent of full-strength leachate. Therefore, a lower percentage implies greater toxicity.
- *Macroinvertebrate (Daphnia magna) Acute Toxicity Test*: A daphnia acute toxicity test [260] is performed by placing 50 mL of leachate into each of three replicate 100 mL beakers to obtain a leachate series of logarithmic concen-

trations from 0–100%. Each beaker is inoculated with 10 daphnids. The test beakers are covered with glass watch covers and placed into an environmental chamber. The test is incubated for 48 h. After incubation, the beakers are examined to determine the concentration of leachate that killed 50% (LC_{50}) of the daphnia relative to the surviving population (30 daphnids) in the control cultures. Again, a lower percentage for the LC_{50} value implies greater toxicity.

- *Microtox Bacterium (Photobacterium phosphoreum) Acute Toxicity Test*: The Microtox test [266, 275, 287] measures the light output of the luminescent bacterium, *Photobacterium phosphoreum* (a marine organism), after it has been challenged by a C&R material leachate, and compares it to the light output of a control (reagent blank) that contains no C&R material solution. The degree of light loss (an indication of metabolic inhibition in the test organism) indicates the degree of toxicity of the C&R material leachate.

6.2.4

Chemical Test Methods

A brief summary of the chemical methods [300–307] used in support of leaching and RRR tests follows:

- *ICP*: Inductively coupled plasma atomic emission spectrometry [223] is used for determination of multiple metals. In ICP, liquid samples are introduced into an argon plasma by peristaltically pumping the solution through a nebulizer that creates a fine mist. The argon plasma operating at approximately 8000°K vaporizes the mist and ionizes the elements in the sample. The light emitted from the ICP is focused onto the entrance slit monochromator/photomultiplier and a computer-controlled scanning mechanism to examine emission wavelengths sequentially.
- *IC/HPLC*: The concentrations of selected major anions for 24 h leachate are determined by ion chromatography (Dionex Series 4000i Ion Chromatograph [IC] equipped with a conductivity detector). The concentrations of selected organics in 24 h leachate are determined by high-pressure liquid chromatography (HPLC).
- *TOC*: Total organic carbon (TOC) is analyzed in accordance with those procedures specified by the manufacturer (model DC-190, Rosemount Analytical, Inc., Dohrmann Division) as well as those in the ASTM Standard Method 505A: Organic Carbon (Total): Combustion-Infrared Method [308, 309]. The analyzer determines TOC by calculating the difference between the measured total carbon (TC) and inorganic carbon (IC) content of a sample.
- *GC/GC-MS*: Extraction of organic compounds from the leachate is performed according to EPA methods 1624 and 1625 (GC-MS Methods for Analysis of the Volatile and Semi-volatile Organic Priority Pollutants, [265, 307, 310]) and the protocol developed by Kassim [1] and Kassim and Simoneit [2]. An extraction protocol, developed by Kassim [1] and revised by Kassim and

Simoneit [2], was used and verified for the qualitative and quantitative analyses of different organic classes of leachate compounds. In brief, SWMs were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1). All of the extracts were concentrated to 2 ml and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4×30 ml), the latter after acidification (pH 2) with 6 N HCl. The acidic fractions, previously reduced to 0.5 ml, were esterified overnight with 15 ml of 10% BF₃/methanol. The BF₃/methanol complex was destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4×30 ml of *n*-hexane. The neutrals were fractionated by long column chromatography into six fractions namely: aliphatic, monoaromatic and polycyclic aromatic hydrocarbons, esters, ketones, aldehydes, and alcohols. The gas chromatography-mass spectrometry (GC-MS) analyses were performed with an HP GC (initial temperature 50 °C, isothermal 6 min, programmed at 4 °C/min to 310 °C, isothermal 60 min) interfaced directly to an HP quadrupole mass spectrometer (electron impact, emission current 0.45 mA, electron energy 70 eV, scanned from 50–650 Daltons).

7

Summary and Conclusion

The problems associated with the environmentally safe, sustainable and efficient disposal of waste continue to grow. In many areas, existing landfills are beginning to fill up, and the cost of disposal continues to increase while the types of wastes accepted at municipal solid waste landfills is becoming more and more restricted. One answer to all of these problems lies in the ability of society to develop beneficial uses for these waste products.

The highway construction industry can effectively use large quantities of diverse materials. The use of waste by-products in lieu of virgin materials, for instance, would relieve some of the burden associated with disposal and may provide an inexpensive and advantageous construction product. Current research on the beneficial use of waste by-products as highway construction materials has identified several promising uses for these materials.

Presently, there are more than 4 million miles of roadways in the United States, and 60% of those roads are paved. In building and maintaining roads, highway agencies and contractors use a wide variety of manufactured materials. Increasingly, these materials include industrial by-products and recycled pavements and waste, as well as additives to enhance the performance of the materials. A 1994 survey found that more than 24 waste materials or industry by-products have been used in at least 36 different highway sustainable applications.

Over time, as rain falls and as melting snow runs off the pavement, components of these materials can leach out of the pavement or base and could be

carried by the rainwater or snowmelt to nearby soil, ground, or surface waters. If these materials contain any potentially harmful constituents, the leachate could be harmful to the aquatic environment and ultimately human health. Considerable research has been conducted on the water-quality impacts from highway and vehicle operations, maintenance practices, and atmospheric deposition, and on characterizing the chemical, physical, and biological contaminants in the roadway storm water runoff and their impacts on receiving waters.

While construction and repair materials have historically been held as innocuous, and therefore not of concern to environmental quality, there are legitimate questions about the impact of some of these materials on the environment. Furthermore, recycled and waste materials are increasingly being promoted as environmentally friendly and sustainable substitutes for conventional construction and repair materials, thereby increasing the number of nontraditional materials in contact with surface and ground waters.

In order to assess the environmental impact of solid wastes as road construction and repair materials on surface and ground waters, the present chapter critically reviewed the most commonly used wastes in the road construction industry. This included: baghouse fines, blast furnace slag, carpet fiber dusts, coal bottom ash/boiler slag, coal fly ash, contaminated soils, FGD scrubber material, foundry sand, kiln dusts, mineral processing wastes, MSW combustor ash, nonferrous slags, plastics, quarry by-products, reclaimed asphalt pavement, reclaimed concrete material, roofing shingle scrap, scrap tires, sewage sludge ash, steel slag, sulfate wastes and waste glass. In addition, the general framework, approach, and methodology of a major research project was presented, which aimed to: (1) identify potentially mobile constituents from highway construction and repair materials – whether conventional, recycled, or waste, but excluding constituents originating from construction processes, vehicle operation, maintenance operations, and atmospheric deposition, and; (2) measure their potential impact on surface and ground waters.

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Beneficial Reuses of Scrap Tires in Hydraulic Engineering

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Abstract Scrap tires are a high-profile waste material. There are serious concerns over the ever-mounting scrap tire problem. A need exists for increasing available reuse measures to their full potential and developing new and feasible scrap tire reuse alternatives. The growing interest in utilizing waste materials in engineering applications has opened the possibility of constructing hydraulic structures with scrap tires. Applications of scrap tires in hydraulic engineering benefits the environment by reducing the waste, yet one may ask whether scrap tires leach compounds that may adversely affect the environment. Before uses of scrap tires in hydraulic engineering practices, it is important to consider and evaluate any possible environmental implications, for example, potential surface water pollution, and groundwater and soil contamination. This chapter focuses on state-of-the-knowledge about the reuses of scrap tires in hydraulic engineering projects and discusses existing and new utilization methods for potential source reduction, which may be effective in solving the waste tire problem. In this chapter, the problems associated with scrap tires are identified, the physical and chemical properties of tire material are summarized, existing scrap tire applications in hydraulic engineering are reviewed, new applications are developed and analyzed, technical and economic feasibilities are investigated, and environmental impact is assessed. Several case studies are presented.

Keywords Environmental impact · Hydraulic structures · Leachates · Scrap tires · Toxicity · Waste reuses · Water quality

List of Abbreviations and Symbols

D_o	Tire outside diameter (mm)
LC_{50}	Lethal concentration for half mortality
LOEC	Lowest observed effect concentrations
LWSC	Low water stream crossings
NOEC	No observed effects concentrations
MCL	Maximum contaminant level
RWM	Rubber World Magazine
TCLP	Toxicity characteristic leaching procedure
TMU	Tetrahedron module units
USEPA	United States Environmental Protection Agency
USEPA OSW	United States Environmental Protection Agency, Office of Solid Waste
USEPA OSWER	United States Environmental Protection Agency, Office of Solid Waste Emergency Response
V	Tire volume including space enclosed (cm^3)
V_m	Tire material volume (cm^3)
W	Tire weight
XXX	Tire cross-section width in millimeter (mm)
YY	Tire aspect ratio (cross-section height to width)
ZZ	Tire rim diameter in inches

1 Introduction

1.1 The Problem – a Hazardous Waste

Scrap tires management has a serious concern over the past decades and become a growing problem in recent years. Scrap tires represent one of several special wastes that are difficult for municipalities to handle. Over 242 million scrap tires are generated each year in the United States. In addition, between 2 and 3 billion waste tires have accumulated in stockpiles or uncontrolled tire dumps across the country. Millions more are scattered in ravines, deserts, woods, and empty lots. Stockpiles of scrap tire are located in many communities, resulting in public health, environmental, and aesthetic problems [1, 2]. The continuing accumulation of waste tires has led to several concerns of varying severity [1]:

1. Tires are breeding sites for rodents and mosquitoes that can spread serious diseases.
2. Large tire piles often constitute fire hazards.
3. Uncontrolled tire dumps are unsightly and fire hazards creating acrid smoke and leaving behind a hazardous oily residue.
4. Landfilling scrap tires is unacceptable for some reasons. Whole tires are hard to landfill because they tend to rise to and break through the surface liner and float to the surface. Tires take up landfill space. The void space in tires makes them unsuitable for land burial. Whole tires have been banned from many landfills, e.g., in Iowa and Oregon since 1991 [3]. Shredded tires take up less space, but space could be saved if the tires were utilized as raw material.
5. Scrap tires present unusual disposal problems. Disposing of tires is becoming more expensive.
6. Waste tires have to be somewhere. They tend to migrate to the least extensive use of disposal option.
7. Tires should be utilized to minimize environmental impact and maximize conservation of natural resources. At present, the reuses do not accommodate all tires, and disposal must be utilized to a large degree.

1.2 Reuses of Scrap Tires

Because rubber tires do not easily decompose, economically feasible and environmentally sound alternatives for scrap tire disposal must be found. Recycling, reuse, and recovery of scrap tires are among existing source reduction measures. Current recycling/reuse alternatives include: (a) reuse of whole tire in civil engineering (Fig. 1); (b) applications of split or punched tire in mats, belts, dock bumpers, washers, insulators, etc.; (c) shredded tire applications in lightweight road construction material, gravel substitutes, and sludge composting; and (d) ground rubber products. Whole tire recycling does not require



Fig. 1 Scrap tire retaining wall constructed in 1991 in Chapel Hill, North Carolina

extensive processing. All of the recycling alternatives listed above are being used to varying degrees [1].

However, the total usage of discarded tires for recycling into new products and reuses in engineering projects have not reduced the amount of tires in landfills and illegal dumps. It is estimated that less than 7% of scrap tires generated annually were beneficially used in various engineering projects, including whole tire applications (0.1%) and processed tire products (6.5%). The whole tire applications in civil engineering include bank and shore protection structures, artificial reefs, septic system drain fields, breakwaters, dock bumpers, playground equipment, and highway crash barriers [1, 2].

Scrap tire applications in civil engineering do not hold the potential to completely solve the scrap tire problem, but they do have the potential to consume more than they consume now (0.1%). Increasing available recycling and reuse measures to their full potential and exploring new reuse alternatives will significantly reduce the amount of scrap tires. A need still exists for the development of more practical uses for scrap tires. As a part of the possible solution, scrap tire applications in hydraulic engineering can help in easing the waste tire problem. In addition to existing applications, scrap tires may be utilized in various hydraulic engineering practices involving surface water and groundwater, such as erosion control, soil conservation, drainage, habitat enhancement, and rain trap.

1.3

Practical Issues

In the past, there were some barriers to increased scrap tire utilization. Economic barriers refers to the high costs or limited revenues associated with

various waste tire utilization methods, which make the uses unprofitable. Non-economic barriers are a number of constraints on utilization. These include technical concerns such as lack of technology information or concerns regarding the quality of products or processes. The barriers also include aesthetic reason, health, safety, and environmental issues [1]. The barriers need to be overcome in order to have more widespread uses of scrap tires. To do so, technical, economic, and environmental questions need to be answered. There is also a need to perform research on new methods of recycling and reusing tires.

Hydraulic projects, including bank/shore protection, harbor protection, water drainage, rain entrapment, and habitat enhancement, may have great potentials of consuming a considerable portion of scrap tires generated in many areas of the country if economic and technical feasibilities and minimum adverse environmental impact can be shown. Before uses of scrap tires in hydraulic engineering projects, it is important to consider any possible environmental implications. Such implications include potential surface and ground water contamination and associated risks. In this chapter, issues to be addressed on scrap tire reuses in hydraulic engineering include description of scrap tire characteristics, evaluation of existing scrap tire applications, development of new methods of scrap tire reuses, technical analysis for engineering design, economic feasibility with respect to cost and benefit, and assessment of environmental impact of hydraulic structures made of scrap tires.

2

Characteristics of Scrap Tires

2.1

Physical Properties

2.1.1

Geometrical and Dimensional Description

The cross section of a passenger car tire has two main components, tread and sidewall. Passenger car tire treads are reinforced with steel belts, whereas only liners support the sidewalls, as shown in Fig. 2. The strength of the tread is generally greater than the tire sidewall.

A typical size specification for passenger car tires is XXX/YY RZZ, where XXX is the cross-section width in millimeters, YY is the aspect ratio (of the cross-section height to its width) in percent, R is the abbreviation for radial construction and ZZ is the rim diameter in inches. By utilizing its size specification, the outside diameter and volume of a tire are estimated. The outside diameter, D_o (mm) can be expressed as

$$D_o = 2XXXYY + 25.4ZZ \quad (1)$$

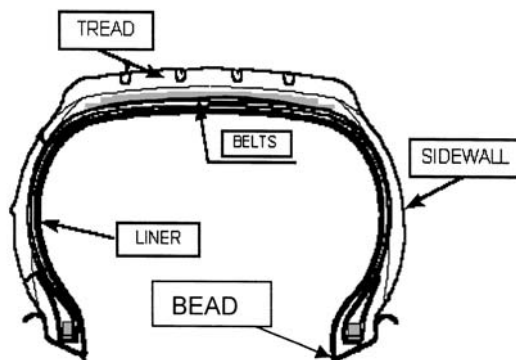


Fig. 2 Cross section of a typical automobile tire

Assuming a cylindrical object with a diameter of D_o and a height of XXX, the volume of the tire including space enclosed, V (cm^3), can be estimated by

$$V = \frac{\pi}{4000} (D_o)^2 \text{XXX} \quad (2)$$

Laboratory measurements of passenger car and truck tires were conducted in previous investigations by Gu et al. [4] and Kjartanson et al. [5]. The widths of truck tire tread studied range from 18 to 24 cm, while passenger car tires have tread widths in the range of 16–20 cm. The outside diameters of truck tires investigated range from 99 to 107 cm and passenger car tires measured from 59 to 65 cm.

2.1.2

Mechanical Features

Scrap tires have retaining strength and flexibility characteristics that make them potentially attractive as a basic construction material. They are relatively small and easy to handle, and their geometric configuration lends itself to a “building block” approach in constructing larger modules.

Scrap tires have desirable strength characteristics for hydraulic structures, but are not individually massive in size. Tires also have the characteristics of being elastic; they are capable of deforming up to 30% without permanent change in shape [6, 7]. Due to the relative inertness of tires, internal structural breakdown is slow. Therefore, they are capable of maintaining strength and flexibility characteristics over long periods of time, even under unfavorable conditions. The capacity of the tire to deform under large forces gives it potentially greater dissipative capabilities than more rigid materials. For instance, in bank/shore protection by tire structures, erosion can be substantially reduced if the majority of the attacking wave energy can be dissipated by breakwaters before reaching the shoreline.

Another possible feature of tire structures is associated with the entrapment of sediments. In certain configurations the nature and geometric properties of the tires may, for example, enhance the accretion of sand along and on a beach.

2.1.3

Laboratory Measurements of Tire Unit Weight

The purposes of these laboratory measurements are to determine the average unit weight of a tire (including rubber, steel, and other materials) and to estimate the volume of a tire. Water displacement tests were carried out on six whole scrap tires of three different sizes. For each test, a scrap tire was weighed before submerging into water. The volume of water displaced by each tire was measured.

Table 1 shows the mass of the six tires before submergence, the volume of water displaced and their respective unit weights, in which W is the weight of tire material, V_m is the volume of tire material, and W/V_m is the unit tire weight. The average tire unit weight is 1580 kg/m^3 . The average specific gravity of tire is 1.59. The specific gravity of rubber is 1.15. Referring to the same table, Goodyear tires have also produced the highest unit weight among the tires tested.

Based on its size specification, the total volume of each individual tire, including space, is estimated by using Eq. (2), in which a cylinder is assumed. The ratio of rubber, steel and other materials to the total tire volume including space, i.e., the volume of solid materials of the tire can then be determined. Presented in Table 1 are computational results for outside tire diameter (D_o), tire material volume (V_m), tire volume (V), and material percent of total tire volume (V_m/V). The average tire material content is about 8%.

Table 1 Results of measurements of tire mass and material volume

Brand	XXX (mm)	YY	ZZ (in)	25.4ZZ (mm)	D_o (mm)	W (kg)	V_m (cm^3)	W/V_m (kg/m^3)	V (cm^3)	V_m/V (%)
Goodyear Integrity	205	65	15	381	647	8.28	5200	1592	66,863	7.8
Goodyear Recatta 2	205	65	15	381	647	8.60	5400	1592	66,863	8.1
Michelin XZ4	195	75	14	356	649	7.75	5200	1490	64,508	8.1
Goodyear Vector	195	75	14	356	649	8.09	4500	1798	64,508	7.0
Grappler II	165	80	13	330	594	6.00	4000	1500	45,724	8.7
Grappler II	165	80	13	330	594	6.25	4000	1563	45,724	8.7

2.2
Chemical and Biological Characterization of Tire Materials

The very characteristics that make them desirable as tires, long life and durability, make disposal almost impossible. The fact that tires are thermal-set polymers means that they cannot be melted and separated into their chemical components. Tires are also virtually immune to biological degradation. Some ingredients used in the manufacture of tires are toxic to aquatic organisms [8–10]. There may be a potential for toxic materials to leach from tires to water. Some potentially toxic constituents released into the aquatic environment may be from weathering of tires.

The basic ingredients of a tire include fabric, rubber, reinforcing chemicals (carbon black, silica, resins), anti-degradants (antioxidants/ozonants paraffin waxes), adhesion promoters, curatives, and processing aids. Typical materials composition of a tire are synthetic rubber, natural rubber, sulfur and sulfur compounds, silica, phenolic resin, oil (aromatic, naphthenic, paraffinic), fabric (polyester, nylon, etc.), petroleum waxes, pigments (zinc oxide, titanium dioxide, etc.), carbon black, fatty acids, inert materials, and steel wire. Table 2 lists the major classes of materials used to manufacture tires by the percentage of the total weight of the finished tire that each material class represents. Scrap tire ash analysis results show a list of compounds: aluminum, arsenic, cadmium, carbon, chromium, copper, iron, lead, magnesium, manganese, magnesium dioxide, nickel, potassium, silicon, sodium, sulfur, tin, and zinc.

Tires contain various types of additives in addition to varying proportions of natural and synthetic rubber. These additives includes organic polymers, such as ozone scavengers (paraphenyldiamines), oil-based plasticizers, paints, and pigments (e.g., zinc oxide, titanium oxide). Metals, such as copper and zinc, are usually present in trace amounts in many steel-belted tires. Some types of additives are used in rubber curing during tire manufacture. For example, benzothiazoles result from the degradation of substances used as antioxidants and from curing compounds used in rubber manufacturing [11]. Spies et al. [11] also identified benzothiazoles in estuarine sediments and attributed their presence to the weathering of tires in the watershed. Chemical tracers present

Table 2 Typical composition of passenger tire by weight

Composition	Weight
Natural rubber	14%
Synthetic rubber	27%
Carbon black	28%
Steel	14–15%
Fabric, fillers, accelerators, antiozonants, etc.	16–17%
Average weight	New 8–11 kg Scrap 6–9 kg

in tire leachates may be useful in tracking the fate of toxic chemicals from tires and of urban runoff.

3

Beneficial Reuses in Surface and Ground Water Structures

3.1

Purposes

The problem of waste tires can be turned into an opportunity. Many benefits have resulted by focusing on an alternative way to utilize the bulky waste, as opposed to how to dispose of it. One of the alternatives is utilizing waste tires to control streambank erosion and streambed grade. In addition to saving valuable public and private land or property threatened by erosion, this option has other benefits. It provides a use for problem tires, has financial benefits, and increases public awareness in the area of natural resource conservation and solid waste management.

The widespread availability and durability of tires has led to their use in the marine environment for breakwaters/coastal defense structures and as artificial reefs for promoting fisheries. Tires have a low density and have been used in floating breakwaters. Shorelines can be protected and strengthened by tire structures. The void space in tires facilitates the construction of artificial reefs to attract fish. Scrap tires can be utilized to drain surface and subsurface water, including storm sewers, cross road culverts, low water stream crossings, and subsurface drainage pipes. They can also be used for trapping rainfall and irrigation water in golf courses and lawns.

3.2

Scrap Tires Reuse Methods

Scrap tire applications in engineering can be in the forms of whole tires and processed tires. Reuses of scrap tires in hydraulic engineering applications in the form of whole tires perhaps have better economic and technical feasibilities than processed tires. Hydraulic structures in surface water and groundwater projects constructed by using whole scrap tires include tire pipes or highway culverts, small overfall dams, riprap, breakwaters, retaining walls, low water stream crossings, and artificial reefs for habitat enhancement. Fastening systems for connecting the tires and fill materials to provide structure weight are needed in whole scrap tire applications. Whole scrap tires have broader applications in hydraulic engineering than processed tires because whole tires meet project needs while do not require processing costs.

Processing methods include shredding, splitting in halves, cutting sidewall/beads, and baling. A number of products, in the form of processed tires, can be made from scrap tires that have applications in erosion control, soil conserva-

tion, ravine crossing, and horizontal drains [12]. Scrap tires are gathered from customers and delivered to a plant where the tires are sorted and processed. The tires are shredded into pieces 15–45 cm in length.

Truck-tire pipes were made by cutting the bead and sidewall from heavy truck tires and stacking and compressing beads/sidewalls [13]. The bead and sidewall are cut from heavy truck tires to make pipes for roadway cross drainage by stacking and compressing the bead/sidewalls to 2.4 m, held in place with rebars wrapped length-wise around the pipe walls and welded [13]. Sidewalls and faces cut from scrap tires can also be used on erosion control structures.

Using split (half) scrap tires, Tire Farms, a California Corporation under The Ford Odell Group's initiative for responsible environment [14] invented and developed a rain trap system for golf courses or lawns.

Another product of processed tires is tire bales. Car and truck tires are compressed into bales by a baler. The processing cost for bales manufactured from whole scrap tires could be high as heavy machines (balers) are needed. In addition, due to low unit weight of rubber and large voids, tire bales do not meet the weight requirements of most hydraulic structures. Therefore, tire bales have limited applications in hydraulic engineering.

In addition to hydraulic engineering applications, processed tires can be utilized in other civil engineering applications, such as shredded tires and rubber-sand as lightweight backfill [15] and natural clay-shredded tire mixture as landfill barrier materials [16].

3.3

Scrap Tire Structures in Hydraulic Engineering

3.3.1

Erosion Control

3.3.1.1

Overfalls for Stream Grade Control

Small overfall dams for stream grade control can be made of scrap tires. Channel degradation is a natural event that can occur in any stream or river, especially acute in erodible deep loess region. As streams erode deeper and wider, the structural safety of numerous roads, bridges and other infrastructures is affected. The widening of the channel also causes the loss of valuable farmland, which can never be reclaimed once it occurs [17]. Grade control structures are overfalls that raise the streambed elevation, which decreases the slope of the flow line for a given reach upstream, and thus reduces the streamflow velocity within that reach and the rate of channel degradation [18].

As a low cost alternative to concrete and natural rock in stream channel stabilization, small overfall dams using whole scrap tires for stream grade control are developed by Gu et al. [4]. In this application, the entire mass of a stream grade structure (overfall) is composed of whole scrap tires that are tied together

and filled with materials to provide adequate resistance to erosion, uplifting, and overturning due to flowing water. The tire structures recycle a hazardous waste material that has become problematic and at the same time provide a relatively inexpensive method of stabilizing degrading streams.

3.3.1.2

Bank Protection Structures

Hydraulic structures using scrap tires for bank protection include tire mats, revetment (retaining walls, seawalls, revet mattresses), and tire-concrete units. In search for economical bank-protection structures, the use of scarp tires as a less-expensive alternative is desirable, considering the costs of the metal and concrete used in reinforced-concrete construction, especially in developing countries. Whole scrap tires can be utilized for surface erosion control, beach and slope protection, and stream bank stabilization. In these applications, scrap tires are banded together and partially or completely buried on unstable slopes. Tires can be used with other stabilization materials to reinforce an unstable highway shoulder or protect a channel slope remained stable and can provide economical and immediate solutions. In bank protection structures, tires are laced together by steel cables and used as a protective layer or *mat* over stream banks or soil embankments. The top, toe, upstream and downstream ends of the *mattress* are tied into the banks. Used tires with metal cords were shown to be an excellent construction material that can partially replace reinforced concrete for protection of river banks and canal walls [19].

3.3.1.3

Breakwaters and Revetments

Experimental testing indicated the potential value of using discarded tires as a construction material for low cost shore and harbor protection. Two types of modular assembly methods with available connecting materials were examined by Armstrong and Peterson [6]: floating tire breakwaters and tire revetments. Floating tire breakwaters provide wave attenuation in marinas and small harbors in both salt and freshwater. Tire revetment mats hold the promise as a low cost approach to certain shore erosion problems.

Breakwaters are barriers off shore that protect a harbor or shore from the full impact of the waves. They were found to be effective on small-scale waves. The tires perform well in applications where floats are needed. Scrap tires for breakwaters and floats are filled with materials, usually foam. The concept employs scrap tires as a durable container for holding the floatation material together.

3.3.2 Drainage

3.3.2.1 Subsurface Drainage Pipes

In the early 1990s, the Louisiana Transportation Research Center [20] conducted a simple feasibility study of utilizing scrap tires in roadside ditches. Whole tires were placed side by side to form a conduit. The constructed culvert was able to drain adequately with negligible head loss during moderate rains. An innovative 330 m long culvert system using whole truck tires on previously undisturbed land was constructed near Fort Dodge, Iowa. The culvert system was constructed to reduce the groundwater level and to divert surface water runoff away from buildings. Kjartanson et al. [5] investigated the design and performance issues in the reuse of scrap tires as subsurface drainage culverts.

3.3.2.2 Roadway Culverts

Culverts (pipes) in roadway cross drainage works passes stream channels under roadways. Scrap tire pipes made of truck tire bead-sidewalls have been used at over 27 locations in Oklahoma, Texas, and Arkansas [13]. In most cases, installations were made by county departments. The tire pipes were installed in rural or small-town environments, ranging from a drive giving access to a field to a rural subdivision road; most were on county roads. Traffic volumes at most sites were relatively light.

3.3.2.3 Low Water Stream Crossings

There is an increasing need for replacement of many old, unsafe bridges on low volume roads. Many communities have bridges that are no longer adequate, and are faced with large capital expenditure for replacement structures of the same size. In this regard, Low Water Stream Crossings (LWSCs) can provide an acceptable, low cost alternative to bridges and culverts on low volume and reduced maintenance level roads. There are two common types of LWSCs: unvented ford and vented ford with pipes. Unvented fords are similar to overfalls used in stream grade control. Reinforced concrete, crushed rocks are most widely used materials for unvented fords. The application of scrap tires in LWSCs is similar to that in stream grade control structures.

A vented ford is one of LWSCs that has pipe(s) under the crossing that accommodate low flows without overtopping the road. High water will periodically flow over the crossing. The pipe(s) or culverts may be embedded in earth fill, aggregate, riprap, or Portland cement concrete. Corrugated metal, plastic and precast concrete are commonly used materials for pipes in vented fords

(LWSCs). Scrap tires may also be used to replace these more expensive pipe materials if they adequately designed. A vented ford for LWSCs is a type of roadway cross culverts. In addition to the ford, the pipes in the vented ford can be made of scrap tires as that in the roadway cross drainage.

3.3.2.4

Tire Pipes in Storm Water Sewers

Concrete, metal or plastic pipes are conventionally used in stormwater sewers for urban surface runoff drainage. A stormwater sewer pipeline is laid parallel to the ground surface with a cover of more than 0.9 m. Scrap tire pipes may be used as the construction material of storm drainage systems in small towns if the pipes can provide required flow capacity.

3.3.3

Artificial Reefs for Habitat Enhancement

Scrap tires have been employed in the large-scale construction of reefs and fish attractors in marine environments and to less extent in freshwater (canals) and have been recognized as a durable, inexpensive and long-lasting material, which benefits fishery communities [21]. As an alternative use, the creation of artificial reefs using scrap tires has been actively and successfully pursued in the State of New Jersey, Southwestern United States, and the South Australia to produce artificial habitats for marine fish and invertebrates [22, 23]. There are two types of reefs: sinking and floating.

Sinking or bottom artificial reefs are constructed by splitting tires and then stacking them in triangular fashion and using concrete for necessary ballast. They then provide habitat for marine organisms and fish. In New Jersey [22], cooperative tire reef projects have enabled a Reef Program to construct large-scale artificial reefs at little or no cost to the state for construction materials. The State's role in the cooperative programs is to specify tire unit designs, ensure quality control of unit construction and direct deployment operations, as well as conduct follow-up physical, biological and use surveys needed to evaluate tire reefs.

Floating tire breakwaters for wave attenuation and shore/harbor protection (see above) can make excellent floating artificial reefs for habitat enhancement [24]. Five floating tire structures in Narragansett Bay were monitored and evaluated by the University of Rhode Island. The air-buoyant tire structures were so productive that the marine growth had to be removed at least once a year to prevent the structures from sinking. The effectiveness of the non-polluting floating-tire structures was demonstrated by the more than fifty highly successful floating tire breakwater structures that were constructed in both fresh and salty water environment.

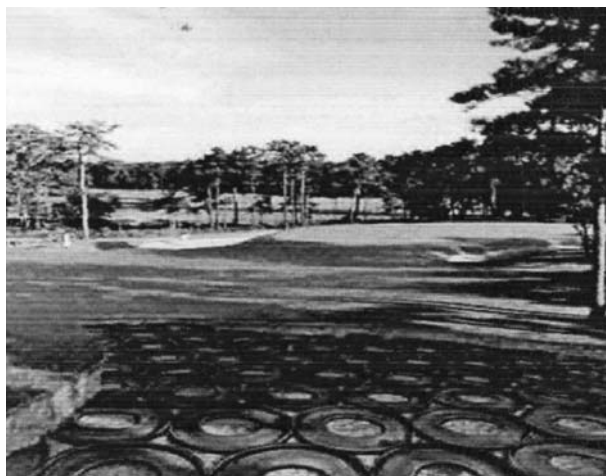


Fig. 3 Rain trap system showing split tires embedded under a fairway of a golf course

3.3.4

Rain Collection Systems

Modern golf courses are doing an excellent job of applying the exact amount of irrigation needed – no more, no less – to satisfy the demands of turfgrass. When there are periodic rainfalls of over 13 mm, within hours, that beneficial water has percolated downward beyond the root depth and is lost. The soil, already near field capacity, cannot retain the rainfall. A rain trap system using split scrap tires developed by Tire Farms of The Ford Odell Group [14] can catch and reservoir that rainfall for golf courses or lawns (Fig. 3). In natural soil, available water is only about 15% of soil volume. The rain trap system stores water at about three times that amount, or full saturation level. The system can save between 10% and 50% on golf course irrigation. Additionally, 4.7 days' supply of water is safely stored within the root zone. For an average golf course, this translates into an annual savings of 60 million gallons of pumped water. The rain trap system uses 1.2 million tires during the construction of an average golf course.

4
Technical Feasibility – Design and Construction

4.1
Erosion Control Structures

4.1.1
Overfalls for Stream Grade Control

4.1.1.1
Structure Dimension and Volumetric Analysis

Figure 4 shows a typical layout of a stream control overfall using scrap tires. The estimated number of tires required for various grade control overfalls with different proposed geometrical dimensions is presented in Table 3. For fish passing as required by natural resources agencies, the height of the overfall is limited to a maximum height of 1.2 m and the downstream slope is limited to 1:4 (vertical to horizontal) or milder.

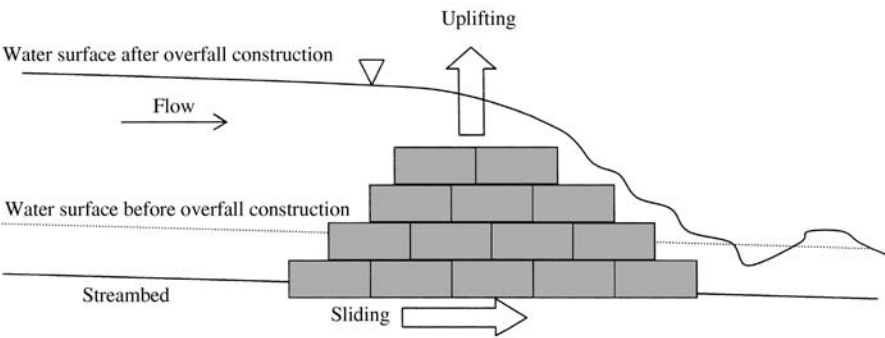


Fig. 4 Scrap tire overfall for stream grade control and stability

Table 3 Scrap tire overfalls in a 9.1 m (30-foot) wide channel

Top width (m)	Height (m)	Upstream slope (V:H)	Downstream slope (V:H)	Volume (m ³)	Number of tires
1.5	1.22	1:2	1:8	84.4	1583
1.5	1.22	1:1	1:8	77.6	1456
1.5	1.22	1:1	1:4	50	937
1.5	0.61	1:1	1:8	38	717
1.5	0.61	1:1	1:4	16.4	307

V:H=Vertical to horizontal.

4.1.1.2

Stability of Scrap Tire Overfalls

A low drop grade control structure of whole scrap tires (Fig. 4) may fail externally by sliding on a plane within the tires above the foundation or along the contact between the tires and soil foundation and by uplift due to overflowing water and internally by breaking the fastening system or tearing the tire rubber itself. Sliding along the foundation of the structure may be resisted by the shear resistance between the soil surface and the bottom layer of tires. Because the damage to fastening systems and the pullout strength of the connecting materials from tires may also cause structure failure, the fastening systems and connection to the tires should be strong enough to resist all potential hydraulic forces. Uplift due to overflowing water can be overcome by properly designed weight of the structure, i.e., the required unit weight.

Theoretical studies were performed to analyze stream flows and forces acting on the grade control structures [4]. The calculated horizontal and vertical forces are used to determine the required stability (Fig. 4). The pullout strength of a binding system or tires and the unit weight of the structure (tires and fill materials) must be adequately designed to resist uplifting, internal breaking-down and sliding. The safety factor for overcoming uplift is computed from the vertical forces and the weight of the structure, i.e. the ratio of the weight to the vertical forces [4]. The factor of safety against sliding is determined by comparing the river bottom shear stress and the horizontal reaction. The safety factor of the fastening system is the ratio of the strength of the system to the hydraulic force applied to the structure.

4.1.1.3

Construction

To connect tires into a coherent structure, bindings between and within layers are needed. This binding system is built to resist shear forces between riverbed soil and structure bottom and between tire layers and hydraulic forces generated by flowing water. Three fastening methods were identified through laboratory measurements of tensile and shear strengths [4] to provide sufficient resistance strength to a tire grade control structure. They are nylon or steel cable, bolts and nuts (combination of machine bolts and nuts), and lag screws and washers.

After tires are placed and fastened in designated construction area, various types of materials could be used to fill up voids in the structure for providing the required weight to overcome uplifting. Based on laboratory direct shear strength tests and hydraulic resistance experiments [4], three types of fillings are recommended: construction rubble, sand and gravel, and flowable mixture of loess, cement, and sand.

To increase stability and reduce sliding of the whole structure, a key-in structure may be used. It is suggested that key-in is used to insert the tire structure into the riverbed and walls of the channel. The dimension of key-in portion is

about two tires wide and three tires deep. These tires are fastened to the bottom and two ends of the proposed structure.

After the whole structure is built, a fastened tire blanket could be used as upstream and downstream riprap to reduce scouring or erosion on riverbed and protect the riverbank. This tire blanket should be either tied with the body of grade control structure or anchored to the subjacent soil.

In case actual in-stream flows exceed the design flow, the tire grade control structure may not provide enough unit weight and resistance to hydraulic forces. Anchoring of the tire structure to the riverbed could help to hold it from floating and sliding. Steel rod with screw and plate is one of commonly used earth anchors. For secure gripping and holding power, anchors are screwed into riverbed. Steel piles may also be used for anchoring purpose.

A layer of coating can be used on upstream and downstream section of grade control structure. The purpose of coating is to protect exposed area from erosion. Concrete or bituminous materials may be used for coating.

4.1.2

Tire Blocks for Bank Protection

Traditional riverbank protection structures are made of reinforced concrete in the form of L-shaped slabs 1.2 m wide, 5 or 7 m high, and 30 cm in wall thickness.

With the application of scrap tires, U-shaped reinforced-concrete bank-protection structures are placed side by side along the river or canal to be protected. Used truck or bus tires of the same type are stacked so that one arm of each of two neighboring concrete units projects upward through their open centers (Fig. 5). Thus, adjoining U-shaped units are securely linked by piles of tires. The width and thickness of the concrete pillars (0.25×0.25 m, Fig. 5) and the width of the U-shaped unit are adjusted to fit the diameter of scrap tires used in the structure. When scour occurs under the tires, they automatically drop to fill the cavity and more tires can be added at the top, keeping the pro-

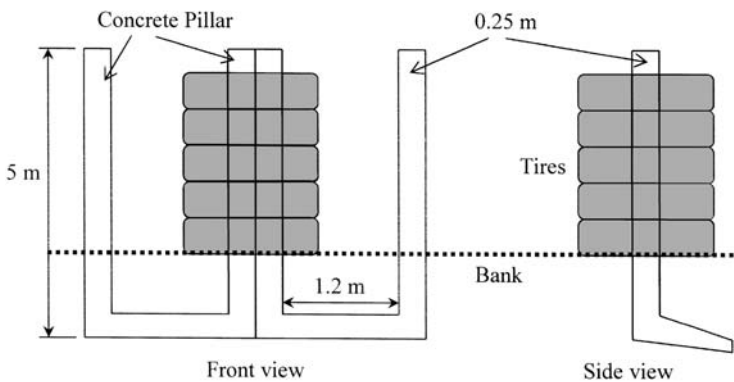


Fig. 5 Reinforced concrete bank-protection structure with scrap tires

tection structure intact. The tires protect the concrete pillars against cavitation wear and mechanical damage from mudflow action. They are also an improvement over previous methods that used unconnected concrete slabs, which could be individually displaced by erosion.

4.1.3
Tire Mattresses as Lake/Sea Shore and Harbor Protection Structures

Tire mattresses are used to attenuate wave, control shore and bank erosion, and protect lake/sea shores and harbors. To facilitate construction of large protection structures, intermediate tire modules are suggested. The design of tire modules best utilizes the irregular surface tires present to incoming waves. This irregular surface will interact more effectively with the wave than a flat, similar-sized structure made of stone or concrete. Using tire modules interlocked to form a mat or mattress instead of stacked or bundled tires made the module mat a promising method of shoreline or harbor protection as they require less material, anchoring and labor during construction.

The tire modules are constructed by connecting together 18 tires to form a modular unit (Fig. 6). The tires are interconnected with high strength rope, cable, or chain, using appropriate fasteners. The fastening or connecting materials should be of suitable strength and corrosion resistance to withstand wave

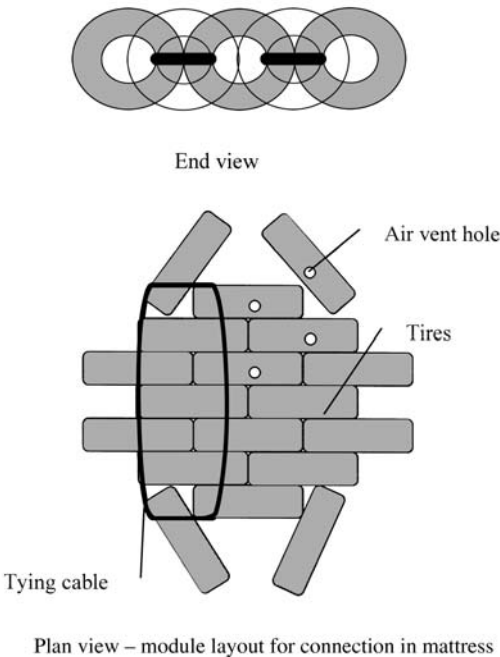


Fig. 6 Basic 18-tire module

forces over the expected service life. Nylon rope, corrosion-resistant cable or chain, and formed steel rods may be used, but each has certain operational limitations. To form a single-layer tire mattress, modules are connected to each other by strapping material similar to that used in their assembly. Mattresses are built to meet length and width requirements specific to each site application.

Tire structures used for shore and harbor protection fall into two categories. Floating tire breakwaters are built in locations offshore to attenuate incoming waves for harbor protection. Revetments type structures located directly on the shoreline are built to dissipate wave energy remaining at the shore.

Floating breakwaters are constructed by building mattresses in shallow water and then pulling to desired location by boat. Mooring is accomplished with anchors, concrete blocks, or driven timber pilings, depending wave and bottom conditions. Short-term floatation (about one year) for the tire mattress breakwater is provided by air trapped in the crowns of the tires. Should longer-term floatation be required, securing thermoplastic foam or sealed plastic bottles in a few or all of the tires of each module can ensure the buoyancy of the breakwater. Scrap tires for breakwaters and floats are filled with materials, usually foam, which displaces 100 kg water and can be used to float a number of devices such as marinas and docks and serve as small breakwaters.

A floating breakwater may also be constructed with a rectangular array of scrap tires interlocked together in a manner that entirely eliminates the use of tying cables to lash the tires together except for the use of cables in anchoring the floating array in position [25]. A unique tire splice interlocks the tires together so that only tire material is used to construct the floating body, eliminating the need for lashing by cable, ropes which are subject to corrosion and deterioration.

The tire mattress concept can also be used as an onshore/offshore revetment (revet mattress). This application offers direct protection of beach and bluff areas. The revet mattress will be subject to the entire power of a breaking wave whereas the floating breakwater only interacts with the upper portions of the wave form. The design and assembly is similar to that used in the floating breakwater. The offshore portion of the revet mattress can be left floating or sunk to conform to the bottom, which may trap sediments.

4.2

Drainage Systems

The design of surface water and groundwater drainage systems, including roadway cross culverts, low water stream crossings – vented fords, subsurface drainage pipes, and stormwater sewer pipes consists of two parts: hydraulic design and structural design. Open channel flow principles, culvert hydraulics, and the theory for pressured flow in pipes are used in hydraulic analyses of the drainage systems. Procedures were developed by Gupta [26], Yang [27], and Normann et al. [28], applying conservation laws (including continuity, energy, and momentum equations), Manning's equation, critical flow equation, frictional head loss, and local or minor energy losses. The theory, principles, and procedures

can be used in the analysis and design of scarp tire drainage systems. A design flow capacity and a length of the culvert or pipe are selected first. As the size of scrap tire is known, the slope and number of pipes are adjusted so that the pipes are adequate for conveying the design flow.

A conduit built with whole scrap tires by steel bandings is suitable for low or moderate water flowrates. The roughness coefficient of the tire culvert is an important parameter for hydraulic design. A value of 0.05 was estimated by Yang [27]. The tire culvert is designed for partial flow only due to the high roughness and to avoid buoyancy effects associated with air trapped in the top of the tires. The maximum water depth inside the pipe is limited to 75% of the pipe diameter. For underground pipes, the range of soil depth above the tire pipes is limited by allowable pipe deflection, which is determined by the type and degree of compaction of the backfill soil and the surface load. Yang [27] recommended 0.3–1.2 m for minimum soil covers and 6–45 m for maximum soil covers.

Cross roadway drainage pipe can also be made of scrap tire beads and sidewall (Fig. 7), which are usually used as culverts at small streams and ditches on county or rural subdivision roads. The pipe material is produced by cutting the bead and adjacent sidewall from a scrap tire. The pipes are made using a hydraulic press to compress about 80 tire bead-sidewalls to a length of approximately 2.4 m. Four number 3 rebars are then wrapped lengthwise around the pipe walls, 90 degrees apart, and welded. Rebars are steel rods, commonly used in reinforcing concrete. Field connections between two end-to-end tire pipe sections can be made with a flexible belt, which is wrapped around the two abutting pipe ends and cinched in place with a strap. The pipes can be used as gravity flow drainage conduits where soil provides support to the pipe walls.

4.3

Artificial Reefs

The sinking or bottom artificial reefs for habitat enhancement with scrap tire units are constructed either by splitting and stacking or by stacking and com-

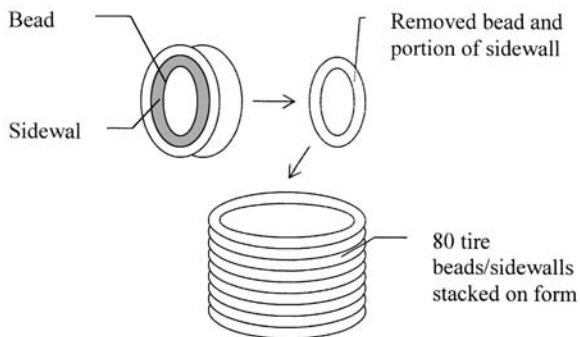


Fig. 7 Construction of tire pipes using beads/sidewalls

pressing tires, and then pouring concrete into the central cylinder of each stack to bind the tires together and provide the necessary ballast [22]. The units are constructed by splitting tires like bagels leaving about six inches attached and then stacking them in triangular fashion [23]. Holes are drilled through this stack and about 22 kg per tire of concrete are poured in the holes to anchor the reef. The 900-kg 0.91-m high reefs are then hauled by barge 6 to 20 km off the coast and dumped in 18–30 m deep water. They then provide habitat for marine organisms and fish. Tire units are designed to be stable and durable on ocean reef sites. It is desirable that the units stay without breaking-down for a long period.

Each of these reefs is made up of modules consisting of 28 scrap tires strapped together with polyester tape fastened by stainless steel clips. The tires are formed into tetrahedron module units (TMUs) with concrete ballast in the basal tires. They are placed at carefully selected locations and in a manner to minimize any adverse environmental effects. Underwater monitoring programs are needed on each of these reefs to see if all reefs attract fish and support a growing population of benthic organisms. It is expected that the longevity of the materials will be retained for a minimum of 20 years.

The floating tire breakwaters for wave attenuation and harbor protection (see above) can make excellent floating artificial reefs for habitat enhancement [24]. These floating reefs are placed in waters that are from 1.2 to 6 m deep. The design of the floating tire reefs uses the eighteen-tire modular building units as described above. The units may be laced together to form large rectangular open grid floating mats identical to the breakwater structures, or they may be interconnected in circular patterns for amore pleasing overall aesthetic effect. Variations in height are possible by adding modules below to vary the thickness or by combining constructions such as hanging a curtain on the mat structure. Floatation is provided by trapped air, foam or sealed plastic bottles.

4.4

Rain Collection System

After proper irrigation, a soil is at full field capacity and turfgrass root hairs now draw off water that adheres to the soil grains. As the water thins out, the turfgrass root hairs have an increasingly more difficult time attracting water. The cohesive attraction of water to the soil grain is greater than the root hairs' ability to extract that water. This point of turfgrass starvation, or about 10% water, is known as the permanent wilt point. "available water" is that which is actually used by the grass. In natural soil, available water is only about 15% of soil volume. The rain trap system stores water at about 3 times that amount, or full saturation level.

The rain trap system made of split tires are embedded 38 cm under a fairway of a golf course or a lawn (Fig. 8). The principle behind the rain trap system is as common as a household flowerpot. When one waters plants, all excess water is saved in the saucer below the pot. Split scrap tires do the same job of collecting and reusing water but do it by the acre. In natural soil, Available wa-



Fig. 8 Rain trap system using split scrap tires to collect and reuse irrigation water in Santa Rosa, California, installed May 1996

ter is only about 15% of soil volume. The rain trap system stores water at about three times that amount, or full saturation level.

Civil engineering technique can assure uniform embedment of rain trap system and low installation cost. Three corresponding pieces of specialized equipment complete the operation simultaneously. In a single process, the ground is excavated, the pre-split tires are precisely planted, the tires are covered, and the earth is compacted and ready for topsoil. Two installation methodologies are identified, either of which can be employed without interference with the normal earth-moving process of building a golf course. Placement of the split tires requires close coordination with whichever earth-moving method is selected for individual application.

The first is to use standard golf course earth-moving equipment and factor its use with the cut and cover necessary to implant the split tires. With this operation, the earth mover would cut an additional 30 cm below the grade specified by the architect, moving the material to a location where tires had been placed. The other method under consideration at this time is the use of a fine grader to excavate for the tires after the course earth-moving is balanced and before the topsoil is replaced for the final grading. This would involve excavating a slot, and covering the just placed tires with the excavated material directly from the fine grader.

5

Economic Feasibility – Cost and Benefit

It is economically feasible to use scrap tires in hydraulic engineering. Their benefits include waste reduction for environmental protection and lower material costs than conventional used materials in surface water and groundwater structures. In most cases, scrap tires are burned or disposed in landfills, and

therefore can be readily and inexpensively obtained. The availability of scrap tires is normally so great that the only cost involved in obtaining tires is the transportation cost. A conservative figure would be about \$0.10 per tire in Michigan in 1976 [6]. For areas distant from major population centers, a shipping cost of \$0.20 per tire is incurred. Construction costs for most hydraulic structures utilizing tires, such as bank and shore protection, surface and sub-surface drainage and artificial reefs, may be low enough that an individual property owner can afford to install a type of the applications.

5.1

Erosion Control

Erosion control applications of scrap tires, which are banded together and partially or completely buried on unstable slopes, can provide economical and immediate solutions. Construction costs were reduced by 50 to 75% of the lowest cost alternatives such as rock, gabion (wire-mesh/stone matting), or concrete protection.

5.1.1

Stream Grade Control

Gu et al. [4] estimated that for a structure of 35 m long, 3 m and 17 m wide on top and bottom, respectively, and 1.2 m high, the costs of fastening systems range from \$9000 to \$65,500, including connecting materials and labor, in Iowa in 2000. Nylon cable appears most expensive. Nylon ties are marginal. The nylon ties and cables have a greater material cost and are significantly (4–6 times) higher in cost than the other two options (bolts and nuts and lag screws). The cost of fill materials (a mixture of cement, sand and loess) increases as the cement used increase and ranges from \$2600 to \$9600. These costs do not include that for mobilization or earth moving, transportation, and mixing the loess with cement and sand. Mobilization cost depends on the specific site condition and location and travel distance. The total structure cost is in the range of \$16,000 to \$23,000 if bolts and nuts or lag screws are used for fastening systems and labor and transportation costs are excluded from fill materials costs, depending on cement percentage and mobilization distance.

5.1.2

Bank/Shore and Harbor Protection

In the application of tire blocks for bank protection, U-shaped concrete units are securely linked by piles of tires. This construction method makes it possible to reduce the amount of reinforced concrete required for bank-protection structures by more than half. In comparison with the traditional structures used for the same purpose, a saving of more than 50% of reinforced concrete is obtained. The inoperative part of the structure is significantly reduced.

Costs for constructing floatation devices are determined on a dollar per pound basis. A one-half to three-quarters cost savings can be achieved by using scrap tire floats over wood, wood-fill, or other alternatives. The tire floats cost approximately \$0.13 to \$0.18 per kg in 1989, whereas the economically closest alternative, foam-filled plastic, costs \$0.22 to \$0.31 per kg of floatation [1].

Construction costs for tire mattress protection structures (revet mattress and floating breakwater) include materials (primarily shipping), connection, moorings and pilings, labor, and equipment usage. Labor costs will vary from place to place. Using the 1976 prices in Michigan, Armstrong and Petersen [6] estimated that the total cost of shore/harbor protection by a floating tire breakwater (with three modules) was \$69 per meter and by the revet-mattress was \$184 per meter. These costs fall into the low-price category for shoreline protective structures, compared to typical shoreline protection methods costing \$380 to \$1312 per meter protected.

5.2

Drainage

Because of the difficulty in disposing of used tires, they can usually be obtained for free or even along with a disposal payment. Thus, the material costs of scrap tire pipe for drainage are limited to small items (rebars, welding supplies, and rebar coatings). Other expenses include transportation costs and labor and equipment. It is expected that the beneficial uses of scrap tires in surface and groundwater drainage allow tire pipes to sell for lower prices than other drainage pipe materials such as corrugated steel, fiberglass, or plastic. This lower cost of tire pipe may be partially offset by increased transportation and installation costs due to their shorter lengths and heavier unit weights.

5.3

Habitat Enhancement

The costs of floating artificial tire reefs are similar to that of floating breakwaters, about \$69/m in 1976 (see above). Costs for constructing bottom or sinking reefs are about \$3.50 per tire in 1989 in New Jersey [1]. This cost is somewhat offset by charging disposal fee, for example \$1 per tire in Ocean City and \$25.25 per ton in Cape May County, New Jersey. This compares to the average of \$45.25 per ton to landfill the tires in the northeastern United States. Since haulers save money by taking tires to the reef builders, tire supply is not a problem.

In New Jersey [22], since no state funds are available to subsidize reef construction, cooperative programs have been developed with other public (county) agencies and private companies to construct and deploy tire units at no cost for the Reef Program. Following construction, private companies are contracted to transport the units to the reef site. Each county charges its residents a nominal fee to cover the cost of binding and ballasting materials, labor and barge transportation. Two private companies are also involved in reef unit construction

projects. These companies charge tire disposers a per tire fee which is used to cover the costs of unit construction and deployment and also generate a profit. Cooperative tire reef projects have enabled the Reef Program to construct large scale artificial reefs at little or no cost to the state for construction materials.

5.4

Rain Trapment

The rain trap system developed by Tire Farms, The Ford Odell Group [14] has value as a means to reduce irrigation costs and fertilizer consumption. It also has the inherent environmental advantage of reducing groundwater contamination. By recycling scrap tires, we obtain a cost free, virtually indestructible construction material. The rain trap system will not only protect groundwater from maintenance chemicals; it will also reduce the amount and frequency of fertilizer application. In an average golf course, fertilizers percolate beyond reach of the turfgrass root hairs. The rain trap system preserves a significant amount of the original application by preventing percolation and loss to groundwater. The tires in the system act as a barrier between fertilizers and the groundwater below.

The economic benefits to the golf course (water and fertilizer savings) once the system is installed will be significant. Spending less time and money on maintenance, golf course owners will automatically experience an increase in profitability. The system can save between 10% and 70% on golf course irrigation while relieving the nation's horrendous, ever-mounting, scrap tire problem. The rain trap system uses 1.2 million tires during the construction of an average golf course.

6

Environmental Impact Assessment

6.1

Beneficial Effects

Successful hydraulic engineering applications can, in addition to construction material cost saving, create beneficial impacts of scrap tires in hydraulic structures on the environment, which is primarily waste reduction, relieving the nation's horrendous, ever-mounting, scrap tire problem. A hydraulic structure may consume thousands of scrap tires. The rain trap system uses 1.2 million tires during the construction of an average golf course. Moreover, scrap tires are proven to be benign in the environment, for instance, in rain trap system, one of the hydraulic applications.

The rain trap system installed in golf courses can help in meeting requirements for groundwater protection from maintenance chemicals because the tires act as a barrier between fertilizers and the groundwater below [14]. The

rain trap system will not only save irrigation water and protect groundwater but also reduce the amount and frequency of fertilizer application. In the rain trap application, tires protect the environment by trapping and reusing the fertilizers and other additives, which are applied to turfgrass. This reuse allows lighter applications and temporary storage so the compounds can further break down. The next substantial rainfall will flush out the tires and the cycle repeats itself.

6.2

Potential Problems

Applications of scrap tires in hydraulic engineering benefits the environment through waste reduction, yet people naturally ask, for example, whether scrap tires leach compounds that may adversely affect the environment. Practical issues and potential problems related to environmental impact of scrap tires in hydraulic structures include chemical leaching, toxicity, soil contamination, water pollution, structural integrity, and aesthetical feature.

Use of recycled materials such as scrap tires in engineering projects should not pose a problem with respect to environmental impact and human health. Scrap tires used in hydraulic structures may have the potential of chemical or metal leaching into the surface water or groundwater. The water may then serve as a pathway to transport these chemical contaminants to human and environmental receptors. When determining and conducting beneficial uses of scrap tires in hydraulic engineering applications, one must assess risk to human health and the environment. Contaminant leaching and subsequent transport are believed to be the primary risk pathways (post-construction) and both of them depend on in situ conditions. Practical leaching and preliminary impact assessments are necessary. In order to assess risk, it is important to quantitatively predict the impact of the various physical, chemical, and biological processes that occur in the water upon the fate and transport of these chemical contaminants. The chemical fate and transport processes in the surface water and groundwater need to be analyzed to quantify the potential for the contaminants to reach receptors.

In surface water applications, the issue of physical integrity and aesthetics of hydraulic structures must be addressed as scrap tires are widely accepted as a suitable construction material. Poor deployment and construction practices may, however, lead to tires washing off after storms and result in environmental problems. The stability and integrity of a scrap tire structure must be maintained to prevent structural failure. This problem can be solved by improved design and construction with sufficient fastening and anchoring.

Another concern over the use of scrap tires in hydraulic structures is that the aesthetic characteristics of protective structures using scrap tires may be less than desirable to some observers. Nevertheless, the tradeoff with cost and ease of construction will determine the relative importance of aesthetic attitudes.

6.3

Chemical Leaching to Seawater

A review of the scientific literature has yielded some information on the environmental impact of tires and in particular, the leaching of heavy metals and organic compounds from tires into sea water. Preliminary results of tire and seawater leaching studies are presented by Collins et al. [29]. These identify zinc as the major leachate (totaling 10 mg/tire after three months). Diluted leachates have not shown significant effects of the growth of the phytoplankton phaeodactylum and isocrysis [29]. The work by Stone et al. [30] to characterize the sea water leaching of tire compounds demonstrated that tire exposure had no detrimental effects on two species of marine fish, pinfish and black sea bass.

An investigation of toxicity of scrap tires leachates in estuarine salinities was conducted by Hartwell et al. [31] to determine if tires are acceptable for artificial reefs. It was found that tire leachates are toxic to some marine species; and their toxicity varied inversely with salinity. Toxic effects were not apparent at 25‰ salinity. This may be due to differential leachability of toxic chemicals, differential interaction of salts and toxicants, and an effect of salinity on tolerance of the organism, or some combination of these factors. Toxicity diminished substantially with sequential extraction and quickly, rather than gradually and steadily over several weeks. Similar results were observed in freshwater experiments [32]. The toxicity values do not suggest a substantial threat by tire reefs to water quality. The use of tires in higher salinity environments appears to pose little direct toxicological risk to resident organisms. However, bioaccumulative effects are possible.

In the laboratory study, shredded scrap tires were leached in a modified toxicity characteristic leaching procedure (TCLP) extraction method in synthetic saltwater solutions for three sequential seven-day periods [31]. Test salinities were 5, 15, and 25‰. Acute toxicity tests were conducted with larval sheepshead minnows *Cyprinodon variegatus* and daggerblade grass shrimp *Palaemonetes pugio*. Mortality decreased following multiple sequential leaching periods. Toxicity decreased with increasing salinity. The fish were more sensitive than the grass shrimp. Dilution series toxicity bioassays were performed with fish and grass shrimp at 5‰ salinity and at 15‰ with fish only. The 96-h LC₅₀s (lethal concentration for half of the test animals) for fish were 10% leachate at 5‰ and 26% at 15‰. The 96-h LC₅₀ for grass shrimp at 5‰ was 63%. The 96-h lowest observed effect concentrations (LOEC) for fish survival were 12.5% at 5‰ and 25% at 15‰. The 96-h LOEC for grass shrimp survival was 50% at 5‰. Growth LOEC values were 12.5% at both salinities for fish and 50% for grass shrimp at 5‰.

Chemical analyses revealed no specific components as the cause of observed toxicity. Antagonism between sea salt and toxic chemicals is hypothesized to cause differential toxicity at varying salinities, as opposed to differential solubility of the toxicants. Extrapolation of laboratory results indicates that proposed tire reefs should not pose a serious threat to water quality in Chesapeake

Bay. No observed effects concentrations (NOEC) were an order of magnitude or greater above field concentrations calculated from simplified methods. Toxic substances appear to leach from the surface of the tires not from the tire matrix. The use of tires in higher salinity environments appears to pose little direct toxicological risk to resident organisms. However, because unknown toxic chemicals were present in leachates at all test salinities, no assessment can be made regarding persistence, fate, transport, or possible bioaccumulative effects.

6.4

Leachates to Fresh (Surface) Water

In all situations where scrap materials come into contact with surface water, there will be a concern regarding the potential for contamination of water by the material. Nozaka et al. [33] found no harmful substances leached from tire material soaked in fresh water while the results of Kellough's [34] freshwater tests suggested that some factor in tire leachate was toxic to rainbow trout. Evidence [35] suggested that tires are unlikely to cause danger to trout and other aquatic life primarily because the rates of water flow can provide sufficient dilution to prevent the effect. Barris [36] studies a 32-acre pond half filled with 15 million tires. All metal and organic compounds tested were either below detection limits or below regulatory limits except Iron. While toxicity caused by zinc was observed in laboratory tests by Nelson et al. [21], it is unlikely that zinc concentrations leached from the tires used in artificial reefs in canals (freshwater) would ever cause acute or even chronic toxicity. Tests with whole tires showed that zinc concentrations declined over time. Chemistry tests for organic compounds also indicated that these chemicals would not be a problem. Therefore, the use of tires in water would not result in adverse changes in water quality.

The use of tire reefs in aquatic environments which have relatively small volumes (e.g., canals) with small dilution capability may raise water quality concerns. Nelson et al. [21] conducted three laboratory tests using plugs cut from tires and whole tires to identify tire leachate and performed a risk assessment of water quality effects. Toxicity identification procedure developed by USEPA [37] was used to evaluate water quality impacted by tires. Toxicity testing results show the presence of zinc, cadmium, lead, and copper above background. All organic compounds tested for were below detection limits. Tests with whole tires showed that the amount of zinc declined over time and toxicants decreases with continuous leaching of water. If water is diluted or continuously flushed, tire shreds should not pose a problem, especially in a marine or reservoir environment which provides a large dilution factor or assimilative capacity. It was believed that the use of tires in artificial reefs in water would not result in deleterious changes in water quality [21].

A laboratory study was conducted by Day et al. [32] to determine if automobile tires immersed in fresh water leach chemicals, which are toxic to aquatic biota. Three tire types were examined – tires obtained from a floating tire break-

water, road-worn tires from the same vehicle, and new tires. Whole tires were immersed in 0.3 m³ of water (natural groundwater) and subsamples (0.04 m³) of water were removed at 5, 10, 20, and 40 days for use in acute static lethality tests. Overlying water from both new and used tires was lethal to rainbow trout (*Oncorhynchus mykiss*) but leachate from used tires was more toxic (96-h LC₅₀s range from 11.8 to 19.3%) than leachate from new tires (96-h LC₅₀s range from 52.1 to 80.4%). In addition, leachate remained relatively toxic to rainbow trout over time (8 days for new and 32 days for used) after tires were removed from the aquaria indicating that the chemicals responsible for toxicity degrade slowly and are non-volatile. No toxicity to cladocerans (*Daphnia magna*; 48-h exposure) or fathead minnows (*Pimephales promelas*; 96-h exposure to leachate from 20 and 40 days only) was observed with these same leachates. Tires from a floating tire breakwater, which had been installed for several years did not release chemicals. In separate experiments, concentrated leachate from tires immersed for 25 days in water inhibited bioluminescence in the marine bacterium. Several other screening tests (e.g., nematode lethality/mutagenicity and bacterium motility inhibition test) were not sensitive to tire leachates. Further studies to identify the toxic compounds and to determine the extent of toxicity under field conditions of dilution are necessary.

6.5

Impact on Groundwater and Soils

When scrap materials are placed in contact with groundwater, they may potentially cause groundwater pollution and soil contamination. Spagnoli et al. [38] found that the long-term immersion of tires in water creates two main groundwater contaminants, iron and manganese. However, in most cases, these contaminants are considered secondary issues that could affect the color and taste of drinking water. Opinions appeared divided over whether the two contaminants would cause a significant groundwater problem in septic system leach fields.

Park et al. [39] presented measured data, using USEPA toxicity characterization leaching procedure (TCLP), of metal and organic compounds that were below detection limits or regulatory levels. However, zinc at 0.38 to 0.63 mg l⁻¹, lead at no detection to 0.015 mg l⁻¹, iron at no detection to 0.23 mg l⁻¹ and manganese at 0.082 to 0.3 mg l⁻¹ were detected using American Foundry Society procedure. After conducting some laboratory and field leaching studies, Minnesota Pollution Control Agency [40] concluded that scrap tire may impact groundwater quality because of some elevated metals at leachate pH of 3.5 and PAHs at pH of 8 and recommended that the use of scrap tires is limited to the unsaturated zone. The studies revealed that under low pH conditions metals may be leached whereas at high pH organics may be leached. Laboratory and field leaching tests carried out by Edil et al. [41] indicated that tire may contribute organic compounds to groundwater but the potential leaching of toxic pollutants from scrap tires, i.e., potential for pollution, is minimal. It was concluded by Edil et al. [41] that scrap tires leached very small amounts of substances and have

little or no effect on groundwater. Bosshner et al. [42] also concluded that leachate from tire chips is not likely to have adverse effects on groundwater.

For applications in the rain trap system, the results of the EPA's toxicity characterization leaching procedure (TCLP) indicate that none of the tire products tested exceeds proposed TCLP regulatory levels. Most compounds detected are found at trace levels, (near method detection limits), from 10 to 100 times less than TCLP regulatory limits and U.S. EPA drinking water standard maximum contaminant level (MCL) values. The Florida Department of Environmental Regulation released its final report on tire leachability in potential usage environments. The study, which evaluates the leachability of shredded tires in different aquatic environments, finds that scrap tires pose no harmful effects when used in applications that are above the water table [14].

The study of water quality effects of tire chip fills placed above the groundwater table by Humphrey et al. [43] showed no evidence that tire chips increased the concentrations of metals that have primary drinking water standard. They did not increase aluminum, zinc, chloride, or sulfate which have secondary (aesthetic) drinking water standards. However, under some conditions, iron levels and manganese may exceed secondary standards. Organics were below detection limits. Downs et al. [44] conducted an investigation of water quality effects of using tire chips below the groundwater table through laboratory leaching tests, simulation of subsurface conditions, and small-scale field trials. Laboratory leaching tests indicated that concentrations of TCLP regulated metals and organics did not exceed limits. The field study showed iron, manganese exceeded standards ($300 \mu\text{g l}^{-1}$ and $50 \mu\text{g l}^{-1}$) at the site. Downs et al. [44] recommended that tire chips be used above the groundwater table or where increased levels of iron and manganese can be accepted.

Some reduction of leachate from scrap tires to surface and ground water may be achieved by soils. Al-Tabbaa and Aravinthan [16] investigated the way to reduce the general leaching of heavy metals from shredded tires to acceptable levels. This is achieved by mixing shredded tire with a clayed soil as clays have some ability to adsorb heavy metals. In the scrap tire applications to river grade control structures and low water stream crossings, loess in fill materials and river bottom soils (clay) may assist to reduce leaching of heavy metals to stream water by adsorbing heavy metals if any leach out of scrap tires. In other applications, such as bank protection, drainage pipes, and culverts, soils in contact with tires may serve as a buffer for attenuating possible leaching of heavy metals to water through adsorption before they enter stream water.

7

Conclusions and Recommendations

A large number of used tires are disposed every year. Existing reuses of scrap tires in hydraulic practices, such as bank and shore protection and artificial reefs for habitat enhancement, were reviewed and their potentials, engineering

and economic feasibilities, and environmental impact were analyzed. New areas of applications have been identified and discussed, including stream grade control, low water stream crossings, surface and sub surface drainage, and rain trapment. Studies and analyses presented in this chapter indicated that hydraulic structures built with scrap tires are technically adequate, economically feasible, and environmentally desirable for their waste reduction potentials.

In grade control and drainage applications, considering their sizes and aesthetics, scrap tires are most suitable for small-scale projects on small streams and in small towns and communities. They include overfalls, low water stream crossings, subsurface drainage, storm-water runoff drainage, and roadway cross drainage.

One of the benefits of scrap tire reuse in hydraulic engineering is lower material cost than conventionally used materials in surface and groundwater structures. The availability of scrap tires is so great that they can be readily and inexpensively obtained with only transportation cost. The total cost of using scrap tires in hydraulic structures, including tire processing costs, can be ranked according to reuse methods as (from low to high): whole scrap tires, split tires, cutting beads/sidewalls, shredded, and bale.

The investigations and results to date have examined the potential environmental impact of scrap tires on marine environment (salty water), surface (fresh) water, groundwater, and soils. The methods used in previous studies included laboratory tests and measurements and field monitoring with various testing procedures. Leachability tended to depend on influent solution pH. Toxicity varied with salinity and time. Previous studies and assessments demonstrated that use of scrap tires in surface water and groundwater is safe to the environment in most cases. However, previous studies also indicated some chemical leachates from scrap tires in surface and ground waters. Therefore, applications of scrap tires in some extreme conditions should be avoided, such as in extreme pH values, small water volumes for assimilative capacity, low velocity or dilution capability, and where iron, zinc, and manganese not acceptable. Tire applications should not be made in extremely acidic conditions. It is preferred that scrap tires be used above the groundwater table over below the table, if possible.

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Hazardous Organic Chemicals in Biosolids Recycled as Soil Amendments

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Abstract The generation and disposal of biosolids produced at municipal wastewater treatment plants is a major environmental issue. Approximately 900 kg of biosolids on a dry basis are produced from the treatment of 1 million gallons of wastewater. These solids are typically dewatered on site and disposed of at landfills, incinerators or on agricultural fields. Disposal of sewage sludge on agricultural fields recycles the nutrients captured from municipal wastewater into agricultural soils. However, biosolids applied as soil amendments can contain significant quantities of hazardous organic chemicals derived from the municipal wastewater or organic metabolites produced during waste treatment. These organics have the potential to adversely impact the soil receiving the biosolids, surface and groundwater in the vicinity of application, crops grown on sludge-amended soils, and animals and humans that may consume the crops grown on the soils. This chapter presents a thorough discussion of the fate of hazardous organic chemicals associated with biosolids recycled as soil amendments.

Keywords Sludge · Biosolids · Contaminants · Fate · Transport

List of Abbreviations and Symbols

APnEOs	Alkylphenol polyethoxylates
BOD	Biochemical oxygen demand
C_s	Concentration of organic contaminant in primary sludge, $\mu\text{g/l}$
C_e	Concentration of organic contaminant in primary effluent, $\mu\text{g/l}$
CFR	U.S. Code of Federal Regulations
COD	Chemical oxygen demand
CPs	Chlorophenols
D_{Gair}	Gaseous diffusion coefficient of contaminant in soil
DEHP	Di-(2-ethylhexyl) phthalate
DO	Dissolved oxygen
EPA	United States Environmental Protection Agency
f_{OC}	Fraction of organic carbon
gcpd	Gallons per capita per day
HCH	Hexachloro cyclohexanes
J_w	Water flux in soil
K_H	Henry's Law constant
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
l	Distance traveled by contaminant in soil
LABs	Linear alkylbenzenes
LASs	Linear alkylbenzene sulfonates
MGD	Million gallons per day
ND	Nondetectable
NP	Nonylphenol
NPnEOs	Nonylphenol polyethoxylates
OCDD	Octachloro dibenzo- <i>p</i> -dioxin
ϕ	Porosity of soil
PAHs	Polynuclear aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo dioxins
PCDFs	Polychlorinated dibenzyl furans
q	Volumetric water content in soil
s	Soil bulk density
t_c	Time required by a contaminant for convective travel
t_d	Time required by a contaminant for diffusive travel
TCDD	Tetrachloro dibenzo- <i>p</i> -dioxin
TSCF	Transpiration stream concentration factor
TSS	Total suspended solids
W	Pounds of sludge produced per day
WWTP	Wastewater treatment plant

1

Introduction

Publicly owned wastewater treatment facilities serve around 75% of the U.S. population [1]. Thousands of potentially hazardous organic chemicals used in common household products and commercial/industrial activities are intentionally or unintentionally discharged into sanitary sewers that convey these chemicals to wastewater treatment plants (WWTPs).

Organics in the wastewater entering a municipal WWTP are biologically transformed into carbon dioxide, water and biological solids (bacterial cells). The biological solids (or biosolids) are separated from water by sedimentation. Wastewater sludge is a concentrated slurry of organic and inorganic solids that often serves as a sink for potentially harmful chemicals including persistent organics. The biosolids generated at wastewater treatment facilities are generally disposed at landfills, by incineration, or through application of dewatered or slurry sludge on agricultural fields.

This chapter presents a discussion on issues related to the occurrence and fate of hazardous organic chemicals in biosolids recycled as soil amendments. Sections on biosolids production, treatment and disposal are followed by a review of common hazardous organics present in municipal biosolids, and their fate when the sludge is applied as a soil amendment. The chapter concludes with a brief discussion of the environmental impacts of hazardous organics in biosolids. A thorough reference list of material relevant to the topic of discussion is included at the end of this chapter.

2

Wastewater Treatment and Biosolids Production

Wastewater discharged into sanitary sewers includes domestic sewage, commercial wastewater and to some extent industrial wastewater. The wastewater is typically transported by gravity to a municipal wastewater treatment plant, where the waste is treated before discharge into a receiving stream. In communities that do not have separate storm water sewers, the sanitary sewers may also serve to convey storm runoff to the wastewater treatment facility.

The quantity of wastewater generated by a community is closely related to its population. In the U.S., this amounts to about 120 gallons (450 l) per capita per day (gcpd), but may range anywhere between 50 and 250 gcpd [2]. The wastewater conveyed to a municipal wastewater treatment plant typically contains 0.24 lb (110 g) of suspended solids per capita per day, and 0.20 lb (90 g) of organic matter per capita per day. The major ingredients in raw wastewater and their typical concentrations are listed in Table 1. Raw wastewater may also include hazardous organic or inorganic materials originating from a variety of domestic or industrial activities.

Table 1 Major ingredients in untreated municipal wastewater^a

Wastewater constituent	Typical concentration	Concentration range
Total solids	800 mg/l	300–1200 mg/l
Biochemical oxygen demand (BOD)	200 mg/l	100–400 mg/l
Dissolved oxygen (DO)	~0 mg/l	<1 mg/l
Total nitrogen as N	40 mg/l	20–90 mg/l
Total phosphorus as P	8 mg/l	4–15 mg/l
Fecal coliform	10 ⁷ to 10 ⁸ /100 ml	10 ⁶ –10 ⁹ /100 ml

^a From [2, 3].

Biochemical oxygen demand (BOD) is a measure of the biodegradable organic matter in the wastewater. It is the concentration of oxygen in water that would allow complete aerobic degradation of the organic matter by micro-organisms. The organic content of a wastewater may also be represented by chemical oxygen demand (COD), which is calculated from the amount of chemical oxidants used to completely oxidize the organic material in a wastewater sample.

Figure 1 describes operations at a typical wastewater treatment plant. The sewer main empties into a wet well from where the wastewater is pumped to the surface of the treatment facility. Screens and shredders are utilized as preliminary treatment processes to remove material that may interfere with plant machinery, such as pumps and valves. Sand-sized particles are removed in the grit removal basin and other suspended particles are removed in a primary clarifier or sedimentation basin. The wastewater then enters an aeration basin containing a large concentration of bacteria. The bacteria utilize the organics in wastewater as a food and energy source allowing them to reproduce. A portion of the wastewater organics is mineralized while another portion is converted into bacteria. These bacteria are allowed to settle in a secondary clarifier or sedimentation tank and the clean supernatant is decanted from

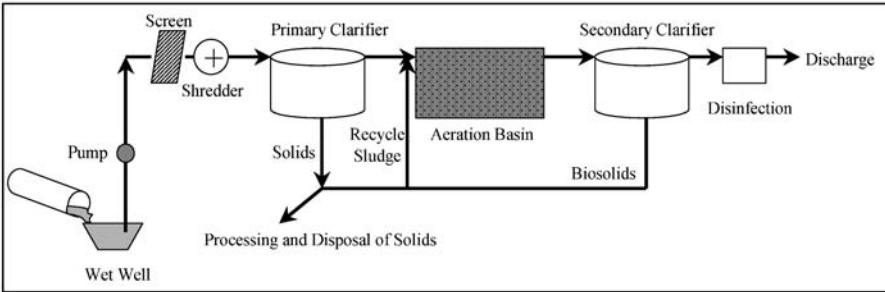


Fig. 1 Schematic of a typical activated-sludge wastewater treatment process

the top, disinfected and discharged into a receiving stream. Some of the settled biomass, known as biosolids or sewage sludge, is recycled into the aeration tank to maintain the desired numbers of bacteria in the basin. When sludge recycle is employed, the waste treatment process is referred to as an activated sludge process. Typically, the larger the organic input to the WWTP, the greater is the amount of biosolids produced at the facility. These biosolids typically undergo further processing before their removal from the WWTP and ultimate disposal.

3 Biosolids Treatment

The disposal of biosolids produced at wastewater treatment plants constitutes a major operational cost for these utilities. A typical WWTP produces about 900 kg (2000 lbs) of dry solids per million gallons of wastewater treated [3]. A medium sized WWTP treating approximately 10 million gallons per day (MGD) may produce 10 to 15 tons of sludge each day. The total sludge produced in a municipal wastewater treatment plant can also be estimated from Eq. (1):

$$W = 0.5 \text{ TSS} + 0.4 \text{ BOD} \quad (1)$$

where W represents the pounds of sludge produced per day, TSS denotes the total suspended solids load (lb/day) in the raw wastewater and BOD is the biochemical oxygen demand load (lb/day) in the wastewater after primary clarification [2].

In most cases, the biosolids have to be processed and stabilized before they can be transported off-site. Stabilization reduces odors and survivability of pathogenic organisms in the sludge. Table 2 summarizes the common sludge processing and stabilization methods utilized by the wastewater industry.

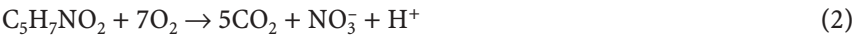
Biosolids are usually thickened prior to dewatering or conditioning. Thickening increases the solids content of the sludge from 1 or 2% to 4 or 5% by removing a portion of the liquid. Thickening processes can reduce sludge volumes to as low as 20% of the unthickened sludge. The thickened sludge generally retains the properties of a liquid. Dewatering may be employed before or after stabilization and is capable of increasing the solids content of the sludge to 25–45%. Sludge dewatering utilizes physical solid-liquid separation processes that result in a smaller volume of biosolids requiring disposal. Although dewatered sludge is 55 to 75% water, these biosolids have properties of a solid and cannot be normally conveyed using pumps and conduits.

Stabilization of sludge is a necessary step before disposal. Stabilization processes reduce odor and pathogen content, and allow for easy dewatering of the stabilized sludge. Although aerobic and anaerobic digestion are the most common stabilization processes for wastewater sludges, other approaches listed in Table 2 are also used. In aerobic digestion, the biosolids slurry is aerated for extended periods of time. In the absence of soluble substrate, microorganisms

Table 2 Common sludge processing and stabilization methods

Sludge thickening processes	Gravity thickening in thickener clarifiers Gravity belt thickening Dissolved air flotation Centrifugation Rotary drum thickening
Dewatering	Pressure filtration in belt filter presses Centrifugation Vacuum filtration Drying beds
Sludge conditioning/stabilization	Aerobic digestion Anaerobic digestion Chemical treatment, e.g., lime addition Heat treatment Composting

comprising the sludge, represented by the molecular formula $C_5H_7NO_2$, undergo endogenous decay as described by Eq. (2):



Lack of organic substrate in the water also results in the death of bacteria, followed by cell lysis and subsequent spillage of cell contents into the water. Some of the organic material released during cell lysis is re-utilized by the live bacteria. The digestion process results in a reduction of as much as 40 to 50% of volatile suspended solids in the sludge. Stabilized sludge does not undergo further biodegradation readily and is, therefore, devoid of putrescible material responsible for offensive odors. Aerobically digested sludge is usually brown to dark brown in color and has an earth/musty odor.

Anaerobic digestion is the preferred method of sludge stabilization at larger wastewater treatment facilities. This approach allows for energy recovery from the waste biosolids and beneficial use of the digested sludge. During anaerobic digestion, biosolids are converted to volatile fatty acids by acidogenic bacteria. A different group of bacteria known as methanogens further transform the volatile fatty acids to methane, carbon dioxide and ammonia. The two types of bacteria coexist in a delicate symbiotic relationship in anaerobic digesters.

Other sludge stabilization processes include lime addition and heat treatment. Addition of lime (CaO or $Ca(OH)_2$) raises the pH of the biosolids above 12 creating an environment not conducive to the survival of microorganisms. The highly alkaline conditions essentially shut down the biodegradation process and render the sludge inoffensive and pathogen-free. Sludge stabilization with heat treatment involves exposure of the biosolids to temperatures as high as 250° C at pressures up to 400 psi for a period of approximately 30 min. The heated sludge is devoid of microbial activity and easily dewatered.

Composting of dewatered sludge is a cost-effective process that converts a waste product into a useful agricultural amendment. During composting, the organic solids in sludge are transformed into a stable, pathogen-free, humus-like material rich in carbon, nitrogen, and phosphorus. Composting usually involves blending dewatered sludge with other organic material such as wood chips, yard trimmings, or straw. Properly composted sludge is an excellent source of organic and inorganic nutrients for horticultural and agricultural plants, and is often used as a soil amendment.

4

Disposal of Biosolids

Approximately 4.6 million dry tons of biosolids were generated in the United States in the early 1970s; the production increased by 50% in approximately 20 years, reaching 6.9 million dry tons by 1998 [4]. The corresponding increase in the U.S. population during this period was only 29%. It is estimated that biosolids production will reach 8.2 million dry tons by the year 2010 [4]. This large-scale generation of biosolids necessitates elaborate management and disposal plans that minimize adverse impacts to ecosystem health and sustainability.

The most common methods of disposing stabilized biosolids include land-filling, incineration, and reuse of sludge as a soil amendment. Municipal landfills are often the final destination for dewatered and stabilized sewage sludge. While composted or chemically treated sludge can be used as daily cover material in landfills, some landfills, called sludge monofills, are designed solely for sludge disposal. Incineration, although expensive, can be a cost-effective disposal option for large urban wastewater treatment facilities.

Stabilized biosolids are rich in organic matter and nutrients that, when applied on agricultural fields, can significantly improve the physical properties and agricultural productivity of soils. Sewage sludge can satisfy crop requirements for other nutrients when used at agronomic rates for nitrogen and phosphorus. In some cases, soil phosphorus levels may need to be monitored and sludge application rates adjusted to correspond to phosphorus rather than nitrogen requirements. The food and agricultural industries have shown apprehension about the safety of farmers and food products, the sustainability of agricultural lands, and the potential for economic and liability risks. Local availability of agricultural land and other local or regional concerns can also impact biosolids disposal options.

A variety of techniques may be used to apply biosolids on agricultural or forest lands. Stabilized sludge can be injected below surface with truck-mounted injection nozzles. Sludge may be spread on land and incorporated in the soil using farm machinery. Dewatered biosolids can be spread on agricultural fields using conventional manure spreaders. Table 3 summarizes typical application rates of biosolids disposed on land.

Table 3 Biosolids application frequency and rates on different land types^a

Land type	Frequency and rate of application
Farmland (hay, corn, soybeans, small grains)	Seasonal or annual, 2–20 dry tons/acre
Forest	Once in 2–5 years, 5–500 dry tons/acre
Range	Once in 1–2 years, 2–60 dry tons/acre
Land reclamation	Once, 60–100 dry tons/acre

^a [6].

Only biosolids that meet the most stringent standards mandated by federal and state regulations are approved for use as soil amendments. EPA’s *Standards for the Use or Disposal of Sewage Sludge* (40 CFR Parts 257, 403 and 503) have resulted in significant reductions in the inflow of toxic pollutants into WWTps through controls at sources and industrial pretreatment facilities [5]. These regulations were designed to assure that the use of biosolids in the production of food crops did not pose a significant health risk to consumers. Part 503’s pathogen criteria defines Class A biosolids as safe for direct public contact, or Class B biosolids, which require site and crop restrictions. Direct testing of pathogens or salmonella or fecal coliforms as indicator organisms is required to confirm Class A designation. Class A biosolids have to undergo advanced treatment such as heat drying, composting and digestion to reduce pathogens to undetectable levels. These biosolids can be bagged and sold as fertilizers.

Restrictions on the use of Class B biosolids require allowing an appropriate length of time for pathogen die-off. These solids cannot be sold for residential use but can be applied on agricultural land. A 30-day waiting period is required before cattle can graze on fields that receive Class B sludge.

The Resource Conservation and Recovery Act of 1976 exempts wastewater biosolids from being categorized as hazardous wastes when the discharge of industrial wastes into sanitary sewers is regulated by state or federally approved effluent pretreatment programs. U.S. regulations for toxic pollutants in biosolids used as soil amendments are based on results of EPA’s risk assessments and annual pollutant loading rates. These regulations allow for some degree of pollutant accumulation in the soil based on the soils’ assimilation capacities. The risk assessment procedure considers various transport and exposure pathways to determine pollutant loading limits and sludge quality requirements for application of biosolids on agricultural or horticultural fields.

EPA’s 503 biosolids rule does not target organic contaminants in sludge. The agency’s initial screening of biosolids from around the nation short listed 12 persistent organic pollutants that included aldrin/dieldrin, benzo(a)pyrene, chlordane, DDT/DDD/DDE, dimethyl nitrosamine, heptachlor, hexachlorobenzene, hexachlorobutadiene, lindane, PCBs, toxaphene, and trichloroethylene [5]. All these chemicals were later exempted from regulation because they fit one

or more of the following criteria: (1) chemical was banned, had restricted use or was no longer manufactured in the U.S.; (2) chemical was detected in less than five percent of samples in EPA's 1990 National Sewage Sludge Survey; or (3) chemical concentration was low enough that estimated annual biosolids loading rates would result in pollutant loading rates that do not exceed EPA's risk assessment criteria. However, since the 1990 National Sewage Sludge Survey, our understanding of organic contaminants in sewage sludge has changed significantly because of advances in analytical techniques and better detection of low-level contaminants in biosolids.

5

Hazardous Organic Chemicals in Biosolids

Many anthropogenic organic contaminants entering into WWTPs are not fully degraded during wastewater treatment and eventually accumulate in biosolids. Wastewater biosolids are comprised predominantly of organic material (50–85% dry weight) [7] with large surface areas (0.8–1.7 m²/g) [8]. Due their low water solubility and high lipophilicity, organic contaminants easily partition into biosolids resulting in their accumulation in biosolids at concentrations several orders of magnitude greater than influent concentrations [9–12]. Reported concentrations of several hydrophobic organic contaminants in raw and treated wastewater and biosolids are summarized in Table 4.

Polychlorinated biphenyls (PCBs), that can be mixtures of up to 209 congeners, were first manufactured in 1929. These are among the most widely detected chemicals in wastewater biosolids. Until the 1960s, PCBs found wide use in electrical insulating materials, artificial rubbers, printing inks, high temperature lubricants, and paints because of their thermal stability, chemical inertness, and high dielectric constant [38]. Although PCBs are no longer produced in the United States because they build up in the environment and can cause harmful health effects, they are still in use in many other countries.

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), often termed 'dioxins', consist of 210 different compounds which have similar chemical properties. This class of compounds is persistent, toxic, and bioaccumulative. They are generated as byproducts during incomplete combustion of chlorine containing wastes like municipal solid waste, sewage sludge, and hospital and hazardous wastes. Industrial processes such as bleaching of wood pulp in the manufacture of paper products, can also produce PCDDs and PCDFs [39].

Linear alkylbenzene sulfonates (LASs) and alkylphenol polyethoxylates (APnEOs) are surfactants that are widely used as industrial detergents, emulsifiers, wetting agents, and dispersing agents [30, 40]. The majority of these compounds is used in aqueous solutions and is eventually discharged through municipal sewer systems into wastewater treatment plants. Compared to their parent compounds, degradation products of APnEOs are more toxic and estro-

Table 4 Reported concentrations of selected organic contaminants in influent, effluent, and biosolids from WWTPs

Compounds	Influent (µg/l)	Effluent (µg/l)	Biosolids (mg/kg)	References
Polychlorinated biphenyls (PCBs)	0.03–0.63	0.01–0.06	0.05–0.93	[13–15]
Polychlorinated dibenzodioxins and dibenzofurans (PCDD/F)	ND– 1.1×10^{-5}	ND– 1.1×10^{-4}	0.01–0.43	[16–18]
1,2-Dichloro-benzene	2.0	2.0	0.02–809	[19, 20]
Linear alkylbenzenes (LABs)	–	–	1.4–73	[15]
Alkylphenol polyethoxylate (APnEOs)	1600–2520	56–102	9–169	[21, 22]
Nonylphenol (metabolite of NPnEOs)	0.69–155	0.50–3	5.4–887	[23–25]
γ-Hexachloro cyclohexane (γ-HCH)	0.01–0.09	0.01	0.01–10	[19, 26]
Hexachloro-benzene (HCB)	ND–0.1	ND	0.01–10	[24, 26]
Polybrominated diphenyl ethers (PBDEs)	–	–	1.1–2.3	[27]
Phthalate esters	1.74–182	0.09–1	12–1250	[28–30]
Acetylsalicylic acid	–	1.5	–	[31]
Clofibric acid	0.8–2	1.6	–	[31]
17α-Ethinyl estradiol	–	0.007	–	[32]
Ibuprofen	3.3	3.4	–	[31, 33]
Iopromide	7.5	8.1	–	[34]
Synthetic musks	–	0.025–0.40	12	[35, 36]
Fluoroquinolone	–	0.045–0.41	–	[37]

genic [41–43]. On the other hand, LAS compounds are more toxic to aquatic organisms than their degradation products that have shorter alkyl chains [44].

Polybrominated diphenyl ethers (PBDEs), mainly used as flame-retardants, have a total of 209 possible congeners. These compounds are being released into the environment more frequently because of their increased use in plastic materials and synthetic fibers. Environmentally significant concentrations have been reported in air, water, soil, sediment, and sewage samples, in aquatic and terrestrial organisms [45], and in human breast milk [46]. Little is known about their toxicity on organisms in the environment; however, there is indication that they are endocrine disrupters capable of affecting the thyroid system [47].

Phthalate esters are manufactured in large quantities (ECETOX, 1995) and have been used in the production of plastics. Di-(2-ethylhexyl) phthalate (DEHP), the most widely used phthalate ester, is persistent during sewage treatment and readily accumulates in sediments and lipid tissues in aquatic organisms. DEHP, a suspected endocrine disruptor [48] has been reported in a variety of media including water, atmospheric deposition, sediments, soil, biosolids, biota [28], and food products [49].

Pharmaceutical compounds and their metabolites such as acetylsalicylic acid (anti-inflammatory), clofibrilic acid (metabolite of lipid regulators), 17 α -ethinyl estradiol (contraceptive), ibuprofen (anti-inflammatory), iopromide (X-ray contrast media), synthetic musks (fragrances), fluoroquinolone (antibiotic), etc. are emerging contaminants that have been frequently detected at low levels in environmental samples [50–52], in biota [53], and even in human tissues [54]. The persistence of pharmaceutical contaminants in the environment has been attributed to human consumption of drugs and subsequent discharges from sewage treatment plants, as well as veterinary use of drugs and nonpoint discharges from agricultural runoff. The long-term effects of continuous, low-level exposure to these compounds are not well understood.

Most hydrophobic organic chemicals in wastewater have a strong tendency to associate with biosolids. Contaminant partitioning into biosolids occurs as a result of adsorption on the surface of the organisms and subsequent transport or diffusion of the adsorbed chemical into the cells. Wastewater solids are comprised of live microorganisms and organic matter derived from dead organisms and their byproducts. The tendency of organic contaminants to accumulate in the biosolids can be reasonably estimated from the octanol-water partition coefficients (K_{OW}) of the contaminants [30]:

$\log K_{OW} < 2.5$:	low sorption potential
$2.5 < \log K_{OW} < 4.0$:	medium sorption potential
$\log K_{OW} > 4.0$:	high sorption potential

Petrasek and coworkers [9] observed a positive correlation between $\log K_{OW}$ and the partitioning of a variety of organic contaminants to primary sludge. These researchers expressed the relationship as Eq. (3):

$$C_s/C_e = 26.5 (\log K_{OW}) - 33.4 \quad (3)$$

where C_s and C_e were the concentration of the organic contaminant in the primary sludge and the effluent from the primary clarifier, respectively. Dobbs and coworkers [11] observed a similar correlation between the aqueous concentration and the concentration of organic contaminants in wastewater solids from primary sludge, mixed-liquor and digested sludge.

The extent of sorption of organic contaminants onto wastewater solids can significantly impact their degradation during the treatment process [55, 56]. With a $\log K_{OW}$ of 4.5, nonylphenol (NP), a metabolic product of nonylphenol polyethoxylates (NPnEOs), is hydrophobic and preferentially partitions into the wastewater solids. Tanghe et al.[57] observed a reduction in NP degradation in lab scale activated sludge reactors when extra microbial or non-microbial organic material such as humic substances was introduced into the reactor.

6
Fate of Hazardous Organic Chemicals in Biosolids Used as Soil Amendments

About 7 million dry tons of biosolids are produced annually in wastewater treatment plants in the United States [4]. Organic contaminants associated with biosolids can be released into the environment during land application, an increasingly common means of sludge disposal (Table 5). A prolonged application of contaminated biosolids on agricultural fields can result in significant increases in residual concentrations of organic contaminants in the soil. Persistence of organic compounds in soils largely depends on their resistance to biotic and abiotic transformation. The potential for surface runoff and leaching can impact their transport into surface water and groundwater. Beck and coworkers [58] used decay curves to describe five typical patterns of persistence of common organic chemicals found in biosolids-amended soils (Fig. 2).

Wild and coworkers [59] investigated the concentrations of polynuclear aromatic hydrocarbons (PAHs) in plot layer (0–23 cm) soil samples of lands that

Table 5 Trends in biosolids disposal: 1993, 1998, and 2010 (projected)

Biosolids disposal methods	1993 ^a	1998 ^b	2010 ^b
Landfilling	38%	17%	10%
Incineration	16%	22%	19%
Land application	36%	41%	48%
Other disposal methods ^c	10%	20%	23%

^a [5].

^b [4].

^c Includes advanced treatment such as composting and other beneficial uses.

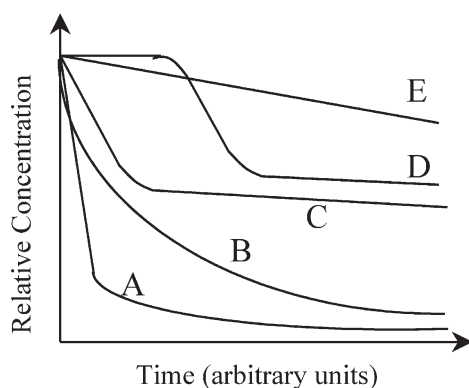


Fig. 2 Persistence of organic chemicals in biosolids-amended soils. A=compounds that are volatile, water soluble, or easily degraded; B & C=compounds with intermediate sorption potential on biosolids; D=compounds whose initial degradation is rate-limited because the microbial population has not acclimated to the compounds; and E=compounds that are non-volatile, relatively water insoluble, and recalcitrant. (after reference [58])

received 25 separate sewage biosolids applications from 1942 to 1961. Total soil PAH concentrations (Σ PAH) increased 5000 times between 1942 and 1961 and subsequently showed a slow decline after 1961. Twenty two years after the last biosolids application, the biosolids-amended soil still contained over three times more Σ PAH than the control soil. The authors hypothesized that following each biosolids application, lower molecular weight PAHs were lost relatively rapidly, while the higher molecular weight, highly hydrophobic, and strongly sorbing PAHs remained as bound residues. Volatilization and degradation are believed to be responsible for the rapid loss of low molecular weight PAHs, while degradation was more important for the removal of PAHs with high molecular weights.

Wilson et al. [60] reported increased soil concentrations of volatile organics, PCBs, PCDDs, PCDFs, and chlorophenols (CPs) in surface soil (0–5 cm) immediately after biosolids amendment. Volatile organics were reduced to control soil levels within eight days of biosolids application. The soil concentrations of PCBs and CPs declined to control plot values within 128 days of amendment. Within 260 days of biosolids application, the levels of PCDD/F did not change significantly and remained at 410 ± 53 ng Σ PCDD/kg and 250 ± 53 ng Σ PCDF/kg, approximately 5 and 1.5 times of the control levels, respectively. Biodegradation was believed to contribute significantly to the decline of PCBs and CPs concentrations in soil amended with biosolids [61]. The recalcitrant nature of PCDD/Fs most likely prevented their significant loss in the soil after biosolids amendment [62].

Surface application of biosolids, a common practice in many countries, creates a relatively thin film of sludge on the soil surface until it is later incorporated into the soil with conventional farm equipment [39]. While on soil surface,

organic contaminants are subject to volatilization [63–68] and photodegradation [69–73].

Volatilization of organic contaminants from soil surface is affected by the physicochemical properties of contaminants, soil properties, and temperature. Organic contaminants with Henry's Law constants (K_H) greater than 10^{-4} are considered to have high volatilization potential [30]. However, losses by volatilization are also limited by soil properties. Adsorption of organic contaminants onto soil organic and inorganic components may reduce their volatilization potential [59, 74]. Ekler [75] showed an inverse relationship between adsorption coefficients and the volatilization rates of thiocarbamates from soil surface. The water content of a soil may affect volatilization by competing with organic chemicals for soil sorption sites [76]. In general, an increase in temperature increases the volatilization potential of an organic chemical [77]. It is conceivable that at high soil surface temperature an organic chemical with relatively low K_H can volatilize from the thin biosolids film on soil surface.

Some organic contaminants may undergo rapid photolysis in biosolids applied to soil at a biosolids application rate of less than five tons dry matter/ha, equivalent to a biosolids film about 0.5 mm thick. The photolysis of organic chemicals in soil does not follow first order kinetics and diminishes rapidly with soil depth because of the strong light attenuating effect of soils [69]. Miller and coworkers [69, 70] observed rapid photodegradation for octachlorodibenzo-*p*-dioxin (OCDD) within several days, resulting in production of the lower chlorinated dibenzo-*p*-dioxins, in a soil depth of 0.06–0.13 mm. However, a slower photolysis degradation rate for tetrachlorodibenzo-*p*-dioxin (TCDD) was observed in the same soils. In a similar study conducted by Schwarz and McLachlan [78] on the fate of PCDD/F in biosolids applied to an agricultural soil, neither photodegradation nor volatilization were observed for PCDD/F within six weeks of summer sunlight exposure. Photolysis of herbicides mecoprop and dichlorprop was detected within two days of light exposure and appeared to be controlled by soil texture and its adsorption capacity [72]. Soil organic matter was observed to have a sensitizing effect on the photodecomposition of these herbicides only in the presence of water. Konstantinou et al. [73] observed higher photodegradation of herbicides triazines, acetanilides, and thiocarbamates in soils with higher organic matter contents.

Once surface applied biosolids are incorporated into soil or when biosolids are applied through subsurface injection, abiotic and biotic processes rather than volatilization and photodegradation play more important roles in degrading organic contaminants. Numerous studies on the degradation of organic contaminants in biosolids have been conducted in the past several decades. Detailed reaction mechanisms for organic chemicals in the environment have been discussed by Larson and Weber [79]. A comprehensive summary on the fate of organic contaminants in biosolids was presented by Jones and Alcock [80]. Degradation of organic contaminants in the biosolids-amended soil environment largely depends on the properties of the chemicals, soil and biosolids, composition of the soil microbial community, and soil environmental condi-

tions. Hesselsoe and coworkers [81] demonstrated that the aggregate size of biosolids affects oxygen availability and, therefore, the aerobic transformation of organic contaminants such as NP in biosolids-amended soils. They found that the degradation of NP was completed within 38 days in homogenous mixtures of soil and biosolids aggregates, while it was retarded to more than 120 days in non-homogeneous mixtures.

The occurrence of heavy rainfall soon after application of biosolids is likely to increase the potential for losses of organic contaminants by surface runoff and leaching. The complexation of organic chemicals with dissolved organic matter and colloidal material may facilitate their movement through soil profile and surface runoff [82–86].

Three parameters, organic carbon-water partition coefficient (K_{OC}), Henry's law constant (K_H), and the biological half-life ($t_{1/2}$), were used by Jury and coworkers [87–90] in a model assessing the downward movement of selected organic compounds after incorporation into surface soil. In this model, the time required for organic chemicals to travel a distance through surface soil by both convective (t_c) and diffusive (t_D) movements were assessed using Eqs. 4 and 5:

$$t_c = \frac{(sf_{OC}K_{OC} + q + aK_H)l}{J_w} \quad (4)$$

$$t_D = \frac{l^2 \varphi^2 (sf_{OC}K_{OC} + q + aK_H)}{D_{Gair} a^{\left(\frac{10}{3}\right)} K_H} \quad (5)$$

where s =soil bulk density, f_{oc} =fraction of organic carbon, K_{OC} =organic carbon partition coefficient, q =volumetric water content, a =volumetric air content, K_H =Henry's constant, l =distance traveled, J_w =water flux, φ =porosity, and D_{Gair} =gaseous diffusion coefficient. The relationships between compound mobility and t_c and t_D are defined in Table 6. This model simulates the mobility of directly applied organic compounds in surface soils. Validation of this model is needed in soils receiving organic chemicals that are incorporated into organic matter in complex biosolids matrices.

Table 6 Convective mobility and diffusive mobility classification (from [91])

Convective mobility			Diffusive mobility		
Classification	t_c (days)	Mobility	Classification	t_D (days)	Mobility
Class 1	>500	Immobile	Class 1	>100	Immobile
Class 2	100–300	Low	Class 2	20–100	Medium
Class 3	30–100	Medium	Class 3	<20	High
Class 4	10–30	High			
Class 5	<10	Mobile			

The uptake of organic contaminants by plants from biosolids-amended soil depends on the physicochemical properties of organic compounds and the physiology of plants [92–95]. Plant uptake of organic chemicals and their distribution within plants have been shown to be affected by (1) the organic chemicals' physicochemical properties, including solubility, vapor pressure, octanol-water partition coefficient (K_{OW}), and Henry's law constants (K_H), (2) environmental conditions such as temperature, air disturbance and soil organic matter content, and (3) plant characteristics, for example the shape of the leaves, type of root system, and lipid and cuticle characteristics and contents [94].

There are a number of different pathways by which organic chemicals may enter vegetation [95]. The major pathways include (1) uptake by roots and subsequent translocation from roots to shoots (i.e., liquid phase transfer) in the transpiration stream, (2) folio uptake of volatilized organic chemicals from the surrounding air (i.e., vapor phase transfer), (3) uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it, and (4) uptake and transport in oil cells which are found in oil containing plants like carrots and cress.

Briggs et al. [92] evaluated plant uptake and translocation of 18 pesticides and found that Eq. (6) correlated the translocation of organic chemicals into plants to the K_{OW} value of the compound:

$$TSCF = 0.784e - \left[\frac{(\log K_{OW} - 1.78)^2}{2.44} \right] \quad (6)$$

where TSCF (transpiration stream concentration factor) is the ratio between the amount of the compound in shoots per ml of water transpired and the concentration of the compound in soil. Figure 3 suggests that organic chemicals

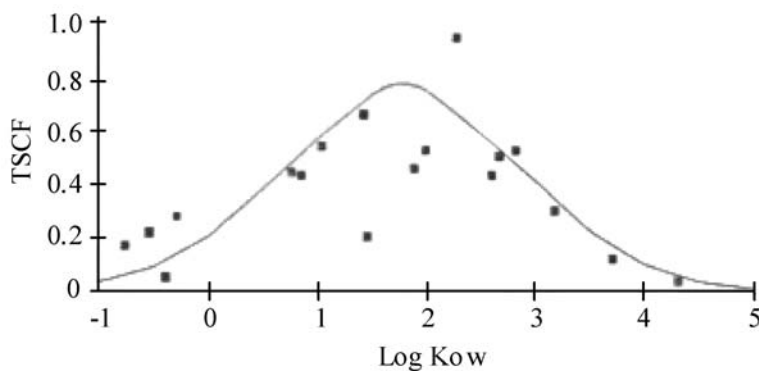


Fig. 3 Relationship between $\log K_{OW}$ and transpiration stream concentration factor (TSCF) [92]

with $\log K_{OW}$ values in the range of 1.5 to 2.5 (with a maximum around 1.8) have a higher propensity for movement into plant root and translocation up the stem into plant leaves. Briggs et al. [92] suggested that the translocation of compounds with lower $\log K_{OW}$ values is limited by the lipid membranes in the root, while those with higher $\log K_{OW}$, their translocation is limited by the rate of transport of the lipophilic chemical from the plant roots to the top of the plant.

7

Environmental Impacts of Hazardous Organic Chemicals in Biosolids

Volatile organics are unlikely to accumulate in biosolids-amended soil, although they can impose a significant negative environmental impact on air quality [96–98]. Little information is available on whether volatile organic contaminants in land-applied biosolids can have negative impacts on terrestrial organisms. Jensen [99] provided an excellent review on the biological effects of linear alkyl-

Table 7 Toxicological classification for organic compounds of primary relevance (from [100])

	Mammalian toxicity (acute)	Ecotoxicity	Aqueous solubility	Persistence	Concentration levels
PCDDs/Fs	H Carcinogenic	Aquatic: H Terrestrial: H Bioaccumulation: H	L	H	L
PCBs	M Tumor promoting Immunotoxic	Aquatic: H Terrestrial: H Bioaccumulation: H	L	H	L
Benzo(a)-pyrene (PAH)	Carcinogenic Mutagenic Teratogenic	H Bioaccumulation: H	L	H	H
LAS	M	Aquatic: H Terrestrial: M Bioaccumulation: H	H	M	H
NP	M endocrine disruptor	Aquatic: H Terrestrial: M Bioaccumulation: H	H	M	H
Tributyltin oxide	H Endocrine disruptor	Aquatic: H Bioaccumulation: H	M	H	H
DEHP	L Endocrine disruptor	Aquatic: M to H Terrestrial: L Bioaccumulation: H	L	M	H

H=high; M=medium; L=low.

benzene sulfonate (LAS) on soil microbial community, soil fauna, and plants. The data summarized by Jensen [99] showed adverse effects at about 10–50 mg kg⁻¹ for microorganisms and at about 90 mg kg⁻¹ for plants and invertebrates.

Litz [100] assessed the ecotoxicity of 44 organic contaminants in biosolids and provided an overview of the compounds found to be of primary relevance (Table 7). Toluene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, 1,1,1-trichloroethene, tetrachloroethene, DDT (incl. DDE, DDD), lindane, 2,4-dichlorophenol, pentachlorophenol, Ugilec, bromophosethyl, silicones, and phenols were proposed as substances of secondary relevance. Litz [100] stated a need for additional information for the following substances: clofibrin acid, chloroparaffins, EDTA, musk xylene, tris-(chloroethyl) phosphate, deca-, penta- and octabromodiphenyl ethers, 2,4,6-trichlorophenol, 2,4-dimethyl phenol, ethynyl estradiol, polyacrylic acid sodium salt, polyacrylamides (cationic), and DNBP (di-*n*-butyl phthalate).

Duarte-Davidson and Jones [94] raised the concern of transfer of biosolids derived organic contaminants from soil to plants and livestock. They proposed that organic contaminants can be ingested by grazing livestock via three routes: (1) associated with vegetation, (2) soil/biosolids adhered to vegetation, or (3) through ingestion of biosolids-amended soil. The rate of transfer is a function of many factors including the physicochemical properties of organic compounds, livestock species, type and form of biosolids applied, season, diet, etc. Following ingestion, compounds may pass through the gastro-intestinal membrane, enter the blood stream or lymph system and become incorporated into tissues and organs.

8 Conclusions

Each year, several million dry tons of biosolids are generated in the United States alone. A majority of these biosolids are applied as soil amendments on agricultural lands. The sludge provides valuable nutrients such as nitrogen, phosphorus and organic matter to farmland. Most wastewater treatment plants that are responsible for the generation of large quantities of biosolids serve large cities. The raw wastewater treated by these WWTPs contains significant quantities of industrial discharges that result in the introduction of hazardous organic chemicals to municipal wastewater. The hydrophobic nature of these chemicals results in their sorption to wastewater sludge. The organic biosolids can bind large quantities of organic contaminants such as PCBs, dioxins, pesticides, petroleum hydrocarbons and pharmaceutical compounds. The presence of these contaminants in biosolids can impact the ability of the sludge to be recycled as a soil amendment. The fate of the contaminant in the environment can be controlled by the properties of the chemical, soil characteristics, and environmental conditions. Decisions about land application of wastewater biosolids containing hazardous organic chemicals should be based on a comprehensive analysis of the environmental impact of the activity.

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A Review of Roadway Water Movement for Beneficial Use of Recycled Materials

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Abstract The purpose of this chapter is to provide a comprehensive review of water movement in roadways so that this knowledge may be used in environmental impact studies of traditional and recycled pavement materials. Long term leaching of contaminants is dictated in part by the hydrology of the roadway environment. To determine the hydraulic regimes in the field, ingress and egress routes and the hydraulic conductivity of the materials need to be known. This paper demonstrates that the major water ingress routes are along cracks, joints, and shoulders. It is shown that both saturated and unsaturated conditions in the field occur, suggesting that the contaminant leaching studies that consider saturated conditions

only may overlook the effects of unsaturated conditions and the effects of wetting and drying. Furthermore, moisture content and unsaturated conditions have significant spatial and temporal variations in pavement systems. The hydraulic conductivity of pavement materials presented in the literature vary significantly due to various pavement designs, however, the hydraulic conductivity of pavement is less significant in influencing pavement system hydraulic regime than are cracks, joints, shoulders, and drainage systems.

Keywords Recycled materials · Pavement · Hydraulic conductivity · Leaching · Unsaturated flow

List of Abbreviations and Symbols

ACOE The United States Army Corps of Engineers
FHWA Federal Highway Administration
L/S Liquid to solid ratio
MSW Municipal solid waste
PCC Portland cement concrete

1

Introduction

1.1

Recycled Materials Use in Roadways

There are nearly 6 million kilometers of roads in the United States (US) [1]. Construction and maintenance of these roadways require use of large volumes of materials. Numerous by-product and waste materials, produced in millions of metric tons per year, have the potential to be recycled in roadway applications (Table 1). The US Highway agencies have been using recycled materials with varying degrees of success for the past 20 years. At least 22 states have approved the use of coal fly ash and coal bottom ash in road construction [5]. The US also has a history of use of recycled asphalt pavement, reclaimed concrete pavement, blast furnace slag, and scrap tires. Theoretically, annual demand for construction materials (350 M tons) is close to the supply (353–859 M tons) of waste materials that have the potential to be recycled in roadway applications [6, 7]. However, the US is far from fully utilizing its recycling potential. Compared with many European countries, there is less than optimum recycling in the roadway environment. For example, reclaimed asphalt pavement, blast furnace slag, coal bottom ash, coal fly ash, and municipal solid waste (MSW) ash are completely recycled in the Netherlands and only partially or not at all recycled in the US [8].

1.2

Incentives for Studying Water Movement in Pavements

Water movement in pavements has traditionally been studied by pavement engineers to understand the relationship between moisture in the pavement and

Table 1 Annual production and use of recycled materials

Waste materials	Production (million metric tons)	% Recycled	Highway applications			
			Asphalt concrete	PCC	Granular base	Stabilized base Other
Agricultural						
Crop wastes	362 ^a	U	CM			
Lumber and wood wastes	64 ^a	U				E
Domestic						
Incinerator ash	7.8 ^a 7.3 ^b 8 ^c	<0.7 ^b 0 ^c	A		A	A
Sewage sludge ash	0.5–0.9 ^{a,c}	U	MF, A	A		
Scrap tires	2.2 ^a 2.3 ^b	U	ACM, A			E
Glass and ceramics	11.3 ^a 12 ^{b,c}	2.4 ^b 3.2 ^c	A		A	
Plastic waste	13.1 ^a 14.7 ^b	0.3 ^b	ACM			

^a Adapted from Collins and Giesielski [2].
^b Adapted from Schroeder [3].
^c Adapted from Chesner et al. [4].
U=undetermined.
MF=mineral filler.
A=aggregate.
CM=cementitious material.
E=embankment or fill.
F=flowable fill.

Table 1 (continued)

Waste materials	Production (million metric tons)	% Recycled	Highway applications			
			Asphalt concrete	PCC	Granular base	Stabilized base
Agricultural						
<i>Industrial</i>						
Coal ash – Fly ash	43.5 ^a 45 ^b	24	CM	CM	CM	F, E
Coal ash – Bottom ash	12.7 ^a 16 ^b 14.5 ^c	31	A		A	F, E
Coal ash – Boiler slag	3.6 ^a 2.3 ^c	91	A		A	
Advanced SO ₂ control by-products	4.5 ^a 18.0 ^b 21.4 ^c	>1 ^c			A	E
Construction and demolition debris	22.7 ^a	U			A	E
Blast furnace slag	14.1 ^{a,c}	100	A	CM, A	A	
Steel making slag	7.2 ^a 7.5 ^b	96–100	A		A	E
Non ferrous slags	9.1 ^a 7.6–8.1 ^c	U	A	A	A	E
Cement and lime kiln dusts	12.9 ^c	U	MF, A		CM	F
Bag house fines	5.4–7.2 ^c	U	MF			
Reclaimed asphalt and concrete pavements	45 ^{a,c} 94 ^b	73	A, ACM	A	A	E
Foundry sand	9.1 ^a 9.0–13.6 ^c	U	A			F
Roofing shingle waste	9.1 ^a 8.1 ^b 10 ^c	U	ACM, A, M			
Lime waste	1.8	U	MF			F
Contaminated sediments and soils	U	U	A, CM		ACM	
Mineral processing wastes	1600 ^c	U	A		A	

pavement integrity. It is well accepted that moisture shortens pavement life. Water pumping and freeze-thaw phenomena are two examples causing pavement damage in the form of cracking, rutting, and stripping. To examine damaging effects of moisture, water regimes in pavements need to be known. Thus, most of the information about water movement in pavements in the literature has been reported with the intent to understand moisture removal and moisture damage in pavements.

A new interest in water movement in pavements has stemmed from researchers interested in assessing the environmental impact of beneficial use of recycled materials in roadways. In the US, environmental compatibility of recycled materials has been one of the primary concerns in light of stringent solid waste regulations. Decker pointed out that the hot mix asphalt industry wants to ensure that 'linear landfills' are not being built [9]. Similarly, Callahan reported that among 40 surveyed states, all confirmed that a foremost concern was placed on protecting human health and the environment while evaluating beneficial use [5]. The potential for leaching of inorganic and organic contaminants in materials used in roadways needs to be determined to assess the risk posed by recycled material utilization. However, contaminant release mechanisms and contaminant transport depend on the hydraulic regime. Thus, robust leaching and environmental impact assessments need to incorporate knowledge on hydraulic regimes.

The purpose of this chapter is to provide a comprehensive review of water movement in roadways so that this knowledge may be incorporated into fate/transport models for use in risk assessment. The focus of the chapter is on the environmental impact of leaching of contaminants and aspects of subsurface hydrology as they relate to contaminant leaching. More specifically, the goal of this chapter is to provide answers to the following questions:

- Why is knowledge on hydrology necessary for understanding leaching?
- What is known about water pathways and water content in roadways?
- What are typical hydraulic properties of traditional and recycled materials?
- How can knowledge of hydrology be implemented into leaching studies?

1.3

Contaminant Release Pathways

Hazardous constituents may be released into the environment from highway components by: (a) dispersion of fugitive dust, and particulate and volatile emissions into the ambient air; (b) dissolution and transport in surface runoff; and (c) leaching of soluble components in percolating groundwater [4]. Highways may release pollutants to the environment even when recycled materials are not used. Ball et al. [10] listed the primary sources of pollutants found in runoff from road surfaces (Table 2). Many of the pollutants released as part of surface runoff may also be found leaching into the groundwater. In the pavement, possible leachable pollutants include trace metals (e.g., As, Cd, Cu, Cr, Hg, Pb, Zn) and trace organics (e.g., benzenes, phenols, vinyl chloride) [4]. Air quality is

Table 2 Pollutant constituents in runoff from conventional road surfaces (adapted from Ball et al. [10])

Constituents	Primary sources
Particulate	Pavement wear, vehicles, atmosphere, maintenance
Nitrogen, phosphorus	Atmosphere, roadside fertilizer application
Lead	Auto exhaust, tire wear, lubricating oil and grease, bearing wear
Zinc	Tire wear, motor oil, grease
Iron	Auto rust, steel highway structures (e.g., guard rails, moving engine parts)
Copper	Metal plating, bearing and brushing wear, moving engine parts, brake lining wear, fungicides and insecticides
Cadmium	Tire wear, insecticide application
Chromium	Metal plating, moving parts, break lining wear
Nickel	Diesel fuel and petrol exhaust, lubricating oil, metal plating, bushing wear, brake lining wear, asphalt paving
Manganese	Moving engine parts
Cyanide	Deicing compounds
Sodium/calcium chloride	Deicing salts
Sulfate	Roadway beds, fuels, deicing salts
Petroleum	Spills, leaks or blow-by of motor lubricants, antifreeze and hydraulic fluids, asphalt surface leachate, dust suppressants and roadbed stabilizers
PCB	Background atmospheric deposition, PCB catalyst in synthetic tires, spraying of rights-of-way

compromised by volatile constituents such as volatile organics as well as fine particulate matter that contains trace metals and organics [4]. In order to evaluate environmental risks related to the highway environment, each potential release mechanism must be fully investigated.

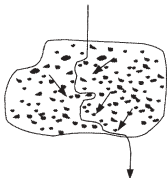
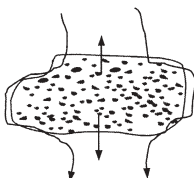
2
Leaching and Hydrology

Estimating long term field leaching is currently still a challenge. Often, researchers or regulators use laboratory data to evaluate field leaching because the mechanisms controlling solubility and release are not entirely known [11]. A large database exists on laboratory leaching of recycled materials in saturated conditions [12]. However, laboratory leaching data needs to be used cautiously

since various leaching protocols with varying design objectives exist across nations and none of the leaching protocols consider the presence of unsaturated conditions (TCLP, the United States; NEN 7343 and NEN 7349, the Netherlands; DIN 38414 S4, Germany; X 31–210, France; TVA, Switzerland) [13, 14]. Application of laboratory leaching data to field leaching may be a serious challenge considering that both saturated and unsaturated conditions exist in the field, and that there is little field leaching data in the literature [15].

Contaminant release depends on the solubility, diffusion, and advection of the contaminant itself. As contaminants solubilize, they diffuse within the particles' pore spaces and across the aqueous boundary layer that surrounds the particles. If the hydraulic regime is governed by "fast" fluxes, advection will quickly remove the released contaminant from the source, thereby leaving the solution unsaturated and allowing more release. If advection is slow, such as in a slow percolation system across unbounded materials, then the solubility may govern the maximum concentration of release. In granular materials (base course, embankments), the release is more often controlled by solubility. In monolithic systems (asphalt concrete, Portland cement concrete (PCC)), the rate limiting step in release of contaminants is more typically diffusion (Table 3). The estimated cumulative release in a percolation-controlled regime can be calculated by the product of liquid to solid ratio (L/S) and the solubility or total availability, as appropriate. In this simple approach, the L/S can be estimated from infiltration rate, height and density of the material, and the elapsed time for release. If contaminant mass transfer dictates the rate of release, a diffusion equation can be used to estimate release [15]. The diffusion approach accounts for unsaturated conditions by normalizing the cumulative release to the period of time that the material was wet [15]. The approaches for estimating cumulative release based on models estimating fluxes using diffusive or solubility limiting rates are examples of methods that relate laboratory data to field leaching. Their predictive ability has been somewhat verified with field observations although more research is needed to test their robustness with respect to other disposal or beneficial use scenarios [15].

Table 3 Characteristics of leaching mechanisms for granular and monolith materials

Material state	Unbound (granular)	Bound (monolith)
Hydraulic regime	Percolation	Advection
Rate limiting step	Solubility	Diffusion
Schematic		

There exists no detailed analysis of leaching of metals from construction materials in field conditions where hydraulic regimes are highly variable. Researchers studying leaching of metals from wastes in landfills currently realize the importance of hydraulic regime with respect to release and contaminant transport [11, 16]. Recently, as a prerequisite to understanding leaching and transport, Johnson et al. have looked into various modeling approaches to describe water movement through landfills [17]. The contaminant release mechanism and contaminant transport depends on the hydraulic regime, however, the consideration of water contact time has not gone beyond variation of the L/S in leaching protocols. In the waste management research realm, relatively little attempt has been made to model leaching and hydrology together.

3

Routes of Water Ingress and Egress

Current engineering practice in the US is predicated on the fact that water enters the pavement despite efforts to prevent it. Elsayed and Lindly [18] noted that until the study by Ridgeway [19], high water table and capillary water were thought to be the primary causes of excess water in pavements. Recently, crack and shoulder infiltration, and to some extent subgrade capillary action, are considered to be the major routes of water entry to the pavement [18, 20]. The significance of infiltration was shown by an immediate increase in edge drain outflow following a precipitation event [21]. Van Sambeek [22] reported that surface water infiltration could account for as much as 90–95% of the total moisture in a pavement system. He also identified transverse and longitudinal joints as major routes of ingress [22]. Similarly, field studies by Ahmed et al. [23] showed that pavement-shoulder joints were a major source of surface infiltration. For routes of egress, Dawson and Hill [20] noted that the lateral or median drain is the most significant route except when a highly conductive underdrain (subgrade unsaturated hydraulic conductivity >0.1 cm/s) is provided. Thus, infiltration through cracks and joints is thought to be the major ingress route and engineered drainage is believed to be the major egress route. Many studies on drainage efficiency report a ratio of precipitation to drainage outflow because of this conception. A simplified schematic and a list for routes of ingress and egress are provided in Table 4 and Fig. 1. No study was found in the literature that examined evaporation, reverse gradient of permeable layers above formation level, or direct rainfall on pavement during construction.

Table 4 Routes of ingress and egress (adapted from Van Sambeek [22] and Dawson and Hill [20])

Direction	From	Route
Ingress	Pavement surface	Construction joints
		Cracks resulting from shrinkage during/after construction
		Cracks resulting from distress due to loading
		Diffusion through intact materials
	Subgrade	Artesian flow
		Pumping action under traffic loading
		Capillary action of lower pavement layer(s)
		Water vapor rising through subgrade soils
	Road margins	Reverse gradient of permeable layers above formation level
		Lateral or median drain surcharging
		Capillary action of pavement layers
	Other sources	Pavement or ground run-off via unsealed shoulder
		Direct rainfall on pavement during construction
		Frost lenses melting during spring thaw
Egress	Pavement surface	Pumping through cracks/joints existing
		Capillary rise and evaporation through cracks
		Diffusion/evaporation through intact material
	Subgrade	Infiltration to permeable, low water-table subgrade
		Capillary action of subgrade
	Road margins	Gravitational flow in aggregate to lateral or median drain
		Vertical flow in aggregate to open-graded drainage layer below

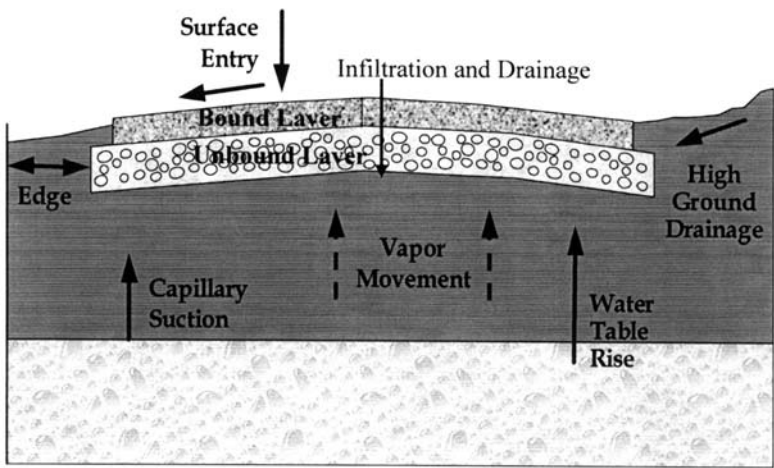


Fig. 1 Routes of water ingress and egress

4

Significance of Drainage

Once in the pavement, water can stay for days or weeks after each saturating rainfall [24]. Considering that leaching occurs mainly in wet conditions, removing water from the pavement is important for minimizing leaching. Similarly, from a pavement engineering perspective, to sustain the strength of the subgrade soil, it is necessary to remove the water from the pavement structure before it reaches the subgrade soil. Cedergren [25] noted that drainage systems were required for all pavements to improve pavement performance. According to Cedergren [25], exceptions for the need of drainage systems include areas in which there is no groundwater or spring inflow, or where the annual rainfall is less than 20 or 25 cm, and no significant amount of snow or ice can enter structural sections. Areas in which subgrades are very permeable and are not subject to freezing, and the natural water table is very deep, do not require drainage systems, nor do pavements that will be subjected to very limited numbers of heavy wheel loads over their design life, for example, on highways with less than 150 or 200 axle loads (8200 kg each) per day [25]. Currently, there does not exist pavement drainage criteria that consider contaminant leaching from recycled or traditional materials.

In the past decade, pavement designers realized that the pavement life could be extended threefold by proper installation and maintenance of subsurface pavement drainage systems [26]. The accepted practice is to remove water to minimize moisture-related problems such as rutting, stripping, cracking and pumping. To remove the water in the pavement, many states adopted the use of drainage systems such as permeable bases and edge drains. Experience shows that this costly practice extends the pavement life only if the subsurface drainage systems are well maintained [26]. Maintenance includes cleaning outlets, replacing rodent screens, flushing or replacing outlet pipes, repairing damages, and deepening ditches. Current belief supports installation of drainage systems only if routine maintenance can be provided to them. In the absence of maintenance, pavements become flooded and susceptible to increased water damage as well as higher leaching of contaminants. Unfortunately, in a national survey, several of the states admitted that proper maintenance was not practiced [26].

5

Moisture Content in Pavements

5.1

Effect of Groundwater Table

Groundwater conditions may affect the moisture in pavement systems and may be the major factor influencing subgrade water content if the ground water table is within approximately 6 m from the surface [27]. Capillary water and

water vapor may migrate towards ground surface and increase the moisture content especially in subgrades. Development of a perched water table may also increase head buildup in subbase layers [21]. Both Chu et al. [28] and Ksaibati et al. [29] noted that deeper groundwater table results in lower moisture content in base and subbase layers.

5.2

Temporal and Spatial Variability

Moisture related pavement problems are often amplified in cold regions where frost penetration or freeze-thaw cycles occur. During winter months, water trapped in pavements form ice crystals that melt when temperatures rise. Because pavements are not homogenous, ice crystals are distributed randomly and result in uneven, differential heave and damage [30]. During thawing, moisture content increases and the pavement is weakened. In some regions, subgrade thawing occurs only once whereas in relatively milder areas, continuous freezing and thawing may occur depending on the climate and amount of deicing salts used on the pavement. In cold regions, the thaw period may spread over several weeks if the frost has penetrated more than three meters below the surface [31]. To reduce the frost effect, existing material may be replaced by frost durable material or an insulating layer within the pavement structure may be preferred due to lower cost [32]. Geotextiles may be used as capillary barriers to reduce the unsaturated flow of water toward the surface caused by freezing or evaporation [33]. Laboratory results suggest that addition of lime to clay soil increases frost resistance and may be an alternative solution for frost susceptible subgrades [34]. More information on common and alternative materials for road and airfield insulation and their performances can be found in studies by Dore et al. [35] and Esch [36]. Xu et al. [37] presented mathematical models of water flow and heat transport in frozen soil.

Moisture conditions in pavements can be spatially variable. Thus, higher or lower leaching may be expected in various locations in the pavement. Roads are three-dimensional structures. Longitudinally, major differences arise from changing subgrade properties and water table levels. When these two variables remain constant, longitudinal variability is likely to be minimized. Variability of moisture conditions among horizontal components of pavements such as the surface layer, base, subbase and subgrade depends on material type, crack formation, and proximity to the groundwater table. The transverse variability is often summarized by the term 'edge effects'. Typically, close to edges, moisture contents are higher due to greater infiltration. More frequent occurrence of cracks along and closer to shoulders typically indicate edge effects. A study by Gordon and Waters emphasizes laterally heterogeneous moisture conditions and their consequences by stating that the performance of the pavements is dictated by edge effects, regardless of the pavement thickness and shoulder details [38]. In the presence of a paved shoulder, edge effects can be delayed but not stopped.

The volumetric water content in the pavement varies considerably (3–45%) not only because of material or design differences but also because of spatial differences such as lateral variability including edge effects along the shoulders or wheel path location [38, 39] or vertical variability [40]. Temporal variability of water content in the field in the short term based on precipitation events [41] or in the long term based on seasons [42] or time passed after construction [43] has also been reported. The high variability in water content indicates that both saturated and unsaturated conditions occur in the field. Thus, contaminant leaching studies should consider the presence of variably saturated conditions in the field.

6

Hydraulic Conductivity of Pavement Materials

The hydraulic conductivity of traditional and recycled materials is a key factor for determining the types of hydraulic regimes occurring in roadways. Typically, Darcy's Law is used to determine the flow rates as a function of the hydraulic conductivity and the hydraulic gradient. To predict the hydraulic regimes, both saturated and unsaturated hydraulic conductivity values are needed. However, determination of unsaturated hydraulic conductivity is difficult and time consuming because the unsaturated hydraulic conductivity is a nonlinear function of the water content. Even though the unsaturated hydraulic conductivity of soils has been widely documented in the literature, not much information exists on unsaturated hydraulic properties of traditional and recycled pavement materials. Thus, this chapter focuses on saturated hydraulic conductivity values of traditional and some recycled materials.

6.1

Asphalt Concrete and PCC

Many researchers showed that it is difficult to establish a linear relationship between porosity and hydraulic conductivity of asphalt concrete [44–46] because many factors such as interconnectivity (e.g., some air voids are trapped by asphalt and mineral fillers), shape, and size of air voids affect the hydraulic conductivity [47]. Still, the porosity of asphalt concrete has been used to categorize it as impermeable (below 6–7% porosity) or free draining (>15% porosity) [48]. Terrel and Alswailmi [44] noted that both the impermeable and the free draining asphalt concrete have significant advantages such as higher strength and less susceptibility to moisture damage over the medium void range asphalt concrete, which is typically used in the United States. Porous asphalt pavements with better skid resistance in wet weather are common in Europe and are also in use in the United States. For these types of pavements, susceptibility of porous asphalt mixtures to clogging may be of concern if the road is used by vehicles that have dirty wheels or carry earth [49].

In PCC, the pores exist in the cementitious matrix of concrete and in the interfacial regions with the aggregate [50]. Similar to the asphalt concrete, the hydraulic conductivity of PCC is also more complex than a simple function of porosity. There is some evidence that the hydraulic conductivity of concrete may be more closely related to the pore volume over a certain threshold value of diameter (e.g., 500 or 1000 nm) rather than to the mean diameter of pores or total porosity [51]. The hydraulic conductivity of concrete, which depends on the size, distribution and continuity of pores and total porosity is modified during the hardening of concrete. Bakker [52] described the fresh concrete as a granular structure with continuous capillary pores. During the hardening period the hydration products glue the particles together and block the capillary pores. These processes increase the strength of the material and decrease the hydraulic conductivity. The hydraulic conductivity of hardened concrete also depends on the temperature during hydration. Higher curing temperatures increase the hydraulic conductivity of PCC if traditional (as opposed to recycled) materials are used [52]. Thus, the type of raw materials (cementitious materials and chemical admixtures) used, the type and extent of chemical reactions during hardening, and curing temperature affect pore size distribution and hydraulic conductivity of PCC.

The hydraulic conductivity of asphalt concrete and PCC may vary eight orders of magnitude because of different designs (Table 5). Typically, the hydraulic conductivity of PCC ($<10^{-7}$ cm/s) is less than the hydraulic conductivity of dense graded asphalt (10^{-2} to 10^{-4} cm/s), Superpave asphalt (10^{-5} to 10^{-1} cm/s), and porous asphalt concrete (10^{-2} to 10^1 cm/s). Less data was found on the hydraulic conductivity of PCC possibly because PCC is assumed to be essentially impermeable. However, if there is cracking, the hydraulic conductivity of the asphalt concrete or PCC may vary significantly depending on the width, depth, and spacing of the cracks. Higher leaching is expected to occur at cracked locations.

6.2

Bases/Subbases/Embankments

A permeable base layer may be stabilized or unstabilized. To provide a more stable construction work area, permeable bases may be stabilized with a cement or asphalt binder with only a slight decrease in hydraulic conductivity ($<10\%$ of the initial material hydraulic conductivity) [60]. Stabilized bases have lower coefficients of hydraulic conductivity (0.08–1.14 cm/s) than those of untreated permeable bases (1.14–7.6 cm/s or higher) [61, 62]. Tandon and Picornell [63] suggested that the best alternative material for base layers is gravel stabilized with 5% cement, which provides the required stiffness, strength, and drainage.

For adequate drainage, Baumgardner [64] and the FHWA suggested the use of 0.34 cm/s for a minimum hydraulic conductivity value for a base layer, whereas Lindly and Elsayed [65] noted that a range of 0.18–0.36 cm/s is typically used for drainage design. The US Army Corps of Engineers (ACOE) differentiates be-

Table 5 Hydraulic conductivity values of asphalt concrete and PCC

Sample	Coefficient of hydraulic conductivity (10 ⁻⁵ cm/s)	Air voids (%)	Source
Coarse-graded asphalt Superpave samples from I-75, Columbia	0–976	4.0–12.1	[45]
Coarse-graded asphalt Superpave samples from I-10, Columbia	2–638	1.9–8.7	
Coarse-graded asphalt Superpave samples from I-10, Escambia	13–927	6.3–11.8	
Fine-graded Marshall Mix Field samples	14–52	5.9–8.3	
Coarse-graded asphalt Superpave Lab fabricated samples	22–145	6.5–8.3	
Laboratory prepared asphalt Superpave mixtures	10–10,000	3.5–15.0	[53]
Porous asphalt mix specimens	62,900–535,900 ^a	15.6–23.9	[49]
Porous asphalt mix specimens clogged with soil	1,300–337,600 ^a		
Open-graded coarse asphalt mixture	27,000–148,000	4–11	[44]
Dense-graded Superpave wearing course specimens	10,200–11,600 ^a		
Dense-graded mix specimens from I-10	176–529 ^a		
Dense-graded mix specimens from I-12	35 ^a		
Asphalt concrete mixture specimens	0–20		

^a Pseudo-hydraulic conductivity, measured at turbulent conditions.
^b Variability within 24 m longitudinal to pavement may vary up to one order of magnitude.
^c Results may not be representative since such low hydraulic conductivities are difficult to measure.
^d Most of the samples had rutting and cracking. Samples are from I-75 Atlanta, Georgia.

Table 5 (continued)

Sample	Coefficient of hydraulic conductivity (10 ⁻⁵ cm/s)	Air voids (%)	Source
Open-graded friction coarse	2069	16.7	[54] ^d
Open-graded friction coarse with 16% crumb rubber	5502	15.8	
Open-graded friction coarse with mineral fillers	3203	19.9	
Open-graded friction coarse with cellulose fibers	8552	16.2	
Open-graded friction coarse with styrene-butadiene (SB) polymer	1801	13.9	
Open-graded friction coarse with SB and cellulose fibers	8121	19.2	
Various hot mix asphalt pavements (field and lab measurements)	100–16,000 ^b		[46]
Cements containing 0, 28.3, and 66% slag		4.2–20	[55]
Concrete mix (cement, slag, fly ash, silica fume, no aggregate)		1–7	[56]
Cement concrete after curing for 56days ^c	0.000001–0.0000026	3.9–6.1	[57]
Fly ash blended cement		~35	[58]
High strength concrete	0.00005		[59]
No cracks, 25 mm thick sample	0.0002		
No cracks, 50 mm thick sample	0.0003		
50 µm crack, 25 mm thick sample	0.0006		
50 µm crack, 50 mm thick sample			
250 µm crack, 25 and 50 mm thick samples			

tween open-graded and rapid-draining materials that have coefficients of hydraulic conductivity of greater than 1.8 cm/s and 0.35–1.8 cm/s respectively [66]. Recommendation by the National Stone Association for unstabilized permeable base is on the order of 0.49 cm/s. State Departments of Transportation often differ in their specifications ranging from greater than 0.35 cm/s for New Jersey Department of Transportation to a range of 0.35–6.4 for Pennsylvania Department of Transportation [66]. On the other hand, European researchers noted that for mean annual rain intensities greater than about 400 mm, the adequate draining capacity is greater than 0.5 cm/s [67]. Excluding the values cited by Zhou et al. [62] for untreated base materials and the European recommendation by Alonso [67], a minimum value common to sources cited above seems to be the coefficient of hydraulic conductivity noted by Baumgardner [64], which is 0.34 cm/s. Similarly, Elsayed and Lindly [18] noted that a minimum laboratory hydraulic conductivity of 0.36 cm/s is often preferred by designers. The compiled hydraulic conductivity data of base/subbase layers varied almost four orders of magnitude both below and above this value because both free draining and impermeable bases are currently used (Table 6).

If the hydraulic conductivity of the base material cannot be measured, one approach to estimate the hydraulic conductivity is to examine the gradation of the material (percent passing as a function of sieve size). The gradation is important because the extent of fines in the material affect the hydraulic conductivity considerably [81]. Cedergren charts and Moulton nomographs, the two common methods for estimating the hydraulic conductivity of aggregate base layers from the gradation curve, have been updated by another empirical relationship given by Lindly and Elsayed [65]. To estimate the hydraulic conductivity of asphalt or Portland cement stabilized bases, Lindly and Elsayed [65] provided a regression that uses the percent asphalt cement and porosity information in addition to the gradation curve. However, the correlation is for open-graded materials and may not be useful for dense-graded asphalt-treated bases. Yet, since the addition of two to three percent asphalt cement has markedly less effect on hydraulic conductivity than the aggregate gradation, approaches used for untreated bases may closely approximate the coefficient of hydraulic conductivity for treated bases [22].

Hydraulic conductivity and water regimes in embankments are not as widely discussed in the literature as asphaltic concrete, PCC, base, or subbase layers. There is some literature on the use of recycled materials in embankments, however most of these focus on strength and workability of the material rather than its hydraulic conductivity. Kim et al. [82] presented a knowledge-based expert system for utilization of solid flue gas desulfurization by-product (a coal combustion by-product) in highway embankments and note that the hydraulic conductivity of solid flue gas desulfurization by-product may range from 3.1×10^{-9} to 1.6×10^{-4} cm/s at 28-day curing while its hydraulic conductivity in place may gradually decrease with aging. Partridge et al. [83] noted that compacted waste foundry sand used in embankments is not a free draining material. Its laboratory and field hydraulic conductivity ranges from 0.1×10^{-5} to

Table 6 Hydraulic conductivity of base and subbase layers

S,U ^a	Type of base	Hydraulic conductivity (cm/s)		Source
		Field	Lab	
	Recommended for drainage (see Appendix for more values)			
S	Mn/DOT Permeable Asphalt stabilized base		0.34	[18, 64]
U	Class 5 Dense-graded base	1.16×10 ⁻⁴	0.35–0.71	[69]
U	Base or		0.001	[23]
U	subbase		0.00043	
U	No 24 sand with 6% passing No 200 sieve		0.000038	
U	No 53 stone with 5% passing No 200 sieve		0.000043	
U	used by		0.068	
U	No 53 stone with 10% passing No 200 sieve		0.038	
U	Indiana DOT		0.025	
U	No 73 stone with 10% passing No 200 sieve		0.009	
U	No 53B base with 2.5% passing No 200 sieve		0.00022	
U	No 53B base with 5% passing No 200 sieve		8.1–13.0	[70]
S	No 5D hot asphalt concrete base		7.5–11.0	
S	Asphalt stabilized gravel/slag/limestone		9.5–20.0	
S	Portland cement stabilized gravel/slag/limestone			
U	Untreated gravel/slag/limestone			
U	Untreated aggregate base (IDOT specification 41–21)	0.046	0.4–3.35, 0.044 ^b	[71]
U	Untreated aggregate base (ODOT specification No. 304)	0.00503	0.036–0.4, 0.018 ^b	
U	Untreated aggregate base (DOT specification No. 310)	0.0154	0.007–4.2, 0.0077 ^b	
U	New Jersey untreated drainable base	0.611	2.6, 0.252 ^b	
S	Portland cement stabilized free draining base (AASHTO No.57)	5.85	11.9	
S	Asphalt stabilized free draining base (AASHTO No. 57)	3.93	10.1–13.2	

^a Based on design calculations.

^b Moulton estimation.

^c Pseudo-coefficient of hydraulic conductivity.

S=stabilized.

U=unstabilized.

Table 6 (continued)

S, U ^a	Type of base	Hydraulic conductivity (cm/s)		Source
		Field	Lab	
S	Asphalt treated open-graded base		0.17–1.45	[62]
U	Permeable base		14.1	[72]
U	Dense-graded base material – Limestone	0.35–1.7 ^a	0.05–0.75	[63]
U	Dense-graded base material – Iron-Ore		0.004	
U	Dense-graded base material – Sand and Gravel		0.04	
S	11 Open-graded large stone asphalt base mix samples	0.06–1.47 ^c		[47]
S	2 Asphalt treated drainable base mix	2.4–3.6 ^c		
U	Fine to coarse-graded aggregate		0.0003–0.5	[73]
U	Open graded untreated base layers from roadway samples		0.075	[74]
S	Asphalt treated permeable base		0.086	
S	Cement treated permeable base		0.059	
U	Aggregate from stockpile for treated permeable base		0.063	
U	Untreated permeable bases (range)		≥1.14–7.6	[61, 62]
S	Treated permeable bases (range)		0.08–1.14	
S	Open-graded asphalt treated base		0.05–0.8	[65]
U	Dense and open-graded aggregate bases		0–1.0	[18]
	Geotextile layer (used to reduce pumping)		0.15	[75]
	Geotextile used in drainage trenches		0.28–1.66	[30]
	Till subgrade north of Montreal	0.000005–0.0001		

Table 6 (continued)

S, U ^a	Type of base	Hydraulic conductivity (cm/s)		Source
		Field	Lab	
S	Permeable asphalt stabilized base		0.35	[41]
U	Dense-graded base (Class 4 special)		0.000135	
U	Dense-graded base (Class 5 special)		0.000220	
	Pea gravel used in edge drains		0.35	
U	Dense-graded (Class 4 special)		0.000038	[76]
S	Permeable asphalt stabilized base		0.35	
U	Subbase in Searsmont, Maine	0.0004–0.01		[77]
U	Subbase in Cyr Plantation, Maine	0.000006–0.001		
U	Subbase in Passadumkeag, Maine	0.0001–0.007		
U	Subbase in Lebanon, Maine	0.0005–0.001		
U	2% fines subbase		0.000068 or 0.000190	[78]
U	12% fines subbase		0.000014 or 0.000053	Two values are
U	Free draining		0.031 or 0.31	from two different
				testing apparatus
U	Base course materials		0.00013–0.00058	[79]
U	used in Western Australia. Clayey-sand		0.000005–0.00024	
U	Also used in shoulders. Quartzitic crushed rock		0.00008–0.00023	
	Clayey-gravel			
U	Compacted natural gravel used in low volume		0.00000025–	[80]
	bituminous surfaced roads in Kenya and Botswana		0.000000045	

7.1×10^{-5} cm/s. Bhat and Lovell [84] examined the design of flowable fill by using waste foundry sand as a fine aggregate. They note that the hydraulic conductivity of flowable fill is low (2.6×10^{-6} to 1.2×10^{-5} cm/s) and that the hydraulic conductivity does not necessarily decrease with increasing contents of fly ash possibly because the advantage from the fine particle size of fly ash is outweighed by the uniform spherical shape of these particles.

7

Infiltration Through Cracks

Formation of cracks is a widespread phenomenon in both asphalt concrete and PCC pavements. In PCC, before application of an external load, bond cracks may occur in concrete at the mortar-aggregate interface, with negligible cracking in either the mortar or aggregate phases [85]. Cyclic loading propagates cracking, and with extension and widening of microcracks, a network of cracks may form. Slate and Hover reported that the increase in bond cracking is negligible at applied loads up to 30% of ultimate load [86]. Environmental conditions and especially freeze-thaw cycles enhance crack development. Expansive soils underlying pavements also contribute significantly to cracking. Causes of cracking and other deterioration resulting in surface roughness can be determined by profilometers that provide accurate and reproducible longitudinal profile data [87]. Often cracks are referred to as transverse and longitudinal cracks. Roberson [88] related crack formation and type to material problems (Table 7). Frabissio and Buch [89] reported that pavements containing slag or recycled concrete coarse aggregate appear to have more transverse cracks than those using natural gravel or carbonate aggregates. They suggested that slag and recycled pavement have a greater tendency for shrinkage cracking when proper curing considerations are neglected. With so many factors promoting

Table 7 Cracking types and causes [88]

Pavement type	Cracking	Material problem
PCC	Corner	Follows pumping
	Diagonal	Follows moisture build up
	Transverse	
	Longitudinal	
	Punch out	Deformation following cracking
Asphalt concrete	Longitudinal	Strength
	Alligator	Drainage
	Transverse	Freeze thaw cycling
	Shrinkage	Suction (i.e., moisture loss)

crack formation and growth, many pavement structures are subjected to undesired conditions arising from cracking.

The presence of cracks as well as joints significantly increases hydraulic conductivity of the surface layer. Higher leaching may be expected in areas that have cracks and joints. Studies as early as 1952 have pointed to the enhancement of water permeability due to crack formation. The effect of cracks in water permeability of pavements is so significant that some authors believe infiltration through the surface layer depends on the extent of cracking rather than the hydraulic conductivity of the material itself [90]. Cedergren and Godfrey [91] noted that up to 70% of surface runoff can enter a crack no wider than 0.8 mm if there is no obstruction at the bottom of the crack. Similarly, Barksdale and Hicks [92] noted that it is possible for as much as 70–97% of rainfall to enter open joints with opening of 0.9–3.1 mm when dry conditions exist beneath the pavements.

There is continued interest to find methods to minimize the undesirable effects of cracking. In asphalt concrete, mineral fillers such as rock, dust, slag dust, hydrated lime, hydraulic cement, fly ash and loess may be used to increase density and strength of asphalt concrete mixture. A laboratory study by Tawfiq et al. [85] suggests that addition of mineral filler such as silica fume and fly ash reduces the extent of crack formation, and thus the hydraulic conductivity of concrete. Yet, more of the studies focus on sealing of cracks rather than preventing them. In asphalt pavements, the cracks may be sealed to not only minimize water penetration, but also to renew skid resistance, fill ruts, retard raveling, restore ride quality, reduce stresses due to traffic and reduce effect of thermal variations. Sealing appears to be an effective method for blocking water ingress since laboratory studies show that hydraulic conductivity of seals is quite small (Table 8). On the other hand, there is data suggesting that for PCC pavements, the presence of crack/joint sealants does not play a significant role in altering surface infiltration rates over dense-graded materials [94]. Christopher and McGuffey [26] attributed the failure of sealing to the short life span of sealants (2–3 weeks). Similarly, Hagen and Cochran [69] noted reduced or no flow through the sealed joints during the first two weeks and observed significant infiltration on the third week after a big rain event. Sealants were ineffective although they seemed to be in good condition.

In the US one approach taken to prevent moisture penetration has been to seal the top and bottom surface of the asphalt mixture. At present, it is believed that sealing does not prevent water penetration [60], although sealing of shoulder joints may significantly reduce infiltration [95]. Sealing can slow infiltration and may prevent particles from entering the pavement. On the other hand, several studies have suggested that surface sealing did not hinder rutting and stripping partially because routes of evaporation were blocked, causing moisture accumulation within the asphalt concrete mixture [48].

Other than sealing, several variables affect the water movement in cracked surface layers. For example, the type of base may influence the water flow through cracks in PCC pavements. The water flow in PCC pavements with open

Table 8 Hydraulic conductivity of seal as measured using a falling head test [93]

Material tested	Water head (cm)	Measured hydraulic conductivity (cm/s)	Average hydraulic conductivity (cm/s)
Slurry seal	20	5.2×10^{-5}	3.9×10^{-5}
		5.2×10^{-5}	
		1.2×10^{-5}	
	5	1.1×10^{-7}	2.0×10^{-6}
		3.0×10^{-6}	
		2.8×10^{-6}	
Micro-surfacing	20	5.2×10^{-6}	1.1×10^{-5}
		2.8×10^{-5}	
		0.0	
	5	0.0	0
		0.0	
		0.0	
Seal coat	20	0.0 ^a	0
	5		0

^a Seal coat specimens exhibited no permeability to water with a head of 20 cm for a measurement period of 72 h.

bases may be greater than the water flow in PCC pavements with densely-graded bases [94]. Koch and Sandford [78] documented that in presence of free draining subbase, infiltration through cracks is limited by crack width, whereas in other subbases, it is the subbase that limits infiltration rate. Duration of the rainfall is also relevant. Rainfall of higher duration may result in higher water entrance and flow in pavements than rainfall of short duration, but high intensity [94].

Related to crack conditions, the variables affecting water hydraulic conductivity through cracks are the length, width and spacing of cracks as well as whether the cracks are filled by debris or not [94, 96]. Laboratory tests by Koch and Sandford [78] confirmed that infiltration rates through infilled cracks are significantly higher than infiltration rates through unfilled cracks. Since cracks are free of debris only during their initiation (fresh cracks) and possibly after they are washed clean by pumping or rain events, infiltration rates through debris filled cracks are more representative of field conditions. Finally, on retro-fitted pavements that have an additional asphalt layer on top of old pavement, crack width as observed on the new surface layer may be misleading if the old pavement was already cracked at some other width [78].

8 Modeling

Often, researchers examining contaminant release from waste materials assume that release is either solubility limited or diffusion limited. In real life, the limiting factor may vary temporally depending on the hydraulic regime. In addition, mechanisms other than solubility, such as sorption and ion exchange, may need to be accounted for to fully describe leaching [11]. One approach for estimating contaminant release may be to use numerical models that simulate reactive transport by coupling modeling of water movement with chemical equilibrium. Reactive transport models have been used for many contaminant transport problems, especially since the models have become commercially available, however, their use for studying leaching from waste materials has been limited. In the 1980s many numerical geochemical models and transport models were developed independently. Currently, there are few examples of numerical models that simulate chemically reactive multiple component transport for various hydraulic regimes (Table 9). Multiple component reactive transport models are capable of simulating water flow in variably saturated media (using the Richards equation), physical solute transport (advection, dispersion, and diffusion), and chemical solute transport (potential chemical reactions of complexation, ion exchange, oxidation-reduction, precipitation-dissolution, acid base reaction, and adsorption-desorption). By considering all possible mechanisms affecting release, use of multiple component reactive transport models may improve the ability to predict laboratory and field leaching. The model selected should be able to simulate unsaturated flow.

Ideally, the model selected for simulating leaching should include some other features. To account for crack infiltration, the spatial capability of the model should be at least two dimensions. Among analytical, finite difference and finite element techniques, finite element method is preferable because irregular geometries such as cracks and variable surface geometry (crowning of the road, transverse and lateral cracks) can be handled more easily. Continuous wetting and drying cycles can only be modeled if the model can simulate the hysteresis effect. In addition, the model should handle heterogeneous media so that different layers of the pavement structure can be input in the model. Time varying

Table 9 Reactive multiple component transport models

Reactive transport model	Transport model	Geochemical model	Source
DYNAMIX	TRUST	PHREEQE	[97]
HYDROGEOCHEM	FEMWATER	EQMOD	[98]
MINTRAN	PLUME2D	MINTEQA2	[99]
RT3D	MODFLOW	MT3D	[100]
REACTRAN2D	SUTRA	MINTEQA2	[101]
FASTCHEM	EFLOW, ETUBE	ECHEM	[102]

boundary conditions are also preferable for inputting precipitation and groundwater table depth values. Inclusion of all the factors in the model is complicated and the state of the art in modeling reactive transport is continuously improving. The ideal modeling approach was presented here to demonstrate all factors that may influence the release and transport of contaminants.

9

Conclusions and Research Needs

This chapter showed that hydrology is a key factor affecting the impact of beneficial use of recycled materials. Hydraulic regimes should not be ignored when estimating the environmental impact of traditional or recycled materials used in roadways. The major ingress routes for water are cracks and joints and shoulder infiltration. Knowledge of hydraulic conductivity is essential for determining hydraulic regimes. It was shown that hydraulic conductivity varies significantly because of various pavement designs. Both saturated and unsaturated conditions exist in the pavement and thus information on both saturated and unsaturated hydraulic conductivity of materials used is required. Unsaturated hydraulic conductivity was not discussed in this chapter mainly because little information exists on unsaturated hydraulic properties (soil moisture retention curve) of both traditional and recycled materials. Water content in the pavement is spatially variable. Higher water contents and possibly higher leaching may occur in shoulders or under cracks and joints.

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Evaluation Methodology for Environmental Impact Assessment of Industrial Wastes Used as Highway Materials: An Overview with Respect to U.S. EPA's Environmental Risk Assessment Framework

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Abstract An evaluation methodology was developed for assessing potential ecological risks posed by constituents released from waste and industrial byproducts used in highway construction. This methodology is discussed in the context of United States Environmental Protection Agency's (U.S. EPA) environmental risk assessment framework. Concerted efforts have been made to incorporate important components of the U.S. EPA's risk assessment framework with the Oregon State University (OSU) methodology's own innovative testing

and measurement components for assessing potential ecological risks. The evaluation methodology includes leaching tests that are designed to describe *source terms* (quantification of characteristics of leachate, such as the constituents released, the chemical matrix, the rate of release) and the potential for ecological risk, i.e., *hazard assessment* of industrial wastes used in highway construction). Environmental removal, reduction, and retardation tests combined with an integrated chemical and biological assessment prescribed in the OSU methodology contribute substantially in characterizing the exposure and ecological effects of leachate constituents.

Keywords Waste materials · Reuse · Highways · Ecological risks · Evaluation methodology

List of Symbols and Abbreviations

APHA	American Physical Health Association
ASTM	American Society for Testing Materials
C&R	Construction and Repair Materials
EC ₅₀	Mean Effective Concentration (causing 50% effect)
EEC	European Economic Community
ERA	Ecological Risk Assessment
FFDCA	Federal Food, Drug, and Cosmetics Act
FIFRA	Insecticide, Fungicide, and Rodenticide Act
ISO	International Standardization Organization
LC ₅₀	Mean Lethal Concentration (causing 50% mortality)
NAS	National Academy of Sciences
NRC	National Research Council
OECD	Organization of Economic Cooperation and Development
OSU	Oregon State University
RRR	Removal, Reduction, and Retardation
TRB	Transportation Research Board
TSCA	Toxic Substances Control Act
US EPA	United States Environmental Protection Agency
TOC	Total Organic Carbon

1

Introduction

Researchers at Oregon State University (OSU) developed an evaluation methodology to assess potential ecological risks posed by constituents released from waste and industrial byproducts used as secondary aggregates in highway construction [1–4]. Due to high volume consumption of natural aggregates in highway construction, the transportation industry is under increasing pressure to use non-conventional, waste, and byproduct materials as secondary aggregates. In such activities, a wide variety of materials, including fly ash, bottom ash, recycled asphalt cement, petroleum-based sealants, wood preservatives, and performance-enhancing additives are used. During storm events, there is a potential for leaching of the chemical constituents in these materials and their transport to adjacent surface and subsurface water bodies. Toxic leachate

constituents could result in adverse effects on the ecological health of the streams, ponds, wetlands, and groundwater systems. If such water bodies are used as a source of potable water, adverse human health effects could occur as well.

The Transportation Research Board (TRB) of the National Academy of Sciences (NAS)-National Research Council (NRC) commissioned a six-year study to develop an assessment framework that helps transportation and environmental officials make prudent decisions on suitable reuse of waste and byproduct materials in road construction. This evaluation methodology not only includes its own innovative testing and measurement components but also incorporates several important features of the risk assessment paradigm developed by the United States Environmental Protection Agency (US EPA) [5].

2

Risk Assessment Paradigms

Ecological risk assessment (ERA) is the practice of determining the nature and likelihood of effects of our actions on animals, plants, and the environment. It has emerged as an important part of environmental protection programs employed by industries, government agencies, policy makers, citizens and legislators to support environmental management decisions [6].

Considerable attention has been given to the developments of ecological risk assessment paradigms or framework over the past decade. A paradigm is “a philosophical and theoretical framework of a scientific school or discipline.” As such, it differs from a specific protocol or guidance. Rather, it provides a general conceptual framework for organizing problems and approaches. The NRC proposed a four-step paradigm in a 1983 report, *Risk Assessment in the Federal Government: Managing the Process*. This conceptual model included hazard identification, dose-response assessment, exposure assessment, and risk characterization. The U.S. EPA and other agencies readily accepted this paradigm for the conduct of human health risk assessments. To a limited degree, the paradigm or similar paradigms were applied to certain ecological risk assessments, most notably those related to ocean disposal of sewage sludge [7, 8] and investigations of hazardous waste sites [9, 10]. One of the earliest adaptations of the 1983 paradigm for use in ecological risk assessment is presented in Barnthorse and Sutter [11] and their work provided a starting point for the development of the framework. Major efforts have been undertaken by the U.S. EPA in its 1992 “Framework for Ecological Risk Assessment” [12] and by the NRC in its 1993 “Issues in Risk Assessment” [13].

In 1998, U.S. EPA replaced its *Framework for Ecological Risk Assessment* with a refined *Guidelines for Ecological Risk Assessment* [5]. The U.S. EPA’s risk assessment paradigm has come into more common usage than the NRC paradigm and is considered the prevailing conceptual approach for ecological risk assessment in the United States. Figure 1 illustrates the U.S. EPA model for risk

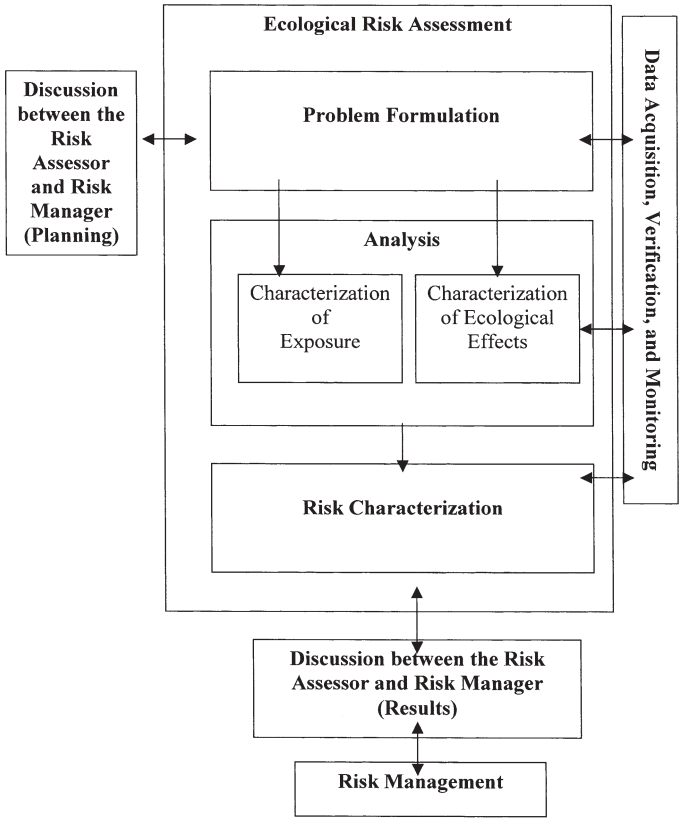


Fig. 1 The U.S. EPA framework for ecological risk assessment

assessment. Various federal and state agencies and private organizations have used the U.S. EPA paradigm to guide ecological risk assessment activities as it provided an acceptable and sufficiently flexible conceptual structure to develop more detailed guidance for risk assessment. In this chapter, an analysis of the evaluation methodology developed by OSU researchers is performed from the perspective of the U.S. EPA's environmental risk assessment framework.

3 Methodology Overview

An evaluation methodology was developed as a practical procedure that provides government agencies (e.g., state departments of transportation) and private industry with a systematic process for assessing the potential environmental impacts resulting from the use of waste and industrial byproducts in highway

construction. To achieve potential benefits, the methodology is simple enough for users not extensively trained in all of its facets and does not necessarily rely upon experimental activities for routine application.

The methodology was also used for assessing the potential impacts of waste and industrial by-products used as secondary aggregates in road construction. The impact of these materials and their mobile constituents on surface and ground water was the primary focus of this study. There was an ongoing concern that increasingly more waste materials were being used as construction materials. This concern, coupled with the implicit need to demonstrate the ability of the protocol to discriminate potentially toxic from non-toxic materials, led to the development of the evaluation methodology.

3.1

Screening Phase

The overall evaluation methodology development was planned in several phases and is illustrated in Fig. 2. The screening phase (or phase I) focused on a broad screening of common construction and repair (C&R) materials to identify the extent of the problem and to guide the succeeding phases. The components of screening phase are:

1. Search database for chemical and toxicological properties of the subject C&R material
2. Identify and evaluate assessment endpoints
3. Perform toxicity screening of subject C&R material
4. Decide whether the subject C&R material is toxic at highest concentration
5. Provide a preliminary description of a conceptual model to assess the fate and transport of soluble toxicants in the surface and soil-water matrix

3.1.1

Database Search

As depicted in Fig. 2, the process starts with a database search to determine whether human health information, ecological toxicity data, or chemical data exist on the subject C&R material.

If data exist on the target material, the time and cost of generating data for the subsequent fate and transport model input are eliminated. In the cases when additional toxicity and chemistry data are required, assistance from specialized laboratories (e.g., universities, independent contractors, state laboratories) will be required.

3.1.2

Assessment Endpoints

Selecting assessment endpoints (e.g., a species, a functional group of species, a community or other entity of concern) are critical because they construct the

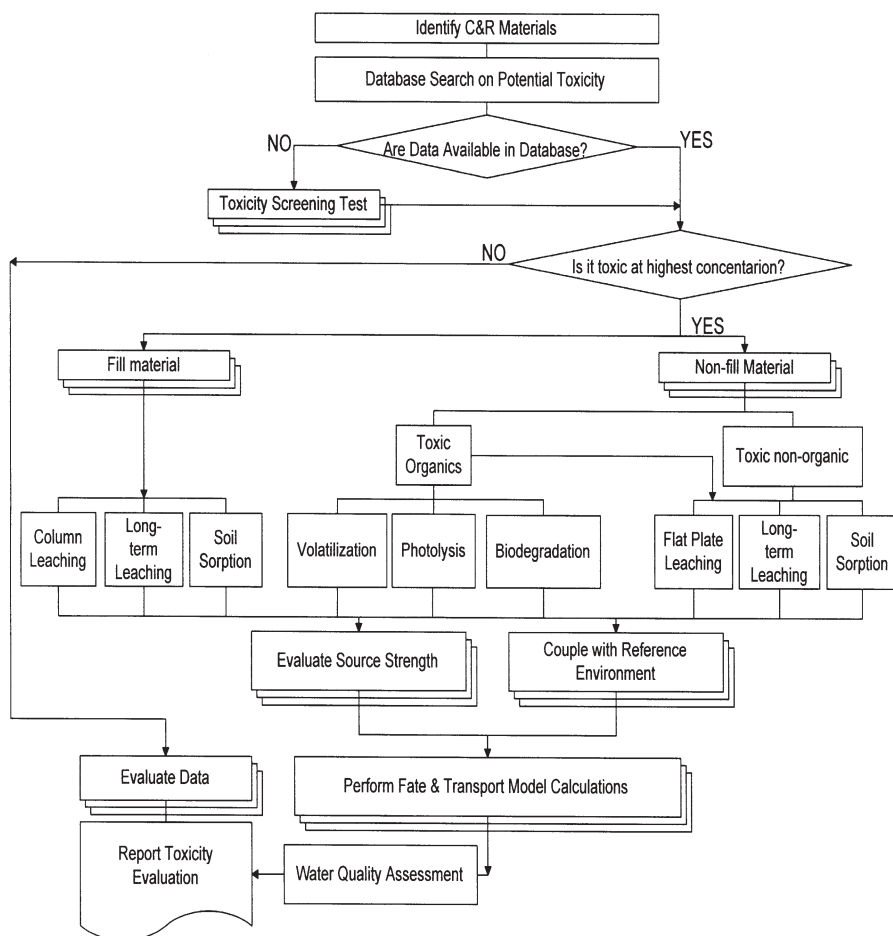


Fig. 2 The OSU evaluation framework for waste materials reuse/recycle in highway construction

assessment framework to address management concerns (protecting the quality of surface and groundwaters) and are central to conceptual model development. For this methodology, freshwater green alga *Selenastrum capricornutum* (currently known as *Raphidocelis subcapitata*) and freshwater macro invertebrate *Daphnia magna* were chosen as the test organisms. *Selenastrum capricornutum* represents plant species while *D. magna* represents animal species.

Some of the criteria used for choosing these test species for use in a toxicity test were sensitivity, ecological importance (in terms of trophic level), wide geographic availability, successful laboratory maintenance, indicator of receiving environment, recognition by environmental and other agencies, and availability of standardized testing protocols.

Freshwater microalgae are the primary producers in the aquatic food chain. Disruptions to this production base would probably cause adverse effects at higher trophic levels [14]. A review of Toxic Substances Control Act (TSCA) and U.S. EPA's ECOTOX databases show that the *S. capricornutum* is more sensitive than other standard test organisms to many common compounds [15]. *Selenastrum capricornutum* is the most frequently used species [16] and is the only plant species recommended by the U.S. EPA for monitoring the toxicity of effluents [17]. Standardized algal test methods currently used were developed during the past 20 years by a variety of organizations such as American Society for Testing Materials (ASTM), European Economic Community (EEC) or Organization of Economic Cooperation and Development (OECD), International Standardization Organization (ISO), American Public Health Association (APHA), and by the U.S. EPA [16]. These tests were designed to be conducted with easily cultured alga such as *Selenastrum capricornutum* that rapidly grows and can be easily enumerated.

Daphnia are one trophic level higher than algae in the aquatic food chain and are one of the most commonly used organisms in aquatic toxicity testing. Species used in our laboratory testing is *Daphnia magna* which are large, commonly available and easy to culture. Often daphnids are more sensitive than vertebrates to a variety of toxicants [18]. Standardized test protocols using Daphnia were also developed by organizations such as ASTM, U.S. EPA, ISO, APHA, OECD and EEC.

Furthermore, algae and daphnia are among the selected species required by various regulatory guidelines such as Clean Water Act (CWA), Toxicity Substance Control Act (TSCA), Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and Federal Food, Drug, and Cosmetics Act (FFDCA) for aquatic toxicity tests [19]. It was considered of critical importance that both a plant and an animal species be selected for testing highway C&R materials. Plants and animals have biological differences that would cause them to react differently (or not at all) to different chemicals.

3.1.3

Toxicity Screening

Test protocols for assessing the toxicity of C&R material leachates were initially developed and later refined as per the U.S. EPA methods [17, 20]. About 100 representative materials were screened for potential impact to the two target organisms, the water flea *Daphnia magna* and the freshwater algae *Selenastrum capricornutum*. Most C&R materials were tested in their "raw" form, not necessarily in the form in which they would be applied in the field. For instance, Portland cement and asphalt cement were tested, in addition to later tests in which they were mixed with aggregates to form Portland cement concrete and asphalt concrete. These tests simulated the worst-case scenario. In general, toxicity tests expose living organisms to materials of concern, and measure the effect in terms of mortality or growth inhibition. Test samples for screening

were prepared for testing by vigorously shaking C&R materials with deionized water at the weight ratio of 1-solid to 4-liquid for 24 h. Samples prepared in this manner represent an extreme, full-strength concentration for the purpose of toxicity screening. If a material does not show toxicity under this worst case scenario, the material can safely be considered nontoxic. Under normal conditions, leaching during wet weather occurs only as a result of the rainwater running on the exposed, flat surfaces of a given material. Resultant leaching has been found to be much less than for the extreme batch tests.

For each material, the leachate is filtered, and the filtrate is then evaluated for toxicity in two primary ways:

1. The aquatic macro-invertebrate *Daphnia magna* (water flea) is exposed to varying concentrations of the leachate, and the concentration (LC₅₀) at which there is 50% mortality is determined as a percentage of the full-strength solution.
2. A similar test is performed on the freshwater algae *Selenastrum capricornutum*, and the concentration (EC₅₀) at which there is 50% inhibition of growth (relative to growth in a control solution) is determined as a percentage of the full-strength solution.

3.1.4

Evaluation Plan and Conceptual Model

Based on the preliminary toxicity results of a waste material and its potential application in the highway environment (e.g., pavement, fill, pile, etc.), a plan for a detailed evaluation of the material and a conceptual model for the particular reference environment are developed. As depicted in Fig. 2, if the test results show no toxicity, no further investigation is required. If the screening tests show toxicity, tests for evaluating the source strength and the effects of reference environments on toxicity and chemistry of the C&R material leachate are performed. The leaching and fate and transport tests required only for the appropriate reference environments are conducted. For example, flat plate leaching is not required for material that will only be used in a fill application.

3.2

Detailed Evaluation

Detailed evaluation is performed to improve the understanding of the leaching processes, source terms, and environmental degradation processes of the material. The critical components of the detailed evaluation phase are: measuring potential contaminant releases from the target material; evaluating contaminant fate and transport as influenced by the environmental removal, reduction, and retardation (RRR) factors and evaluating effects of these contaminants using standard organisms in the laboratory.

Leaching refers to the assimilation in highway stormwater runoff of chemicals and toxins contained in various C&R materials. For purposes of evaluation

of environmental impact, leaching is the process whereby initial concentrations are generated in the runoff (source term). In order to account for the several possible reference environments, three mechanisms were used to study the leaching process: batch (shake tests), column tests, and flat plate tests. The leaching tests are described briefly in the following section. Detailed procedures for these tests are included in Nelson et al. [4].

3.2.1

Leaching Methods

3.2.1.1

Batch Leaching Test

The short-term (24-h) batch leaching test also is conducted to provide leachate (source term) for RRR tests, including volatilization, photolysis, biodegradation, and soil sorption. The leachate is analyzed during the screening process and is utilized to determine the RRR model coefficients. Analysis of the leachate during the toxicological and chemical screening process provides the chemical composition and toxicity data needed for initial evaluation of the test material. This evaluation aids in the scheduling of experiments for each test material. For example, if a material is found to be composed of mostly inorganic matter, then the biodegradation, volatilization, and photolysis experiments are generally not required, as these RRR processes will not affect inorganic chemical concentrations.

For the batch leaching experiments, the resulting data were modeled as

$$C = C_a (1 - e^{-kt}) \quad (1)$$

where C is concentration of leached chemical at time t , t is time of leaching, and C_a and k are coefficients.

The use of Eq. (1) offers the advantage of only two fitting coefficients, a and k . Spreadsheet programs can easily solve such regression equations. However, not all of the leaching curves have proven to be readily fit with this equation. More complex models, such as using two terms, one for the short-term release and one for the long-term release, would provide closer fits over the entire range of the test. However, such models would require much more extensive methods of coefficient estimation.

3.2.1.2

Flat Plate Leaching Test

The flat plate test determines the leaching rate from a defined surface where mass transfer across a solid/liquid boundary controls the leaching or flux rate (expressed in $\text{mg}/\text{cm}^2 \text{ h}$). The flat plate test focuses on release by diffusion from surface pavement construction materials in a simulated on-site experiment. The test material is formed into a 10 cm diameter disk using the Marshall

method of specimen preparation (50-blow compaction) and immersed in 1 l of distilled water in a glass beaker. The material is leached into the water phase, which is continually mixed above the flat plate with a paddle stirrer. Increasing concentrations of the contaminant are measured chemically with time. The flux rate of the compound of interest across the diffusion-controlled surface can then be determined. This flux will represent the transport of chemicals from an in-place, flat and compacted material surface, such as a highway surface.

The flux of contaminants ($\text{mg}/\text{cm}^2 \text{ h}$) is determined by the increase of concentration in the overlying water as a function of time. An exponential function is used to represent the flat plate data. The equation for increase of the concentration of leachate metals or organics is given as

$$C = a t^k \quad (2)$$

where C is total concentration of metals or organics (mg/l), t is leaching time (h), and a and k are coefficients.

The flux, F , of the contaminants is calculated as

$$F = (V/A) dC/dt \quad (3)$$

where F is flux ($\text{mg}/\text{cm}^2 \text{ h}$), V is leachate volume (l), and A is surface area (cm^2).

3.2.1.3

Column Leaching Test

The column experiment is used to simulate the reference environment where the crushed test material (by itself or mixed with an aggregate) is used as a fill material. The laboratory column is filled with the test material and distilled water is pumped through the column. The contaminants are leached from the test material into the flowing water. The concentration of the contaminant of concern is at a peak at the beginning of the test and decreases with time. Hence, sampling should occur more frequently at the beginning of the experiment, depending on the column flow rate and the flux rate of the leached contaminant.

The concentrations of leached contaminants appearing in the effluent from the column are measured over time and the results are plotted in the form of leachate breakthrough curves (C_{metals} or C_{organics} vs time). The effluent concentrations for different flow rates generally follow first-order kinetics, as shown in Eq. (4), with the coefficients fitted by linear regression of the log-transformed equation,

$$C = C_0 e^{-kt} \quad (4)$$

where C is concentration of metals or organics at time t , C_0 is initial concentration at time 0, t is time, and k is first-order leaching rate constant.

The cumulative mass of metals and other leached contaminants appearing in the effluent from the column is measured in terms of number of pore volumes (PV) passed through the column and was determined to follow Eq. (5):

$$M = m (\text{PV})^p \quad (5)$$

where M is mass of metals or organics (mg), m and p are constants, and PV is the number of pore volumes.

Equation (5) can also be used to estimate the cumulative mass of metals and other leached contaminants appearing in the column effluent if time (t) is substituted for number of pore volumes (PV), as t and PV are directly related.

3.2.2

RRR Process Methods

Batch leachate samples (24-h short-term test) are tested for various removal, reduction, and retardation (RRR) processes likely to be encountered as runoff moves away from the highway area. For removal, reduction, and retardation (RRR) process tests, soil sorption tests are conducted for both fill and non-fill materials, while volatilization, photolysis, and biodegradation tests are conducted only on non-fill materials that have organic compounds in their leachates. RRR process tests are described briefly in this following section. Detailed procedures for these tests are included in Nelson et al. [4]. The following is a summary of the test procedures.

3.2.2.1

Soil Sorption

Batch tests (i.e., tests on individual samples) are conducted with soil-plus-leachate suspensions using the standard test soils. The soils are prepared from air-dried samples, sieved through 1/4" screen for mixing with the leachate from the 24-h batch leaching test. The concentrations of leachate in the solution are designed to evaluate the capability of environmental soils to adsorb available contaminants. The soil particles must be fully dispersed within the aqueous phase to achieve complete adsorption.

The adsorption isotherm is obtained from a series of batch reactor data relating equilibrium mass of chemical adsorbed (C_s , mg/g of soil) to equilibrium concentration of the leachate contaminant in solution (C , mg/l). The blank/control sample is the leachate without any soil present. Defining the initial concentration of the contaminant in the leachate solution (without any soil) as C_o , the adsorption mass ratio, C_s (mg/g), is computed as follows:

$$C_s = \frac{(C_o - C)V}{M} \quad (6)$$

where V is volume of aqueous phase (about 1000 ml) and M is soil mass (typically varying from 50 to 250 g).

The values of C_s are plotted as a function of the equilibrium concentration, C . For constituents at low or moderate concentrations, the relationship between C_s and C can be expressed as a Freundlich isotherm, as shown in the following equation:

$$C_s = K_f C^N \quad (7)$$

where K_f and N are coefficients that depend on the constituents, nature of the soil, and interaction mechanisms established with the contaminant.

If N is equal to 1, the C_s vs C relationship will be linear, i.e., the graphical plot will show a straight line. A linear adsorption isotherm is described by the equation

$$C_s = K_d C \quad (8)$$

where K_d is equal to the slope of the linear sorption isotherm and is called the distribution or partition coefficient (l/kg), and is commonly used to describe contaminant partitioning between liquid and solids for hydrophobic organic compounds.

The Langmuir isotherm is based on the concept that a solid surface possesses a finite number of sorption sites. When all the sorption sites are filled, the surface is saturated and will no longer sorb solutes from solution. The Langmuir isotherm is given by

$$C_s = \frac{QbC}{(1 + bC)} \quad (9)$$

where C and C_s are as defined above, Q is the maximum sorption capacity of the surface (mg/kg), and b (l/mg) is a constant related to the equilibrium free energy of adsorption.

3.2.2.2

Photolysis

Photolysis is pollutant oxidation induced by sunlight energy resulting in irreversible alterations of the molecules. Through photolysis, light can affect the chemical composition and toxicity of organic compounds that comprise the total organic carbon (TOC) leached from C&R materials. The rate at which a pollutant photochemically degrades depends on numerous chemical and environmental factors such as the light absorption properties and reactivity of a compound, the light transmission characteristics, and the intensity of solar radiation. For example, polycyclic aromatic hydrocarbons (PAHs) containing three or more rings are able to absorb radiation strongly in the UV-A (320–400 nm) and UV-B (290–320 nm) regions of the solar spectrum. To study the photochemical changes of the substances in leachate in a controlled manner, the use of artificial lighting is required. This study exposes the leachate to a Xenon arc lamp to mimic solar radiation at about 30 Watts/m² in a 20 °C constant temperature room. This light intensity is about one tenth the intensity of ambient sunlight. The control consists of leachate under equivalent conditions without exposure to the light source and stored at 4 °C.

Assuming a first order loss rate, the data are modeled as

$$C = C_0 e^{-k_p t} \quad (10)$$

where C is concentration at time t , C_0 is initial concentration at time 0, t is time, and k_p is first-order rate constant, $1/\text{time}$.

The model coefficients are determined from a linear regression of the $\ln C$ vs t plot.

3.2.2.3

Volatilization

Theoretically, the rate of mass transfer of organic materials from C&R materials is proportional to the difference between the saturation (equilibrium) concentration in the atmosphere and the existing concentration in the leachate solution. The exact organic compounds volatilizing to the atmosphere have not been determined, but it is safe to assume that their atmospheric concentrations are close to zero. Hence, the flux across the water-air interface is a first-order process, commonly assumed for environmental conditions. The volatilization experiments are conducted with 24-h batch leachate placed into 1-l glass beakers. The beakers were placed in a 20 °C controlled temperature room and the test solutions continuously sparged with air at a flow rate of 250 ml/min. Samples were taken daily from the glass beakers and analyzed for toxicity and chemical content. The solution volume was kept constant by adding distilled water after each sampling. The control consisted of leachate under equivalent conditions without sparging with air source and stored at 4 °C. Stated mathematically, the volatilization flux is given as

$$r_c = K_L C \quad (11)$$

where r_c is rate of mass transfer of organic volatilization ($\text{mg}/\text{m}^2\text{-h}$), K_L is surface exchange coefficient (m/h), and C is concentration of organic contaminant in solution (mg/m^3).

Assuming a first order rate process as implied by Eq. (11), concentration vs time can be modeled as

$$C = C_0 e^{-k_v t} \quad (12)$$

where C_0 is initial concentration of organic at time $t=0$ (mg/m^3), C is concentration of organic at time t (mg/m^3), k_v is first-order volatilization rate ($1/\text{h}$) = K_L/h , and h is depth (m).

The model coefficients, C_0 and k_v , are determined from a linear regression of the $\ln C$ vs t plot.

3.2.2.4

Biodegradation

Biodegradation is a process by which organic compounds can be degraded aerobically and/or anaerobically by microorganisms. In general, microorganisms are ubiquitous in the subsurface environment and actively catalyze reactions through enzymatic activity. The rate at which a compound biodegrades in the

subsurface environment depends mainly upon the availability of a suitable electron acceptor and the presence of appropriate microbial consortia. The purpose of this laboratory experiment is to examine the removal of toxic organic compounds associated with construction and repair materials in an aerobic degradation process.

Test material leachate is inoculated with fresh primary settled sewage and a nutrient feed solution to promote degradation. A control reactor consists of leachate under equivalent conditions without inoculation with microorganisms. Assuming a first order biological degradation rate, the data are modeled as

$$C = C_0 e^{-k_b t} \quad (13)$$

where C is organic concentration at time t , C_0 is initial organic concentration at time 0, t is time, and k_b is first-order biological decay constant, 1/time.

The model coefficients are determined from a linear regression of the $\ln C$ vs t plot.

3.2.3

Chemical and Biological Analysis

For all leaching and RRR process tests, samples are taken as a function of time to assess changes in chemical characteristics (presence and concentration of toxicants) and corresponding biological toxicity (algal chronic toxicity bioassay and daphnia acute toxicity bioassay).

3.2.3.1

Chemical Analysis

A summary of chemical methods used in support of leaching and RRR tests is presented here for reference purposes. Detailed procedures for these tests are included in Nelson et al. [4] as follows:

- ICP: Inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian Liberty 160) is used for determination of multiple metals.
- IC/HPLC: The concentrations of selected major anions for 24-h leachate are determined by ion chromatography (Dionex Series 4000 i Ion Chromatograph [IC] equipped with conductivity detector). The concentrations of selected organics in 24-h leachate are determined by high pressure liquid chromatography (HPLC) (Dionex Series 2000 i equipped with UV-VIS detector).
- TOC: Total organic carbon (TOC) is analyzed in accordance with the procedures specified by the manufacturer (model DC-190, Rosemount Analytical, Inc., Dohrmann Division) as well as those in Standard Methods 505A: Organic Carbon (Total): Combustion-Infrared Method.
- GC/MS: Extraction of organic chemicals from the leachate is performed according to EPA methods 1624 and 1625 (Gas Chromatography-Mass Spec-

trometry Methods for Analysis of the Volatile and Semi-volatile Organic Priority Pollutants.

- GC: A Hewlett-Packard (HP6890 plus) gas chromatographic with a flame ionization detector (FID) and MS 5973 detector is used for target analytes qualification and quantification.

3.2.3.2

Biological Analysis

A description of toxicity methods used in support of leaching and RRR tests is presented here for reference purposes. Detailed procedures for these tests are included in Nelson et al. [4] as follows:

- Algae (*Selenastrum capricornutum*) Chronic Toxicity Test: An algal chronic toxicity test is performed by placing 50 ml of leachate into each of the three replicate 125-ml Erlenmeyer flasks to obtain a leachate series of five concentrations, from 0 to 80%. The test flasks are inoculated with algae at a final concentration of 10,000 cells/ml and are incubated in an environmental growth chamber for 96 h. Algae cultured in algal assay medium served as the controls. Samples (1 ml) are transferred from each of the flasks to counting beakers and transported to where they are counted with an electronic particle counter to define the concentration of leachate that inhibits 50% (EC_{50}) of the algal population growth relative to the algal population in the control cultures. The concentration is expressed as percent of full-strength leachate. Thus, a lower percentage implies greater toxicity.
- Macroinvertebrate (*Daphnia magna*) Acute Toxicity Test: A daphnia acute toxicity test is performed by placing 50 ml of leachate into each of three replicate 100-ml beakers to obtain a leachate series of logarithmic concentrations from 0 to 100%. Each beaker is inoculated with ten daphnids. The test beakers are covered with glass watch covers and placed into an environmental chamber. The test is incubated for 48 h. After incubation, the beakers are examined to determine the concentration of leachate that killed 50% (LC_{50}) of the daphnia relative to the surviving population (30 daphnids) in the control cultures. Again, a lower percentage for the LC_{50} value implies greater toxicity.

3.2.4

Model Development

The mathematical model IMPACT [21] is for use in the near-highway environment, i.e., over a scale of meters, and consists of fate and transport analyses related to removal, reduction, and retardation (RRR) processes, plus generation of initial pollutant loadings. More specifically, the transport processes of advection and dispersion (in soil) are coupled to the RRR processes of sorption, biodegradation, photolysis and volatilization. Model output consists of flows, loads (mass), concentration of surrogate chemical (surrogate for toxicity), and toxicity of tested C&R materials in their appropriate reference environments.

Leaching rates in the model are based on the appropriate reference environment; flat plate results are the most appropriate for the highway surface, piling, borehole, and culvert reference environments, while column leaching is appropriate for the fill reference environment. In addition, the model simulates lateral movement away from the highway edge in a shallow aquifer, if desired. Hydrologic response to rainfall is simulated simply using a runoff coefficient and surface roughness values characteristic of highway surfaces, and infiltration through a paved surface may optionally be determined based on empirical studies of cracks. Infiltration into soil (including the highway sub-base) is based on soil properties such as hydraulic conductivity and porosity. While a constituent remains on the land surface, the process of volatilization and photolysis may degrade it. Because the surface residence time of the highway runoff is typically very small, on the order of seconds in the absence of ponding, these two processes are unimportant degradation mechanisms based on data currently available. Biodegradation will continue along subsurface pathways, but is also unimportant for most of the constituents studied in this project because the important toxicity-causing metals do not biodegrade (or volatilize or photolyze).

Hence, the most important RRR process is sorption. The model uses an explicit finite difference scheme to simulate the changes in concentration of the constituent as it migrates through the soil and is subject to advection, dispersion, sorption, and biodegradation (the latter is included for constituents for which this process may be important). As leaching rates decrease with time and cleaner water infiltrates the soil, the desorption process is also simulated. Single-event or long-term (hourly or 15-min) rainfall data may be used to drive the fate and transport simulation. At the bottom of the soil profile, the model predicts flows, concentrations and loads (product of concentration and flow) of the surrogate chemical, and associated toxicity. Surface and subsurface loads and flows may be used as input to surface or subsurface receiving water quality models, if desired. The model may also be run for multiple subsurface soil layers, with differing properties. In this case, outflow from an upper layer serves as inflow to the lower layer.

4 Discussion

The evaluation methodology, as discussed in the previous section, is a simple framework with tiered testing and measurement including chemical and biological assessment, and fate and transport modeling components to estimate potential environmental risks of C&R materials in a highway environment. As a unique screening and evaluation tool it has been organized to help transportation and environmental officials make informed decisions regarding environmental suitability of C&R materials of concern. In developing the methodology, concerted efforts have been made to integrate important components of the U.S.

EPA risk assessment framework and establish a common approach with its paradigm. The U.S. EPA's overall ecological risk assessment process is illustrated in Fig. 1. It consists of three basic elements: Problem Formulation, Analysis, and Risk Characterization.

4.1

Problem Formulation

This step is of fundamental importance as it establishes the scope and direction of the overall assessment. It basically identifies the actual environmental values to be protected (assessment endpoints) and selects methods by which these can be measured and evaluated (measurement endpoints).

4.2

Analysis

The analysis phase is directed by the products of the problem formulation and is further divided into characterization of exposure and characterization of effects steps. Exposure characterization uses the properties of the chemicals and the receiving environment to estimate the extent to which the organisms will be exposed. Effects characterization determines the effects of varying dose or other measures of exposure on organisms, populations or communities.

4.3

Risk Characterization

The effects of exposure and effects assessments are integrated to estimate the magnitude of and the likelihood of ecological risks. These results are fed to risk management processes in which the results are combined with engineering feasibility studies, cost-benefit studies, and political and legal considerations to arrive at a decision about potential ecological risks.

The planning and scoping process defined in the screening phase of the methodology are consistent with the problem formulation phase defined in the U.S. EPA's framework. For instance, problem identification, data gathering, selection of assessment endpoints and development of conceptual model and analysis plan are well described in the screening phase of the methodology.

The strength of the methodology is the arrangement of testing and assessment in tiers. Tiered or phased approach is generally agreed to be the best for evaluating exposure and effects assessment. It is based on iterative process of testing and assessment. At each step, based on data from toxicity tests and measurement of properties of chemicals a decision is made about the hazard based on formal decision criteria or scientific judgment. If more data are sought then the decision is deferred until the next tier of testing and measurement.

Thus, a decision is reached as soon as the available data are believed to be sufficient to make a scientific judgment. This process minimizes time and cost

by beginning with readily available data. In the OSU methodology, when required data are not available in the literature the data collection starts with a simple screening test and continue with additional tests depending on the target material and its potential application in the highway environment. The risk assessment paradigm, however, does not explicitly include tiered testing and measurement.

The detailed evaluation tests that are conducted depend whether the subject material is intended for use as a fill material or a nonfill (e.g., pavement or piling) material and the possible environmental factors that are likely to affect the leachates fate and transport (exposure pathway). Source-term leaching tests that are conducted for fill material include column leaching and long-term leaching, while those conducted for nonfill materials include flatplate leaching and long-term leaching. For evaluation of RRR process, soil sorption tests are conducted for both fill and nonfill materials, biodegradation tests are conducted for both fill and nonfill materials that have organics in their leachates, while volatilization and photolysis tests are conducted only on nonfill materials that have organics in their leachates.

For leaching and RRR processes tests, samples are taken as a function of time to assess changes in chemical characteristics (presence and concentration of toxicants) and in toxicological characteristics (algal chronic and daphnia acute effects). Chemical and toxicity data are then fit to the leaching and RRR process model equations by regression methods. Leaching and RRR process models are then coupled with a highway reference environment and evaluated using fate and transport model. The model then computes the likely concentrations and loads of mobile toxicants at the highway boundary (on the scale of meters from the source).

Thus, approaches for evaluating exposure and effects include measuring contaminant releases from leaching tests (source strength), evaluating fate and transport processes of the released contaminants (exposure pathway) and testing algal growth and daphnia mortality (measures of effects) due to these contaminants. The stressor-response relationship was described using the results of toxicity tests. These toxicity tests are used to measure toxicity statistical endpoints algal EC_{50} , the concentration at which there is 50% inhibition in growth, and daphnia LC_{50} , the concentration at which there is 50% mortality in daphnia population.

Risk characterization involves integrating exposure and effects information. The exposure and effects are considered together because they are both important in estimating risk. In general, risk estimation tends to rely on professional judgment based on certain "decision criteria" or formal mathematical and statistical models. The U.S. EPA guidelines provide a flexible and non-prescriptive approach in the estimation of risk. The risk estimates can be developed using one or more of the following techniques: (a) field observational studies, (b) categorical rankings, (c) comparisons of single point exposure, (d) comparisons incorporating the entire stressor-response relationship, (e) incorporation of variability in exposure and effects and/or estimates, and (f)

Table 1 Characterization of impact categories based on toxicity to aquatic organisms

EC50 or LC50	Impact category
≤10%	Extremely high
>10% to ≤20	High
>20% to ≤75%	Moderate
>75% or inhibition	Low
No observed toxic effect	No impact

process models that rely partially or entirely on theoretical approximations of exposure and effects [5].

The OSU methodology, in its current version, does not prescribe any probabilistic or statistical method for quantitatively estimating risk. However, it provides a basis for making scientific decision on the possible impact of C&R material on surface and ground waters. The OSU methodology prescribes an original approach using the LC₅₀ and EC₅₀ data for making a decision on the level of aquatic impact. The impacts are categorized as “extremely high” to “no impact” according to the ranges of LC₅₀ and EC₅₀ values identified in Table 1. Also, data generated from the evaluation tests and from corresponding model outputs can readily be used in the U.S. EPA’s risk estimation techniques (c) and (d) described above. Furthermore, the IMPACT model can be used to provide concentrations (exposure) and corresponding toxicity (effect) to other probabilistic or statistical models should complex risk estimation methods are needed.

5 Conclusions

A complete methodology for the screening and evaluation of environmental impacts of highway construction and repair materials on surface and ground waters has been developed and validated. The evaluation methodology incorporates a review of existing test data from the literature, a toxicity screening test for preliminary assessment of a proposed material in raw (unamended) form, and a detailed evaluation procedure that incorporates laboratory tests for leaching (source term) and environmental processes coupled with a simulation model for the near-highway environment. Leaching tests include short and long-term batch extraction procedures, a flat plate test for pavement materials (asphalt or Portland cement concrete), and a column test for fill materials. Environmental process tests include soil sorption, volatilization, photolysis, and biodegradation. The leaching tests describe the *source terms* (quantification of characteristics of leachate, such as the constituents released, the chemical matrix, the rate of release) and the potential for ecological risk, i.e., *hazard assessment* of industrial wastes used in highway construction. The analysis

phase of the ERA framework, evaluates both exposure and effects data. Environmental removal, reduction, and retardation (RRR) tests combined with an integrated chemical and biological assessment prescribed in the OSU methodology contribute substantially to characterizing the exposure and ecological effects of leachate constituents. The final phase of the ERA framework is risk characterization that builds upon the results of the analysis phase to develop an estimate of risk, in particular to the assessment endpoints.

A simple toxicity based approach that categorizes the level of potential aquatic impact based on LC_{50} and EC_{50} is used for risk assessment by the OSU methodology. The current scope of the evaluation methodology does not incorporate complex probabilistic or statistical models for risk estimation. Individually, the evaluation methodology can be appropriately used as a predictive tool for hazard assessment in the receiving surface and ground waters. Also, together with probabilistic and statistical tools, the methodology can possibly extend its stated purpose of screening and evaluation tool for environmental impact assessment to probabilistic or statistical risk assessment.

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Leaching from Residues Used in Road Constructions – A System Analysis

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Abstract When residues such as municipal solid waste incineration slag are used as construction materials they are commonly enclosed in a technical construction, which acts as a barrier. This will limit the exposure to water and the atmosphere and thereby delay the resulting leaching process. From a risk assessment perspective there is a great need to qualitative analyze the technical construction, its function, relevant emission scenarios and boundary conditions. The objective is to give a description of the processes and events that are crucial for assessing the leaching of contaminants from roads where residues are used as construction material. One method to describe a complex system is by using *interaction matrices*. The function of the system is broken down into a number of important components, properties and processes through a top-down approach. The method has successfully been used within rock engineering and nuclear waste disposal research, and is here employed on the use of residual materials in road constructions. Based on the analysis of the

system it is concluded that a road ought to be treated as an integrated system instead of treating the system components and processes separately. The role of the road shoulders as water and gas vents remains as the most important mechanism governing emissions from roads where residues are used as an alternative unbound material.

Keywords Road · Residues · Water · Emission

1

Introduction

The linear processing of natural resources is the fundamental error in today's non-sustainable societies. Non-renewable energy resources are used to extract and refine basic material from limited deposits and to manufacture products, which under a short period of time are degraded to waste or residues [1].

Aiming at saving natural resources, residues may be recycled as alternative materials for building and construction purposes. However, at the same time the use of residues such as incineration ashes or crushed concrete may jeopardize the goal of environmental protection since it will imply a risk for environmental impact due to the leaching of contaminants. The alternative fate for these residues is disposal in landfills, which will not be in compliance with the goal of resource conservation but it may reduce the risk for environmental impact in a short time perspective. In a long-term perspective though, the technical barrier will inevitable break and the contaminants will be released.

The leaching behavior of residues is commonly characterized through leaching tests. The results from these tests reflect conditions that in general only are representative on a small spatial scale and a short temporal scale. The aim of predicting leaching processes over a longer period of time under field conditions raises some questions concerning the applicability of the lab test data. A number of parameters may differ if lab and field conditions are compared [2]: temperature, pH, redox conditions, geometry of the material (shape and dimensions), flow field, solute transport volume, the surface area of the solids exposed to water, exposure time and the spatial variability encountered in field-scale. It is also important to acknowledge that when residues are used as construction materials they are commonly enclosed in a technical construction, which acts as a barrier. This will limit the exposure to water and atmosphere and delay the resulting leaching process.

To conclude, the assessment of the risk for a severe environmental impact associated with utilization or disposal of residues requires a detailed qualitative characterization of the system itself. The system is defined by the technical construction (road, landfill, etc.) and the governing chemical and physical processes that control the release of substances from residues under a variety of conditions, spatial and temporal scales. The relevant time span to consider here is of the order of 50 years, which corresponds to the length of life for a road. Meth-

ods and tools, such as substance flow studies and life cycle analysis [3], which incorporate more specific issues into a larger context, are needed in order to successfully balance between the goals of resource conservation and environmental protection.

The objective here is to give a qualitative description of the processes, events, emission scenarios and boundary conditions that are crucial for assessing the leaching of contaminants from a road construction where residues are used as construction material. The function of the system is broken down into a number of important components, properties and processes through a top-down approach. By analyzing these and their interactions a conceptual model can be developed. The conceptual model represents a qualitative description of the system including initial and boundary conditions, state parameters (such as physical and chemical properties of the medium, pH, redox, etc.), processes (water flow, dispersion, diffusion, precipitation/dissolution, sorption, degradation, etc.), their interactions and influence on events and impacts at the system boundary. Based on the conceptual model, mathematical models may be developed with the purpose of testing hypotheses and assumptions made in the conceptual model and, ultimately, to predict emissions.

In order to make quantitative description of a system, simplifications have to be made. The complexity of the system, as described in the conceptual model, must be reduced to something that can be handled mathematically. Still it must be complex enough to capture the essence of the system characteristics. Obviously there is not a unique way of developing a conceptual model based on the available basic information and there is not a unique way of developing a mathematical model based on the conceptual model.

The uncertainty in predictive modeling may be attributed to uncertainty in the design of the conceptual model, uncertainty and variability in the input parameters and limitations in the mathematical models and numerical algorithms. The uncertainty in the input parameters is due to limited data and knowledge, while variability is caused by short or long range variations in time and space. Parameter variations in time may be a result of slow changes of the physical and chemical properties (aging) and variations of the boundary conditions such as rain fall, temperature, mechanical impact etc. The spatial variations are due to the heterogeneity (in different spatial scales) of the material. These heterogeneities may exist initially or arise with time.

The relative effect of the uncertainties above on the performance of the mathematical model depends on the system but the uncertainty in the conceptual model dominates in many cases. The effect of parameter uncertainty and variability depends on the system, and is to some extent possible to quantify by sensitivity and uncertainty analysis. However, uncertainty in the conceptual model is difficult to assess. A qualitative systematic description of the physical and chemical processes, their importance and interactions, and boundary conditions is necessary in order to minimize the uncertainty in the conceptual model.

One method to systematically describe a process system qualitatively is by using *interaction matrices*. The method has successfully been used within rock engineering and nuclear waste disposal research and is employed here to identify crucial process interactions and emission scenarios.

2

Use of Interaction Matrices for Identifying a Complex System

2.1

The Method of Interaction Matrices

The method of interaction matrices was originally developed for analyzing complex rock mechanics [4]. The method has been used for describing and analyzing the emission scenarios associated with the final deep storage of nuclear waste [5] and has also been proposed as a powerful tool for analyzing the emission processes in landfills [6]. The method implies that the processes and their interactions are arranged in a matrix. The procedure promotes an integrated approach; it defines important processes and interactions and identifies crucial scenarios.

The method is a top-down approach based on a combination of graphs and underlying documentation. The overall objective is broken down into a number of important components, properties and state parameters. These are arranged as diagonal elements in the matrix. The other elements represent interactions between the diagonal elements (see Fig. 1). The diagonal elements can be composed of boundary conditions, components of the technical construction, and chemical and physical state parameters. The internal processes, interactions that define the function of the system are identified in off diagonal elements in the matrix.

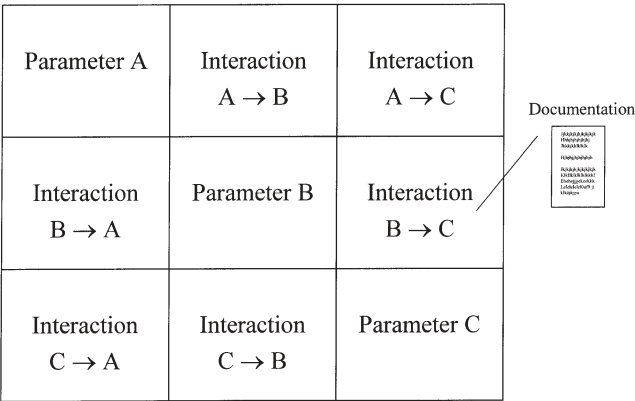


Fig. 1 Principles of an interaction matrix [5]

All interactions are documented in a database using special protocols, including a detailed description of the process including cause and effects, qualitative assessment of its importance and literature references. In this study the description of the diagonal and interaction elements are made in a less formal way.

Examples of external impact on the system are rain, temperature, erosion, etc. The external impact(s) propagates through the system via the internal processes, which has been defined in the off diagonal elements in the interaction matrix. The consequence of a certain external impact or event are clearly described and demonstrated in the interaction matrix. Another type of external impact is unexpected events, which is not a part of the normal conditions.

2.2

Construction of an Interaction Matrix

There is no unique way of setting up an interaction matrix. However, a rule of thumb is to define the diagonal elements so that the processes are extracted from the leading diagonal out to the interaction elements. The number of diagonal elements defines the resolution of the matrix. The method of interaction matrices is suitable for building up a hierarchical system of matrices where every diagonal element is represented of a sub-matrix on the next higher level of resolution. In this way, the level of resolution may be increased or decreased depending on the complexity of the system and the objective of the analysis. At higher resolution the complexity in the interaction elements decreases. At the highest level of resolution, basic physical and chemical processes at nano-scale describe the interactions. The choice of matrix resolution level is a matter of balancing between capturing the essence of the governing processes vs maintaining simplicity and clarity. The general procedure for constructing an interaction matrix is summarized below [5, 6].

The first step is to define the system with respect to system components, physical boundaries, initial and boundary conditions, as follows:

- Definition and description of the diagonal elements
The diagonal elements have to be chosen and arranged in a logical and consistent way in order to facilitate the identification of the interactions; the diagonal elements are preferable arranged so that well-defined interfaces to any adjacent systems are created
- Identification of the diagonal elements and their interactions
Each interaction, its cause and effect, should be described carefully; it is important to be consistent in the definitions and make sure that the actual interaction is a direct interaction between two diagonal elements and that the interaction does not involve another diagonal element as an intermediate step
- Identification of external impacts on the system
External impacts are those, which are associated with the normal conditions as defined by the boundary conditions, but also unexpected features, events

- or process that is not a part of the normal state of the system; the system response to an external impact propagates through the matrix via the interaction elements
- A qualitative assessment of the significance and importance of the interactions
 - It is important that the assessment criteria and principles are documented
- Selection and description of relevant scenarios
 - The most important or critical pathways can be identified by choosing relevant scenarios and by tracking the impact of a certain feature, event or process as it propagates through the system

3

Pavement Construction

3.1

Design and Material

A pavement structure is built in several layers, which from top-down roughly could be categorized into bitumen bound layers (asphalt and an upper road base), unbound layers and subgrade/embankment. Although residues may be used in all layers they have their largest potential as alternative materials in the unbound pavement layers.

Residues that have a significant potential as alternative materials in the unbound material layers are slag from incineration of coal or municipal solid waste and slag originating from the iron and steel manufacturing process, such as blast furnace slag and electric arc furnace slag, and crushed concrete. High concentrations of trace elements characterize most residues and distinguish them from natural materials. These elements are of major environmental concern. The dissolution of trace metals and the subsequent transport process is strongly affected by pH. Residues generated in thermal process and crushed concrete have in common that they are moderately to strongly alkaline. The development of pH depends on the input of protons to the system by acid rain, the supply of protons due to oxidation of sulfides or any organic material and the buffering capacity of the material at different levels. With exception of heavy metals and metalloids that may exist as anionic hydroxo complexes (e.g., Pb, Zn, Cu, Fe, Al, Cr) and anionic oxo complexes (e.g., Mo, As, V, Cr), the solubility of heavy metals is often low in alkali solutions but increases as the buffering capacity is consumed and the solution becomes acid.

At particle scale, leaching of contaminants occurs through a sequence of processes including: transport of the reactant to mass transport boundary layer, diffusion through the boundary layer and micropores to the external and internal reaction surfaces, attachment on the surface, chemical surface reaction(s), detachment of the reaction products and finally the transport out into the bulk solution. The slowest process will govern the overall dissolution rate.

Residues from thermal processes are thermodynamically unstable and react when exposed to water and atmosphere to form more stable mineral phases. The dissolution and weathering of the solid phase and the chemical conditions of the aqueous phase are governed by hydrolysis/hydration, acid-base and redox reactions.

The physical properties of the pavement structure influence the way and the extent to which the unbound materials become exposed to water and air. Air contains acid gases (CO_2 , SO_2) and strong oxidants (O_2), which may react with bases and reductants of the material, respectively, and influence the chemical environment.

The influence of the degree of exposure to air and the resulting pore gas composition is one likely reason for the different leaching behavior when comparing leaching at different scales and experimental setups. For example, different pH levels were observed when comparing a number of leaching experiments carried out on blast furnace slag [7, 8] and steel slag [7, 9, 10]. Here, carbonation and oxidation of sulfides, governed by the exposure to atmosphere, are important processes that control the development of pH. The experiments were performed with the same material but in different scales and experimental setup; columns (saturated and unsaturated), lysimeters placed outdoors on the ground and also lysimeters installed underneath an unpaved road. The varying degree of exposure to oxygen may also reflect itself in varying leachate concentrations of redox sensitive trace elements, such as Cr.

3.2

Road Hydrology

In addition to being a solvent, a reaction and a transport medium water influences the gas transport, and in turn the redox conditions, in porous media. The distribution and movement of water obviously becomes an important factor for leaching of contaminants. Unfortunately only very limited data exists on the movement of water in roads. Studies of water movement in roads were identified as an important future research area in the large European collaborative research project ALT-MAT (ALternative MATerials in road construction) [11].

Field measurements show that the moisture content in a pavement structure typically show a seasonal variation [12, 13]. Data from moisture content measurements in a road in Nantes, France, during a three-year period show a significant seasonal variation in all layers of the road construction [13]. The total moisture content budget on an annual basis was about 80 mm for a road construction (height 120 cm).

Water can enter the road body in several ways. Important potential mechanisms (Fig. 2) are as follow:

- Infiltration through the asphalt layer
- Infiltration through joints, cracks and deformities in the asphalt layer
- Movement of water into the road body directly from surrounding surface- or groundwater

- Lateral movement from the road flanks or edges, driven by capillary, vapor pressure or hydraulic gradients

Rainwater infiltrates directly through the pavement, it may form surface runoff and infiltrate at the edges, it may be stored in depressions at the surface or evaporate. Embanked roads generally become disconnected from the underlying groundwater system and surrounding surface waters and direct infiltration of rain remains as the only water input source to the road system [13].

Two domains subject to different hydrological conditions can easily be identified in the pavement structure:

1. The volume along the shoulders of the pavement structure where water infiltrates at the upper boundary of the domain and moves downward under the action of gravity and capillary forces.
2. The volume under the pavement where normally only very limited infiltration takes place. In this region water movement are dominated by capillary forces.

Note that the boundary between these domains is not fixed. The water that moves downward is spread laterally by capillarity, lateral dispersion and hydraulic gradients. The location of the boundary is therefore dependent on the water flux and the moisture conditions. In the former domain the dissolved contaminants are transported out of the system by advection and dispersion whereas the transport mechanisms in the latter domain usually are diffusion dominated.

The cumulative input of water, expressed as a liquid/solid ratio (L/S), is commonly used to scale up the results from column experiments to expected leaching behavior for infiltration rates encountered at field conditions. This approach works best for advection dominated transport regimes and for constituents that are solubility controlled and dissolves fast enough for local equilibrium to establish. Under field conditions where diffusion-controlled transport regimes are likely to be present the L/S variable is not relevant. Typical examples of when diffusion-controlled transport regimes are present are heterogeneous soils, structured and fractured media. In this particular case, where the diffusion-controlled transport regime constitutes the major bulk of the road construction, the L/S approach obviously fails. Once a certain constituent goes into solution the transport rates out of the diffusion-controlled regimes are in addition to the

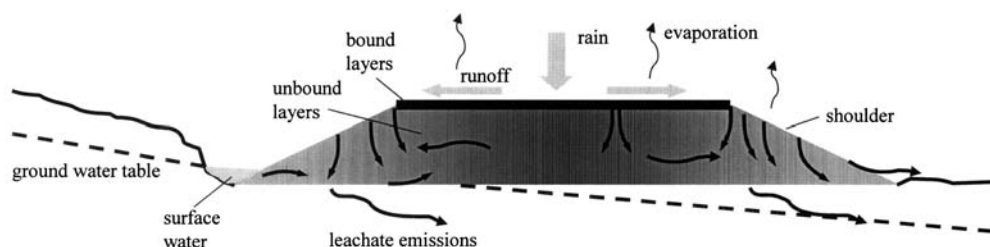


Fig. 2 Road hydrology

physical material parameters controlled by the moisture content, the boundary conditions and chemical retardation processes. The conditions at the boundary between the advection and diffusion controlled regimes are influenced by the water flux in the advection controlled domain.

4

Construction of an Interaction Matrix for a Road System

4.1

Description of the Diagonal Matrix Elements

The cross section of a studied system is defined by the upper boundaries: surface of pavement and the surface of the road shoulders and the lower boundary between the sub-base and subgrade. The obvious candidates for becoming diagonal elements are the physical components of the system: *bound layers*, *unbound layers* and *drainage system* and the state parameter *emission*. Since the focus of this study is the diagonal element *unbound layers*, where residues might serve as an alternative material, the resolution is increased by substituting the element *unbound layers* with its sub-matrix at the next level of resolution. The sub-matrix is composed of the diagonal elements, *road shoulders*, *material properties*, *water content/flow regime*, *water chemistry*, *gases*, and *temperature*.

Finally the diagonal element *Localization*, which induces the boundary conditions, the normal external impact on the pavement construction such as mechanical wear, rain and temperature, etc., is added to the matrix. This gives a total of ten diagonal elements, which are described briefly below. The numbers between brackets define the position in the matrix in Fig. 3 {row, column}.

4.1.1

{1,1} Location

The location defines the boundary condition associated with normal conditions (Fig. 3). A pavement structure is subject to a variety of stress and strain field induced by traffic and climatologic factors such as temperature and moisture. The site of the road is important since it defines the local and regional conditions with respect to these factors. Although not considered here, the locality (geohydrological and geochemical conditions, retardation mechanisms, distance to recipient, etc.) has obviously a large influence on the actual environmental impact on the surroundings in case of an emission from the pavement structure.

1	Location	Traffic load Deposition	Rainfall Surface water conditions	Settlement	Rainfall	Chemistry	Atmosph: Chemistry Pressure	Airtemp Radiation	Ground water conditions	Local depo- sition ex- haust emiss.
2		Bound Layer	Infiltration of surface runoff	Load transfer Settlement	Infiltration Surf runoff Evaporation		Gas and vapour exchange	Heat transfer		
3			Road shoulders		Water intrusion Infiltration		Gas and vapour exchange	Heat transfer		
4		Settlement Cracking		Material Properties	Flow regime	Heterogen reactions	Gas transport	Heat Transfer		Release and retardation mechanisms
5				Loss of bearing capacity	Water: -content -flow	Transport Mixing Reaction	Displace- ment gas	Heat Transfer		Advection Dispersion
6				Heterogen Reactions		Water Chemistry	Heterogen reactions			Reactions Density effects
7				Heterogen Reactions	Displace- ment	Heterogen reactions	Gases	Heat Transfer		
8				Frost Damage	Vaporization/ Condensation	Reaction kinetics	Vaporization Convect.	Temperature	Frost damage	
9					Groundwater Intrusion Drainage				Drainage System	
10									Precip. Clogging	Emissions
	1	2	3	4	5	6	7	8	9	10

Fig. 3 Interaction matrix of a road

4.1.2

{2,2} Bound Layers

The bound layers are a physical component of the system and are commonly composed of a surfacing (asphalt) and bitumen stabilized upper road base.

4.1.3

{3,3} Road Shoulders

The road shoulders are the unpaved edge zones of the pavement structure that declines outward. Here, *road shoulder* is taken as unsealed boundary to the unbound material layers. Which means that the material that constitutes the road shoulders is not assigned a separate diagonal element, instead it is included in the other diagonal elements that are associated with the unbound layers {4,4–8,8}.

4.1.4

{4,4} Material Properties Unbound Layers

This is a state parameter defining the physical and chemical properties of the material. The material in the unbound layers gives the pavement structure its load bearing capacity. The unbound layers are lower road base and sub-base. The strength of a pavement structure can be expressed as the capability to support a certain load without deformation. The bearing capacity is defined by the stiffness and stability. The stiffness of a pavement construction defines the capability to resist deformation and is expressed as elasticity modulus. The stability defines the capability to resist a certain load without permanent deformation. When designing a pavement structure the design load is defined as a number of passing standard axle loads of a certain weight. Permanent (plastic) deformation is due to compaction of the material, relocation of particle sideways or crushing of particles to smaller sizes which may be compacted at a higher density.

Particle size distribution, particle geometry, porosity, and heterogeneity are important material properties that govern hydraulic properties, such as hydraulic conductivity, hydrodynamic dispersivity, and capillary diffusivity. On the other hand, the chemical properties are defined by the mineral phases that constitute the solid phase.

4.1.5

{5,5} Water Flow and Water Content

The following states and phenomena are important:

- Water content (magnitude and spatial variation)
- The influence of the physical heterogeneity on the flow regime: non-uniform flow field, channel/macropore flow
- Transient flow and hydraulic non-equilibrium

4.1.6

{6,6} Water Chemistry

This is a state parameter defined by the chemical composition of the aqueous phase in the unbound layers. The major parameters that govern the mobility of heavy metals are pH, redox, ion strength, and concentration of organic and inorganic complexation agents.

4.1.7

{7,7} Gases

This is a state parameter defined by the partial pressure and movement of gases (mainly oxygen and carbon dioxide) in the unbound layers.

4.1.8

{8,8} Temperature

This is a state parameter, which influences the aqueous chemistry, vapor pressure and gas chemistry.

4.1.9

{9,9} Drainage System

This is a physical component of the system. The purpose of the drainage system is to redirect water from the pavement structure, ground water and surface water as well as infiltrating rainwater. Internationally, various designs of sub-drainage systems exists (see, for example, [14]).

4.1.10

{10,10} Leachate Emissions

Outward mass transport of contaminants at the system boundary. The emissions may spread in the surrounding environment with surface and ground water. Another type of emissions from the pavement structure is the contaminants that originate from the traffic, either deposited on the road surface, and carried to the shoulders of the road by surface runoff, or directly transported and deposited along the road through the exhaust fumes.

4.2

Description of the Interaction Matrix Elements

Short descriptions of the interaction elements are given below. The qualitative assessment of its importance is discussed. Depending on their significance, the interactions have been graded low, medium or high. The grading is illustrated by different shades of gray in Figs. 3, 4, and 5.

4.2.1

{1,2} Traffic Load, Vehicle Emissions Deposition, and De-Icing Salts (*High*)

The traffic flow (intensity, type of vehicles, driving pattern, axle load, etc.) is dependent on the location {1,1} and defines the mechanical load, which is exerted on the pavement structure. The traffic load (type of vehicles, driving pattern, traffic intensity) gives rise to deterioration of the bound layers. There are several types of deterioration [15]. *Rutting*, surface depression in the wheel paths develops fast during the first years but then levels off at a slower rate. *Fatigue* develops first after considerable loadings have taken place but increases rapidly as the pavement deteriorates. *Fatigue* gives rise to series of interconnected cracks. Longitudinal (parallel to the centerline) or transverse cracks are normally not load associated but a result of poor construction or shrinking due to temperature variations or asphalt hardening.

4.2.2

{1,3} Surface Water Intrusion (*High*)

Depending on the location and topography surface water may intrude directly into pavement structure horizontally. In cold regions the presence of snow along the road shoulders may prevent the thaw front to progress at the same speed as into the pavement structure. Under such conditions melt water and rain has been observed to infiltrate at the shoulders, flow into the structure and gradually saturate the pavement structure [12].

The moisture content in road shoulders is governed by climatologic factors such as rainfall, temperature and evaporation and typically show a large variation in comparison with the body of the road. Depending of the moisture contents in the shoulders the capillary potential may drive moisture either in or out of the road body. Moisture is typically transported downwards out of the pavement structure as vapor in the summer and upward, into the structure, during winter [15]. Wallace [16] demonstrated the significance of the shoulders as water entries to the unbound material layers during transient conditions in a theoretical study. The rate of lateral intrusion in the unbound layers will be dependent on:

- Water content in shoulders and depth of any pondage
- Thickness of the unbound layers
- Porosity
- Initial water content of unbound layers
- Hydraulic conductivity and capillarity of the unbound layers

If the subgrade is less permeable a perched water table may develop at the lower boundary of the unbound layers, which will facilitate lateral water movement. Therefore, initial water content, hydraulic conductivity and capillarity of the subgrade are significant for the rate of lateral intrusion.

4.2.3

{1,4} Settlement (*High*)

The external impact on the pavement structure due to settlement or heaving in the subgrade/embankment depends on the locality of the road. Settlements in the subgrade/embankment may give rise to fractures in the unbound or bound layers.

4.2.4

{1,5} Rainfall (*High*)

The location determines the typical rainfall pattern (duration, intensity and seasonal variability). The surface of the bound layers and the shoulders receives the rainwater.

4.2.5

{1,6} Chemical Conditions at Road Surfaces (*Medium*)

The location governs the chemical composition of the aqueous phase at the system boundaries, which will influence the water chemistry in the road body. The chemical composition of the aqueous phase at the system boundary is controlled by the chemistry of the arriving water and the existing conditions at the system boundary. At the road surface the traffic give rise to a local deposition of de-icing salts and contaminants (mainly heavy metals and PAH), which will influence the chemical composition of the aqueous phase at the boundary. The contaminants originate from exhaust gases, brakes, oil/gasoline spill, tire wear and corrosion. The deposition associated with corrosion increases wintertime due to the use of de-icing salts [17]. Contaminants may also originate from the bitumen and aggregate due to wear of the road surface. Also, small particles are produced, which may facilitate transport of various contaminants [18].

4.2.6

{1,7} Atmosphere: Chemistry, Pressure (*Medium*)

The location governs chemical composition of the atmosphere and air pressure, which have a significant influence on the gas composition, and pressure in the road body.

4.2.7

{1,8} Air Temperature and Incoming Radiation (*Low*)

The incoming energy to the system is dependent on the location of the road. The net energy supplied to the surface is divided into change in heat storage in the pavement structure, sensible heat flux and latent heat flux.

4.2.8

{1,9} Ground Water Conditions (*High*)

The local ground water conditions, together with the local rainfall pattern and surface water conditions, govern the amount of water supplied to the pavement structure. A rising groundwater table comes first in contact with the drainage system, which redirects the water and may prevent that the water table rises higher.

4.2.9

{1.10} Local Deposition of Exhaust Emissions (*Medium*)

Some of the contaminants originating from the exhaust (mainly heavy metals and PAH) are deposited directly into the ditches. This emission source may give a significant contribution in addition to the possible emissions from the residues in the pavement structure. De-icing salts may affect mobility of some heavy metals accumulated in the ditches [19].

4.2.10

{2.3} Infiltration of Surface Runoff (*High*)

The surface runoff and rainwater infiltrates at the shoulders. Contaminants and de-icing salts that have deposited on the road surface are carried by surface runoff to the shoulders, where the runoff may infiltrate.

4.2.11

{2.4} Load Transfer (*Medium*)

The bound layers distribute and transfer the load to the unbound layers. The load may give rise to settlement and deformation (compaction, fracturing) of the unbound layers. Settlements are necessarily not directly load associated but can be due to improper construction, settlement of the subgrade/embankment, {1,4}, or loss of bearing capacity due to a high water content, {5,4}.

4.2.12

{2.5} Infiltration, Surface Runoff and Evaporation (*High*)

The rainwater is divided into infiltration, surface runoff and evaporation at the boundary layer surface. Preferably, the bound layers should be impervious and redirect rainwater as surface runoff so that infiltration into the pavement is minimized. However, due to deformities the boundary layers may be an important pathway for water entering the unbound layers. The infiltration capacity depends on the permeability of the pavement and underlying construction layers and presence of cracks and other local deformities of the pavement [13]. If no deformities are present the infiltration capacity for asphalt is typically in the

order of 1×10^{-7} m/s [20]. Deformities of the pavement may drain surface water from large areas and give rise to large infiltration locally [21]. Dawson and Hill [22] refer to investigations where an infiltration capacity of 1 l/h/cm of cracks have been determined.

4.2.13

{2.6} Gas and Vapor Exchange (*Medium*)

Gas and vapor exchange can take place through the bounded layers if significant pathways exist. No information seems to be available in the literature regarding this phenomenon.

4.2.14

{2.8} Heat Transfer (*Low*)

The bounded layers transfers heat between the road surface and the unbound layers.

4.2.15

{3.5} Surface Water Intrusion and Infiltration (*High*)

Rainwater that is carried away as surface runoff infiltrates in the unsealed shoulders of the road and may also move laterally into the road body driven by the capillary potential, hydraulic pressure [16, 23–25], vapor pressure and temperature gradients [13]. Pressure gradients in porous media, also referred to as hydraulic non-equilibrium, typically arise when the flow field is transient and non-uniform.

4.2.16

{3.7} Gas and Vapor Exchange (*High*)

The shoulders of the pavement structure provide an important pathway for vapor and gases out of the pavement structure [12].

4.2.17

{3.8} Heat Transfer (*Low*)

Heat transfer between the road body and the surrounding air takes place partly via the shoulders.

4.2.18

{4.2} Settlement, Cracking (*High*)

Differential settlement or compaction of the unbound layers may cause the bounded layers to crack.

4.2.19

{4,5} Flow Regime (*High*)

Physical properties of the media such as particle size distribution, particle geometry, porosity and heterogeneity govern the flow regime. Non-uniform flow field arise as a result of physical heterogeneity. Channel flow has been observed in pavement structures under field conditions [21, 26–28]. Additional complexity associated with the impact of non-uniform flow on the leaching process is introduced under transient conditions. Important factors that govern the impact are initial and boundary conditions and hydraulic properties of the medium such as particle size and spatial pattern of any preferential flow paths. Also the influence of physical properties of the medium will not be constant during transient conditions. For example, the fraction of mobile water in heterogeneous media has shown to be dependent on the flux [29] and will not remain constant under transient conditions [30].

4.2.20

{4,6} Heterogeneous Reactions (*High*)

Dehydrated residues, such as those formed during thermal processes, will react when exposed to water (hydrolysis and hydration). During the lifetime of a road construction, bases and reductants of the residues in the unbound layers will be titrated with acids (CO_2 , SO_2 , organic acids) and oxidants (O_2) dissolved in the leachate.

The water chemistry and the solubility and toxic metals (heavy metals and metalloids) is mainly controlled by heterogeneous reactions between the solid phase and the leachate, including dissolution/precipitation, sorption/desorption, acid-base and redox reactions. For combustion residues the leaching process may be divided into three phases [31]. During the initial phase easily soluble mineral oxides and salts dissolve and a concentration peak may be expected. For alkaline residues, a strongly alkaline leachate is buffered by dissolution and hydrolysis of alkali-earth and alkali metal oxides. When these solid phases are consumed the pH drops and other less soluble mineral phases, such as metal oxides and amorphous aluminum silicates, start to dissolve and buffer a new lower pH level. Finally, the long term leaching is characterized by the slow dissolution of aluminosilicate glass phases and less reactive magnetic spinel phases.

4.2.21

{4,7} Gas Transport (*Medium*)

The physical properties of the unbound materials govern the resistance for gas transport.

4.2.22**{4,8} Heat Transfer (*Low*)**

The unbound material transfers and stores heat.

4.2.23**{4,10} Release and Retardation Mechanisms (*High*)**

There are several properties related to the solid phase that have a large influence on mass transport. They include the following: diffusion resistance, mineralogy, availability of sorption sites and dispersivity.

4.2.24**{5,4} Loss of Bearing Capacity (*Medium*)**

Significant water content in the pavement structure has various harmful effects on the material properties [15], as follows:

- It reduces the strength of unbound granular materials
- Traffic may induce a high hydrodynamic pressure causing fine particles to move out of the structure so that it loses its supporting capacity
- In cold regions high water content may cause freezing damage
- It may cause differential heaving over swelling soils

4.2.25**{5,6} Transport, Mixing, Reaction (*High*)**

Water is a solvent, a reaction medium, and a mixing and transport medium. The flow of water, the water content and the variations in time and space in the unbound layers are significant for water chemistry and leaching processes. The transport process is governed by a variety of retardation mechanisms.

4.2.26**{5,7} Displacement of Gas (*Medium*)**

Variations of water content may cause displacement of gas.

4.2.27**{5,8} Heat Transfer (*Low*)**

Water transfers and stores heat within the pavement structure.

4.2.28**{5,10} Advection, Dispersion and Diffusion (*High*)**

Dissolved substances are transported out of the pavement structure by diffusion in the water phase and by advection.

4.2.29**{6,4} Precipitation and Dissolution (*High*)**

The pore water in the unbound layers reacts with the solid phase, which change the characteristics of the chemical and physical properties of the materials.

4.2.30**{6,7} Heterogeneous Reactions (*Medium*)**

Degradation of any dissolved organic material generates gases (mainly carbon dioxide and methane) and affects the pore gas composition.

4.2.31**{6,10} Reactions and Density Effects (*High*)**

Homogeneous reactions take place in the aqueous phase. The composition of the water phase influences the solubility of the minerals. Also, the composition of the water may cause density effects that influence the flow and transport process.

4.2.32**{7,4} Heterogeneous Reactions (*High*)**

As previously been described, residues emanating from thermal processes are alkaline, reduced and thermodynamically unstable and reacts when exposed to oxygen and carbon dioxide (and water). The solid phase containing mineral such as metal oxides, salts and non-hydrated calcium silicates transform into more stable mineral forms such as hydroxides, carbonates and hydrated aluminum silicate.

4.2.33**{7,5} Displacement (*Low*)**

The gas pressure and gradients affects the water movement.

4.2.34**{7,6} Heterogeneous Reactions (*High*)**

The pore gases, mixtures of components in air and elements that have been generated in biogeochemical processes, dissolve in the pore water according to its equilibrium constant. The partial pressures of different gases also influence microbiological reactions.

4.2.35**{7,8} Heat Transfer (*Low*)**

The gas phase transfers and stores heat within the pavement structure.

4.2.36**{8,4} Frost Damage (*Medium*)**

Settlement or shrinking/swelling as a result of freezing/thawing, variations in moisture content [32] and temperature may, in addition to deformities of the pavement, cause fissures or fractures of the road body.

4.2.37**{8,5} Vaporization/Condensation (*Medium*)**

The temperature governs the vapor pressure.

4.2.38**{8,6} Reaction Kinetics (*Medium*)**

The temperature in the pavement structure influences the reaction kinetics and the biological processes.

4.2.39**{8,7} Vaporization, Convection (*Low*)**

The temperature in the pavement structure influences the gas transport and the vapor pressure.

4.2.40**{8,9} Frost Damage (*Low*)**

Freezing temperatures may cause frost damage on the drainage system.

4.2.41**{9,5} Ground Water Intrusion, Drainage (*High*)**

Malfunctioning drainage system may cause water to enter the pavement structure through the drainage system [26]. Damaged outlets, improper alignment (line and grade), cover material compaction, damage during construction and clogging due to precipitation [33] are common problems that cause failure of the drainage system [14, 34].

4.2.42**{10,9} Precipitation/Clogging (*Low*)**

In case that the leachate is carried away in the drainage system, the changing environment in the system may cause precipitation and clogging, which will decrease the effectiveness of the system.

5

Crucial Routes Through the Interaction Matrix

The exposure of residues to water and atmosphere controls the aqueous phase chemistry and the leachate quality at the system boundary. The exposure pathways are here evaluated by construction of routes through the interaction matrix via interactions with a *high* degree of significance. The way that the external impacts propagate through the system via internal processes, defined in the interaction boxes, is visualized in the matrices in Figs. 4 and 5. For clarification, the processes have been divided into two groups, which are illustrated in separate matrices.

According to the qualitative assessment, three interactions are highly significant for the water content and flow regime in the unbound layers. These are water entering through the bounded layers {2,5}, the shoulders {3,5}, or the lower boundary of the system {9,5}. These pathways are illustrated in Fig. 4.

5.1

Infiltration Through the Bounded Layers

Lets suppose that a certain location implies a high traffic load on the boundary layers. At a certain point in time, cracks may develop in the boundary layers due to fatigue. The cracks increase the annual infiltration into the road body. The annual amount of rain and its distribution over the year is a local or regional feature. As the water content in the unbound layers increases, some of the bearing capacity is lost, which may cause settlement in the unbound layers. A differential settlement is likely to give rise to further damage to the boundary layer that, in turn, will increase the infiltration capacity and increase the water content and flux in the unbound layers.

5.2

Infiltration Through the Shoulders

Rainwater that falls on the surface of the bounded layer is redirected as surface runoff and infiltrates at the shoulders. Depending on the local topography and surface water conditions water from surrounding areas may also infiltrate in the shoulders. The infiltrated water will be traveling downwards under the force of gravity. As mentioned previously, horizontal water movement will take place due to capillary forces, lateral dispersion and pressure gradients. Under transient conditions hydraulic gradients develop between regions of fast flow and regions under the asphalt with less mobile water volumes [23, 25]. This will result in water flow and convective transport between the regions, driven by the hydraulic gradient, which strive to reestablish hydraulic equilibrium [35, 36]. If the flow becomes steady the hydraulic gradients will attenuate and equilibrium will be established. In response to an unsteady water input pattern at the boundary, the flow system will therefore go through

1	Location	Traffic load Deposition	Rainfall Surface water conditions	Settlement	Rainfall	Chemistry	Atmosph: Chemistry Pressure	Airtemp Radiation	Ground water conditions	Local depo- sition ex- haust emiss.
2		Bound Layer	Infiltration of surface runoff	Load transfer Settlement	Infiltration Surf runoff Evaporation		Gas and vapour exchange	Heat transfer		
3			Road shoulders		Water intrusion Infiltration		Gas and vapour exchange	Heat transfer		
4		Settlement Cracking		Material Properties	Flow regime	Heterogen reactions	Gas transport	Heat Transfer		Release and retardation mechanisms
5				Loss of bearing capacity	Water: -content -flow	Transport Mixing Reaction	Displace- ment gas	Heat Transfer		Advection Dispersion
6				Heterogen Reactions		Water Chemistry	Heterogen reactions			Reactions Desity effects
7				Heterogen Reactions	Displace- ment	Heterogen reactions	Gases	Heat Transfer		
8				Frost Damage	Vaporization/ Condensation	Reaction kinetics	Vaporization Convect.	Temperature	Frost damage	
9					Groundwater Intrusion Drainage				Drainage System	
10									Precip. Clogging	Emissions
	1	2	3	4	5	6	7	8	9	10

Fig.4 Water entering the unbound layers through the bounded layers, the shoulders or the lower boundary of the system

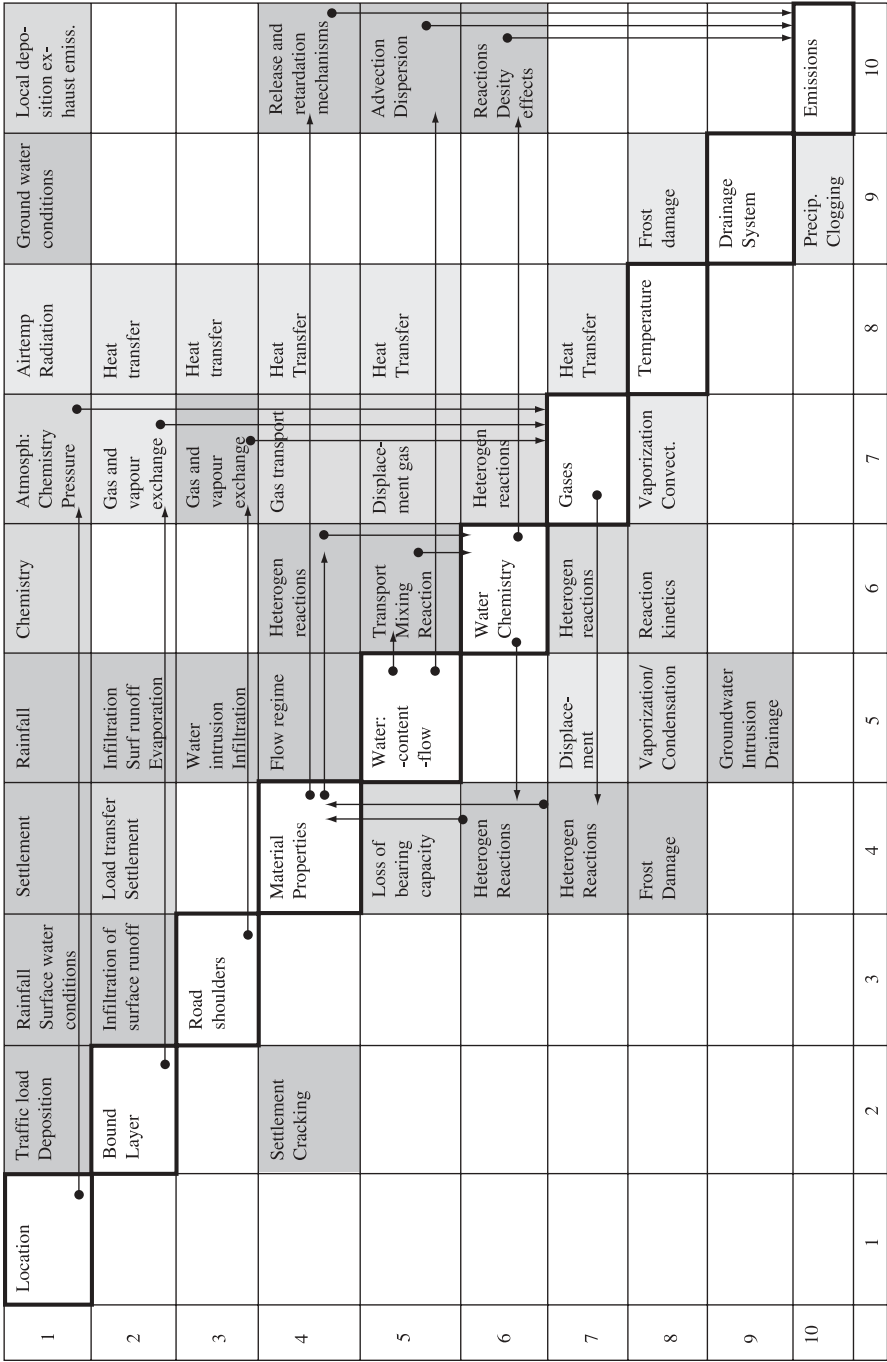


Fig. 5 The exposure to water and gas and the resulting leachate quality at the system boundary

perturbation and equilibrium cycles [37]. Under such conditions the mass transfer flux from road body out in the advection-dominated domains consists of one component driven by the concentration difference and one advective component. Depending on the water input pattern, these transport mechanisms will alternate between working against each other and working in the same direction.

A high water content and flow increases the leaching rate and, just as in the previous example, the high water content may lead to loss of bearing capacity and damage to the boundary layer. The unbound materials in the shoulders will be exposed to a large accumulated infiltration, which will increase the leaching in these regions.

5.3

Ground Water Intrusion

Depending on the local conditions, a rising water table may be a likely scenario for water entering the pavement structure. An efficient drainage system might save the unbound layers from becoming flooded. Otherwise, ground water will intrude the pavement structure and cause the same effect as the previous scenarios.

5.4

Exposure to Water and Gas

The exposure of the unbound material to water and atmosphere and its influence on water chemistry and emissions are illustrated in Fig. 5. When exposed to water and gas unstable minerals dissolves and more stable mineral may precipitate. These reactions change the material properties and control the water chemistry. The dissolved elements are transported under the influence of advection and dispersion out of the system and become an emission.

The major pathways for gas into the pavement structure are through the shoulders and through the bounded layers. Due to its large surface exposed to atmosphere the gas exchange at the boundary of the shoulders is likely to dominate [12]. In presence of water as a reactive medium both the gas and solid phases react together (oxidation, carbonation). The redox condition is controlled, to a large extent, by the pore gas composition and is therefore important to consider.

To summarize, the moisture content and transport rate in the road body is mainly governed by the moisture content and water flux in the shoulders and underlying strata, which define the boundary conditions for the body domain. The composition of pore gas in the unbound layers is a major state parameter that governs the evolution of pH and redox in the unbound layers and as such the mobility of heavy metals. The unbound layers are partially an open system and it is here hypothesized that the gas exchange mainly takes place at the road shoulders.

6

Conclusions

The general leaching behavior in lab scale of residues, such as slag from incineration of coal or municipal solid waste, slag originating from steel manufacturing and crushed concrete are well known. However, predictions of long-term leaching under field conditions are still a challenge.

Despite its simplicity, the interaction matrix captures the central interactions and relations. The matrix clearly illustrates how external impact and events propagate through the system via internal processes defined in the interaction boxes. The exposure to water and atmosphere govern the development of the aqueous chemistry in the unbound layers. The effect of the three significant ways for water, and two different ways for gas, to enter the unbound layers were demonstrated and the following conclusion is made.

For the purpose of predictive modeling of emissions the road ought to be treated as an integrated system instead of treating the diffusion controlled domain and the advection controlled domain separately. Also, high water content does not only increase the emission rate it also affects the material properties negatively. If the unbound material loses some of its bearing capacity the risk for settlements increases. This in turn may cause damage to the bounded layers and higher infiltration.

The role of the shoulders as water and gas vents remains as the most important mechanism governing the emissions from a road where residues are used as an alternative unbound material.

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Forensic Investigation of Leachates from Recycled Solid Wastes: An Environmental Analysis Approach

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Abstract In order to study the environmental analysis and impact assessment (EAIA) of contaminants leached from road construction and repair (C&R) materials, the present chapter introduces an advanced technique called “Forensic Analysis and Genetic Source Modeling”. This consists of an environmental “molecular marker” approach that is integrated with various statistical/mathematical modeling tools. It generally aims to characterize the organic molecular composition of leachates from road construction materials as well as to confirm their source. Accordingly, the main goals in this chapter are to: (1) review different organic contaminants (such as petroleum hydrocarbons, pesticides, phthalates, phenols, PCBs, organotin compounds, and surfactants) leached from solid wastes used as road construction materials and/or their leachates; (2) evaluate the different analytical techniques used for the determination of these organic compounds; (3) discuss the current instrumental developments and advances for the identification and characterization of these contaminants; and (4) present data for a major research program that investigated the environmental impact of highway construction materials on surface and ground waters.

Keywords Solid wastes · Environmental analysis · Fate · Transport · Highway materials · Leachates · Contaminants · Forensic analysis · Source confirmation

Abbreviations

ACZA	Ammoniacal copper-zinc-arsenate
ANNs	Artificial neural networks
ANOVA	Analysis of variance
BSTFA	Bis(trimethylsilyl)trifluoroacetamide
C&R	Construction and repair materials
CCA	Cooper chromated arsenate
CI	Chemical ionization
COMs	Complex organic mixtures
CSIA	Compound specific isotope analysis
DA	Discriminant analysis
DEHP	Di-(2-ethylhexyl)phthalate
DOC	Dissolved organic carbon
DOP	Dioctyl phthalate
EAIA	Environmental analysis and impact assessment
ECD	Electron capture detector
EI	Electron impact
EIA	Environmental impact assessment
EMs	End members
EOM	Extractable organic matter

EPA	Environmental Protection Agency
ESI	Electrospray ionization
FAB	Fast-atom bombardment
FI	Field ionization
GC	Gas chromatography
GC-AED	Gas chromatography with atomic emission detection
GC-FPD	Gas chromatography with flame photometric detection
GC-MS	Gas chromatography-mass spectrometry
GPC	Gel permeation chromatography
HCs	Hydrocarbons
HPLC	High performance liquid chromatography
HTGC-MS	High temperature gas chromatography-mass spectrometry
IDMS	Isotope dilution mass spectrometry
IRMS	Isotope ratio mass spectrometry
ITD	Ion trap detector
L/S	Liquid-to-solid ratio
LC	Liquid chromatography
LIMS	Laser ionization mass spectrometry
LLE	Liquid-liquid extraction
LPT	Linear programming technique
MALDI	Matrix-assisted laser desorption ionization
MMs	Molecular markers
MS	Mass spectrometry
MWC	Municipal waste combustion
NCHRP	National Cooperative Highway Research Program
OCPs	Organochlorine pesticides
PAEs	Phthalic acid esters
PAHs	Polycyclic aromatic hydrocarbons
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PCs	Principal components
PD	Plasma desorption
PGD	Plasma and glow discharge
RIMS	Resonance ionization mass spectrometry
SAR	Structure activity relationship
SFC	Supercritical fluid chromatography
SFE	Supercritical fluid extraction
SIMS	Secondary ionization mass spectrometry
SPE	Solid phase extraction
SPME	Solid phase micro-extraction
SSJ/LIF	Supersonic jet laser-induced fluorescence
SWMs	Solid waste materials
TOC	Total organic carbon
TOF-MS	Time of flight-mass spectrometry
TPs	Transformation products
UCM	Unresolved complex mixtures

1

Introduction

Environmental risk or hazard assessment of organic contaminants in the environment is based on a comparison of two main factors. These two pillars of risk assessment are: (a) the quality and quantity of an organic contaminant in the environment, and (b) the concentration of that contaminant at which no adverse effects to the environment are known.

The first pillar of risk assessment requires the use of state-of-the-art organic analysis techniques coupled with a unique environmental forensic and genetic source confirmation approach. This is done in order to: (a) characterize the contaminant of interest, (b) determine its concentration, and (c) confirm its source. The second pillar of risk assessment and environmental management requires the use of a particular structure-activity relationship (SAR) approach, which can measure the effect of a particular contaminant once it is leached from road C&R materials into the surrounding environment, predict the effects of compounds with similar structures, and model their fate and behavior.

The current chapter presents: (a) an overview of the various possible contaminants (including petroleum hydrocarbons, pesticides, phthalates, phenols, PCBs, organotin compounds, and surfactants), which can be leached from solid wastes that are either disposed in landfill sites and/or recycled as secondary road construction materials; and (b) a discussion of modern environmental forensic techniques, often referred to as “*molecular marker*” fingerprinting, used to identify the sources of contamination. These techniques are based, in general, on the identification of characteristic signatures or markers in leachate samples and the use of these signatures to demonstrate a link between a source and a road construction material. In addition, current instrumental developments and advances in the identification and characterization of these contaminants are discussed thoroughly, and a case study is also presented.

2

Environmental Forensic Concept

The present section provides an outline of the environmental forensic approach, the different types of possible contaminants released from solid wastes (disposed in landfills or recycled as road construction and repair materials), and analytical techniques and advances in contaminant identification and characterization.

2.1

Definition and Terminology

Environmental forensic analysis is defined as a scientific methodology developed for analyzing and identifying contamination-related and other potentially hazardous environmental contaminants, and for determining their sources. It

combines experimental analytical procedures with scientific principles derived from the disciplines of environmental chemistry, engineering, organic geochemistry, and environmental modeling. Environmental forensic analysis can also provide a valuable tool for obtaining scientifically proven data when applied to investigations of leachates from solid waste materials.

Various terms have been used in the literature to describe environmental organic contaminants that are characterized in terms of their molecular structures [1–4]. These terms include: (a) *chemical fossil*, first used by Eglinton and Calvin [5] to describe organic compounds in the geosphere whose carbon skeleton suggested an unambiguous link with a known natural product, (b) *biological markers*, *organic tracers*, *biomarkers*, or *molecular fossils*, used to identify various organic contaminants [1–4, 6–16], and (c) *molecular markers*, used to describe both naturally occurring (biological, and hence biomarker) and/or anthropogenically-derived organic compounds (non-biomarker) present in both aqueous and solid phase environments [1, 17].

2.2

Differences from EPA Analytical Methods

Environmental forensics is effective in many liability cases that aim to successfully identify the party(s) responsible for contamination (i.e., actual source).

Identification of these parties is critical for environmental assessors and managers. In most environmental analysis and impact assessment (EAIA) cases, the presence of chemicals is determined following standard US EPA methods. For instance, EPA Method 418.1 (for analysis of total petroleum hydrocarbons) or Method 8015 (for determining the presence of petroleum in the diesel or gasoline range) is generally adequate for documenting the occurrence of petroleum contamination at a certain site. However, these methods are unsuitable for identifying the types and sources of petroleum in complex contaminated situations. These standard EPA methods were never intended for petroleum product identification. They are not tailored for the analysis of the key diagnostic chemical compounds that comprise petroleum and do not provide sufficient chemical data to perform defensible data analysis for source identification and product differentiation.

An accurate and defensible EAIA approach requires answers to the following questions:

- What are the product types present due to contamination?
- What are the potential sources of contamination?
- Can these potential sources be linked to their original sources?

Answers to these questions require the use of sophisticated contaminant-specific methods of chemical analysis together with, in many circumstances, advanced data analysis, statistical/mathematical modeling and visualization techniques. Successful fingerprinting involves the design and implementation of an investigation including sampling, analytical, and interpretation strategies. The analytical and interpretation strategies are critical to fingerprinting analysis.

The selection of appropriate marker compounds that will differentiate contaminant sources is central to designing an analytical program. Because hydrocarbons, for instance, have a variety of sources (see Sect. 2.3.1), the most important objective in analyte selection is to identify specific markers for both the released/leached hydrocarbon mixture and other potential sources. Markers must have the attributes of uniquely identifying the released/leaching contaminants from other sources, and resistance to alteration (weathering) over time. Most often, the appropriate markers are not known at the start of a fingerprinting study, but are identified during the characterization processes. Successful contamination fingerprinting usually requires analysis of more than one target analyte group. However, analyzing all groups for potential marker compounds results in an expensive analytical program. A tiered approach to target analyte selections is often implemented in analytical designs.

Distinguishing the small differences in characteristic contamination signatures, for instance, requires the use of analytical methods that satisfy the data quality objectives for precision and detection of fingerprinting. As noted above, the standard EPA methods are inadequate for most fingerprinting characterizations. The laboratory selected to perform the more advanced and difficult fingerprinting characterization must be able to analyze the contaminant of interest and its unique marker compounds within the precision and detection limits that the environmental chemist needs to distinguish subtle differences in their signatures.

2.3

Types of Organic Contaminants

Because of the dramatic expansion in environmental organic analysis and the development of commercially available gas chromatograph-mass spectrometer (GC-MS) systems, there have been numerous organic contaminant fingerprints that have been described and identified [2–4, 7–24]. Identities of individual compounds or compositional fingerprints can be determined by highly sophisticated and advanced instruments [23, 25–40], and are used to provide information about the type [22, 23, 34, 41–44], amount [41, 45–48], and source confirmation [1–4, 49] of these contaminants. The following is a summary.

2.3.1

Petroleum Hydrocarbons

Hydrocarbons (HCs) of petroleum origin are widespread organic contaminants that can be found in various solid waste materials and their leachates [1, 17]. The most common groups of compounds are aliphatic and polycyclic aromatic hydrocarbons (PAHs). Of these, the PAHs are toxic, carcinogenic and sometimes mutagenic to both aquatic organisms and ultimately humans [1, 17]. The following is a brief description of each group (detailed information is in Sect. 4.4):

- *Aliphatic hydrocarbons*: They are a diverse suite of compounds (Fig. 1) that have been studied and characterized in terms of their molecular marker composition. They include homologous long chain *n*-alkane series, unresolved complex mixtures (UCM) of branched and cyclic hydrocarbons, isoprenoid hydrocarbons (like norpristane, pristane and phytane), tricyclic terpanes (usually ranging from $C_{19}H_{34}$ to $C_{30}H_{56}$, and in some cases to $C_{45}H_{86}$), tetracyclic terpanes (including 17,21- and 8,14-*seco*-hopanes), pentacyclic triterpanes, steranes and diasteranes [1, 2–4, 6, 11, 13, 16, 50–73].

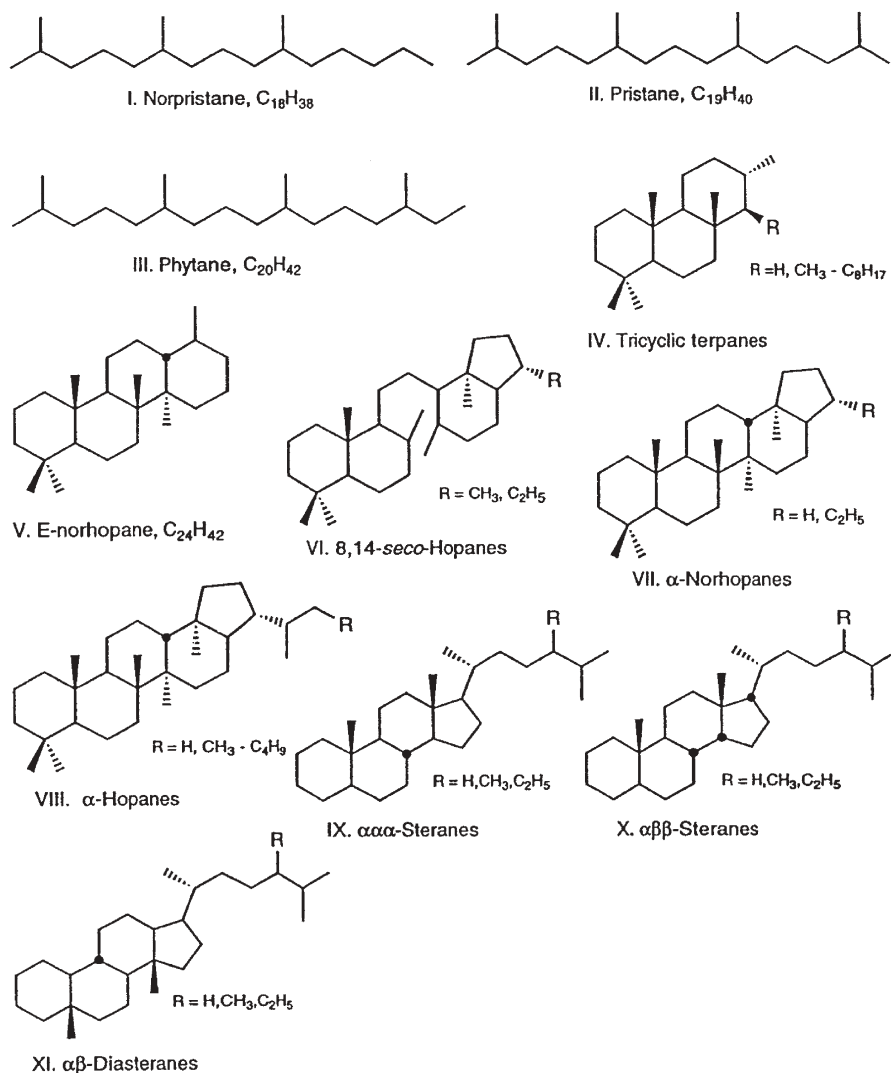


Fig. 1 Chemical structures of some aliphatic hydrocarbons as cited in the text

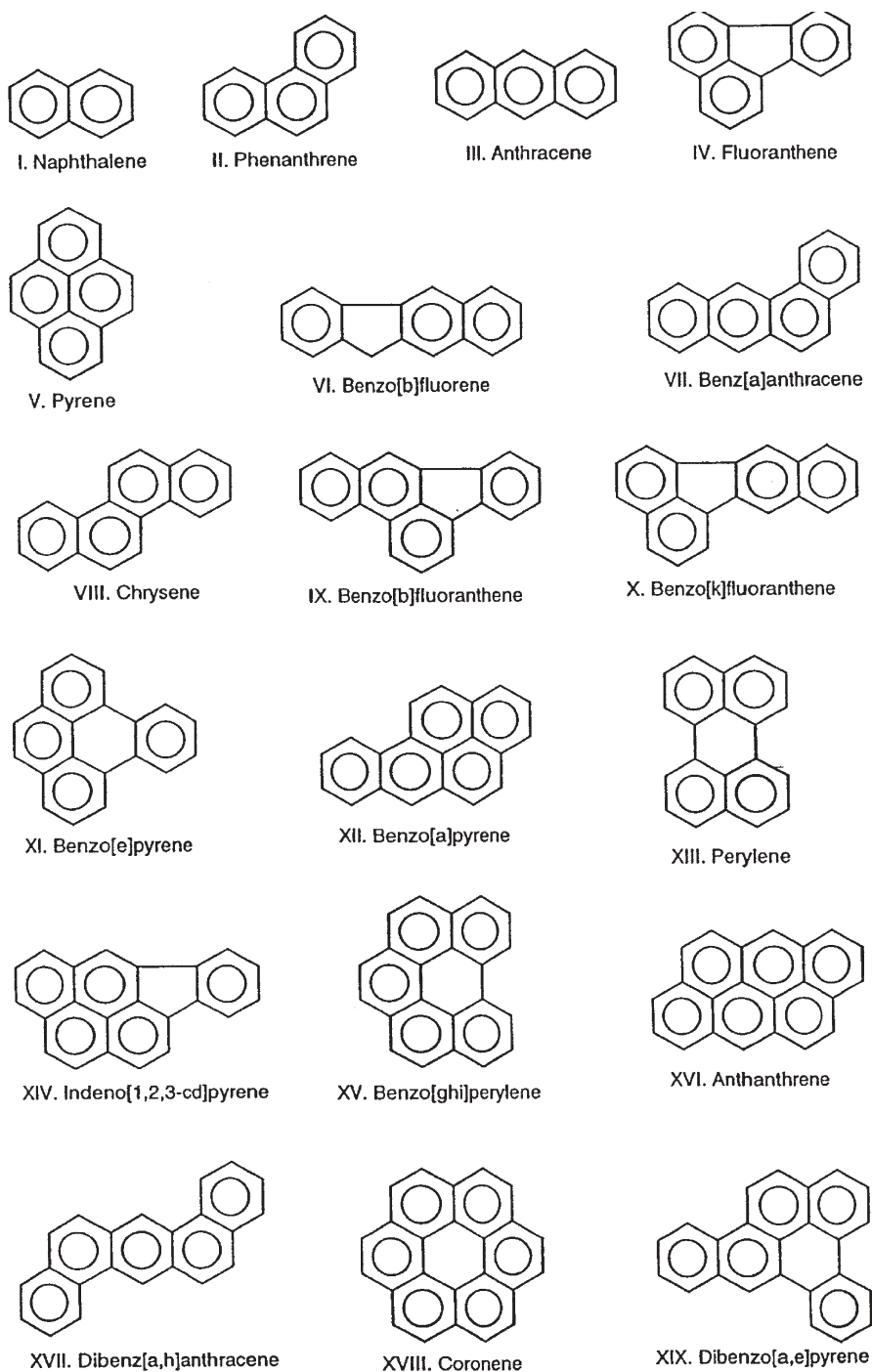


Fig. 2 Chemical structures of some examples of polycyclic aromatic hydrocarbons

- *Polycyclic aromatic hydrocarbons*: PAHs are neutral, non-polar organic molecules consisting of two or more fused benzene rings arranged in various configurations, with hydrophobicity increasing with molecular weight. The parent structures of the common PAHs are shown in Fig. 2, and the alkylated homologs are generally minor, indicating combustion emissions. PAHs are produced from anthropogenic activity such as fossil fuel combustion, biomass burning, chemical manufacturing, petroleum refining, metallurgical processes, coal utilization, tar production, and so on. [74–88].

2.3.2

Pesticides

Several hundred-pesticide compounds of diverse chemical structures are widely used in the United States and Europe for agricultural and non-agricultural purposes, generating large amounts of solid waste materials. Some are substitutes for organochlorines, which were banned due to their toxicity, persistence, and bioaccumulation in environmental matrices. Chemical structures of various pesticides are shown in Fig. 3.

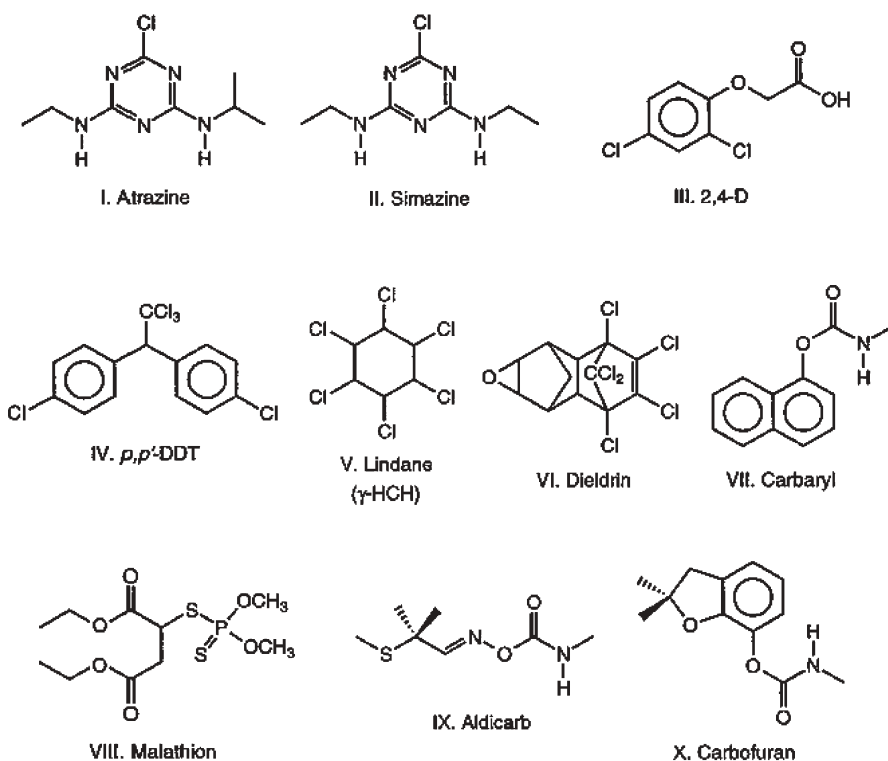


Fig. 3 Chemical structures of various pesticides

Organic pesticides which have been and are still being used belong to numerous different families of organic chemicals that can be grouped in various ways, as follows:

- *Cationic compounds*: Bipyridinium herbicides such as Diquat and Paraquat (Structures I–II, Fig. 3) are the only important compounds of this group that have been thoroughly investigated [89–91]. They are available as dibromide and dichloride salts, respectively, and are used as herbicides and desiccants. These compounds were shown to be toxic to humans [92–94]. The solubility of cationic pesticides is generally high in aqueous solutions, where they dissociate readily to form divalent cations.
- *Basic compounds*: The most important pesticides of this group (Fig. 3) are Amitrole and several members of the family of symmetric(s)-triazines [41, 90, 92, 94, 95]. Amitrole (a herbicide) is soluble in water, with a weak basic character ($\text{p}K_{\text{b}}=10$) and behaves chemically as a typical aromatic amine. *s*-Triazines (Fig. 3), used as herbicides, are substituted diamino-*s*-triazines which have a chlorine, methoxy, methylthio, or azido group attached to the C-3 ring atom. The presence of electron-rich nitrogen atoms confers well-known electron-donor ability to *s*-triazines (weak basicity and the capacity to interact with electron acceptor molecules), giving rise to electron-donor acceptor (charge-transfer) complexes. *s*-Triazines have low solubilities in water, with the 2-chloro-*s*-triazines being less soluble than the 2-methylthio and 2-methoxy analogues. Water solubility increases at pH values where strong protonation occurs (for example between pH 5.0 and 3.0 for 2-methoxy- and 2-methylthio-*s*-triazines, respectively, and at pH 2.0 for 2-chloro-*s*-triazines). Structural modifications of the substituents significantly affect solubility at all pH levels.
- *Acidic compounds*: This group of pesticides comprises different families of compounds with herbicidal action, including substituted phenols, chlorinated aliphatic acids, chlorophenoxy alkanic acids, and substituted benzoic acids, which all possess carboxyl or phenolic functional groups capable of ionization in aqueous media to yield anionic species [90, 96–99]. The following is a summary:
 - Chlorinated aliphatic acids have the highest water solubility and the greatest acidity among this group of compounds due to the strong electronegative inductive effect of the chlorine atoms replacing the hydrogens in the aliphatic chain of these acids. The water solubilities of the phenoxy alkanic acids are low as they have a considerable lipophilic component. Dinitrophenols and pentachlorophenol are generally of intermediate solubility in water, while they are highly water-soluble as alkali salts which represent most of their common commercial formulations.
 - With the exception of Picloram and phenols (Fig. 3), acidic pesticides are considered nonvolatile in aqueous and solid systems [92]. Some ester formulations of these compounds also behave as herbicides. They do not ionize in solution and are less water-soluble than the acid or salt forms.

They are eventually hydrolyzed to acid anions in aqueous and soil systems, but in the ester form are non-ionic and relatively volatile.

- 2,4-D and 2,4,5-T (Fig. 3) are among the most widely known and used phenoxy alkanolic acids. Teratogenic (fetus deforming) effects on rats and mice were reported for 2,4,5-T and the isooctyl ester of 2,4-D, while mortality and physical abnormalities were shown to increase in chick embryos of gamebird eggs sprayed with 2,4-D at rates commonly used in field applications [92, 100]. The most extensively used halogenated benzoic acid herbicides are Chloramben and Dicamba.
- *Nonionic compounds*: Pesticides of this category (Fig. 3) do not ionize significantly in aqueous systems and vary widely in their chemical compositions and properties (water solubility, polarity, molecular volume, and tendency to volatilization). The following are some examples:
 - Chlorinated hydrocarbon insecticides (including Toxaphene, Lindane, Chlordane, DDT and Heptachlor) are among the most widely known and studied group of nonionic pesticides [90, 101, 102].
 - Organophosphates are more toxic than chlorinated hydrocarbons, in particular to humans. Malathion and Parathion insecticides are known to be chemically hydrolyzed and biodegraded by microorganisms in solid phase systems.
 - Substituted urea herbicides are currently commercially available [90], including Benzthiazuron and Methabenzthiazuron. The most important are phenylureas and Cycluron, which has the aromatic nucleus replaced by a saturated hydrocarbon moiety.
 - Phenylamide herbicides (such as Diphenamid, moderately water soluble and nonvolatile), thiocarbamate and carbothioate herbicides (like Thio-bencarb, low water solubility, high vapor pressure) and benzonitrile herbicides (for example Dichlobenil, low water solubility, low vapor pressure) are other examples of nonionic compounds [90].

2.3.3

PCBs

Because polychlorinated biphenyls (PCBs) are potentially harmful to wildlife and man (Fig. 4), there has been continuous development in both the analyti-

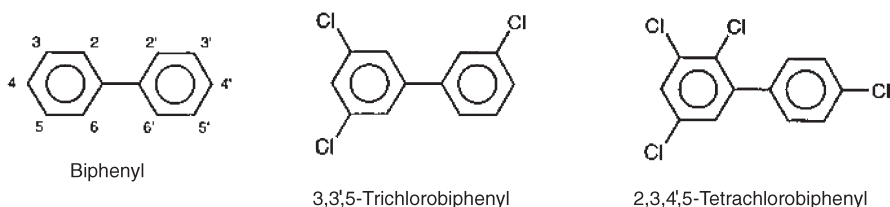


Fig. 4 Examples of chemical structures of PCBs

cal techniques to determine these compounds [38, 52, 103–106] and in the assessment of their biological effects [79, 107–112]. PCBs have been manufactured in substantial amounts since the 1920s [113]. Their uses are in the electrical, paint, pigments, paper and cardboard industries [87, 107, 113–122].

Early analyses of PCBs were made with packed gas chromatographic columns with electron capture detection and industrial formulations to quantify a total value for PCBs [105, 106, 122]. This early technology did not have the resolution to separate individual PCB congeners and the most appropriate method to estimate these contaminants at that time was unquestionably by the summation of the peak heights or areas of the low-resolution chromatogram. Some workers recognized the potential errors in such estimates and attempted to obtain a single response by perchlorination to the decachlorobiphenyl (CB 209) [105, 106, 121, 122]. The need to improve the separation, identification, and quantification of the individual PCB isomers has been reinforced by measurement of the toxic and biological effects of specific congeners [109–111, 123, 124]. With the present methodology and instrumental detection limits for low concentrations [124], it is now possible to measure individual PCBs routinely at levels of pg/kg, and with care at fg/kg.

2.3.4

Phthalates

Esters of 1,2-benzenedicarboxylic acid (phthalic acid esters, PAEs, phthalates) comprise a group of organic compounds used in large quantities by present day society (Fig. 5). The worldwide production of PAEs was estimated to be 4.2×10^9 kg during 1994 [125]. PAEs are mainly used as plasticizers in polyvinyl chloride (PVC) plastics and may constitute up to 67% of their total weight. They are also used in a variety of other products such as cosmetics, ammunition, and inks [126].

Diethyl phthalate – di-(2-ethylhexyl)phthalate (DEHP) (Fig. 5) – is one of the most abundant organic xenobiotics in the environment, accounting for approximately 40–50% of the global annual PAE production [127]. DEHP is an important and popular additive in many industrial products including flexible

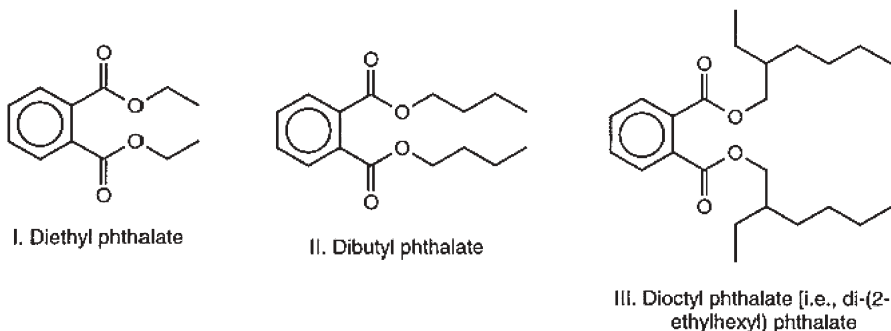


Fig. 5 Common names and chemical structures of phthalates

PVC materials and household products such as paint and glues [126]. The annual global production of DEHP has been estimated to be $1\text{--}20 \times 10^9$ kg [128]. The main sources of DEHP in the environment are incineration, direct evaporation and sewage treatment plants (where DEHP is often found in elevated concentrations in the dewatered sewage sludge). There has been a growing concern regarding the potential health risks associated with DEHP. Although DEHP is considered relatively nontoxic, carcinogenic and mutagenic effects of DEHP on aquatic organisms and laboratory animals have been reported [128, 129]. There has also been an increased focus on likely xenoestrogenic effects of DEHP and its metabolites [128]. On the basis of these findings, the need for a better understanding of the environmental fate of DEHP is evident.

2.3.5

Phenols

Phenol and substituted phenol compounds (Fig. 6) are known to be widespread as components of industrial wastes. These compounds are made worldwide in the course of many industrial processes, such as the manufacture of plastics, dyes, drugs and antioxidants, and in the pulp and paper industry. Organophosphorus and chlorinated phenoxyacids also yield chlorinated and nitrophenols as major degradation products [1]. Pentachlorophenol (Fig. 6), a wood preservative, is the priority contaminant within the group of chlorophenols that has been released most into the environment.

A hydrolysis step is involved in the pulp industry in order to concentrate the cellulose from wood. This uses large-scale processes whereby a liquid fraction, the lignocellulose, is formed as a by-product in the process, and contains high levels of phenolic components and their derivatives. Chlorophenols from the

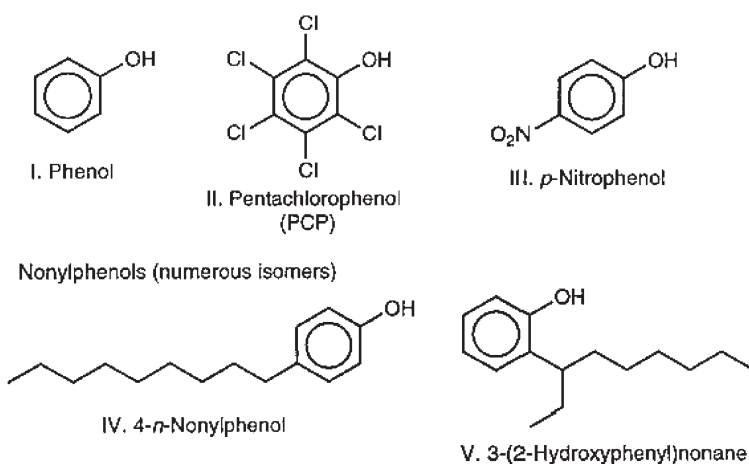


Fig. 6 Names and structures of phenol and substituted phenols

cellulose bleaching process have traditionally attracted most of the interest in the analysis of industrial waste because of their high toxicity.

Phenols and related compounds are highly toxic to humans and aquatic organisms, and have therefore become a cause for serious concern in the environment when they enter the food chain as water contaminants. Even at very low levels (<1 ppb), phenols affect the taste and odor of water and fish [1, 17].

2.3.6

Organotin Compounds

Organotin compounds (Fig. 7) are used worldwide as insecticides, fungicides, bactericides, acaricides, wood preservatives, plastic stabilizers, and antifouling agents [21, 27, 130]. Due to their high toxicity for aquatic organisms, the application of tributyltin (TBT) and triphenyltin (TPT) (Fig. 7) as marine antifouling agents has been restricted [131–134]. Despite these restrictions, TBT and TPT, as well as their major metabolites dibutyltin (DBT), monobutyltin (MBT), diphenyltin (DPT) and monophenyltin (MPT) are still found in natural waters at concentration levels that may be critical for the most sensitive organisms [131–134].

Despite the partial restrictions imposed on TBT by most countries, it is estimated that around 1200 tons yr^{-1} of TBT are used for the protection of ship hulls [135]. Exposure of humans to butyltin compounds used as stabilizers or as biocides in household articles has been regarded as one of the sources. Widespread usage of the organotin compounds motivated numerous studies in order to elucidate environmental contamination and impacts [135–138].

2.3.7

Surfactants

Surfactants (Fig. 8) represent one of the major and most versatile groups of organic compounds produced around the world [139], resulting in major inputs to solid wastes. Their main uses are: industrial, 54% (cleaning products, food and industrial processing); household, 29% (laundry, dishwashing); and

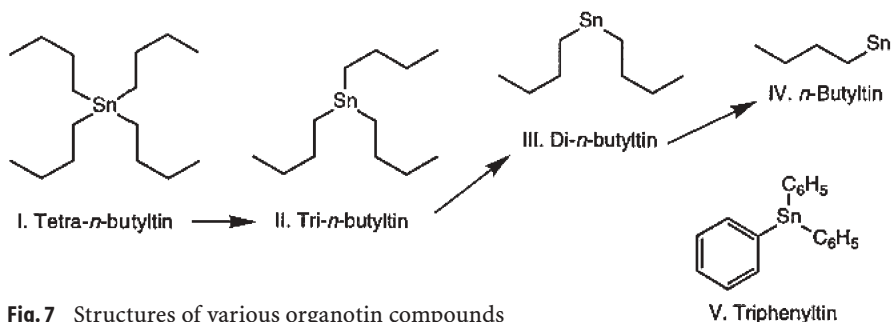
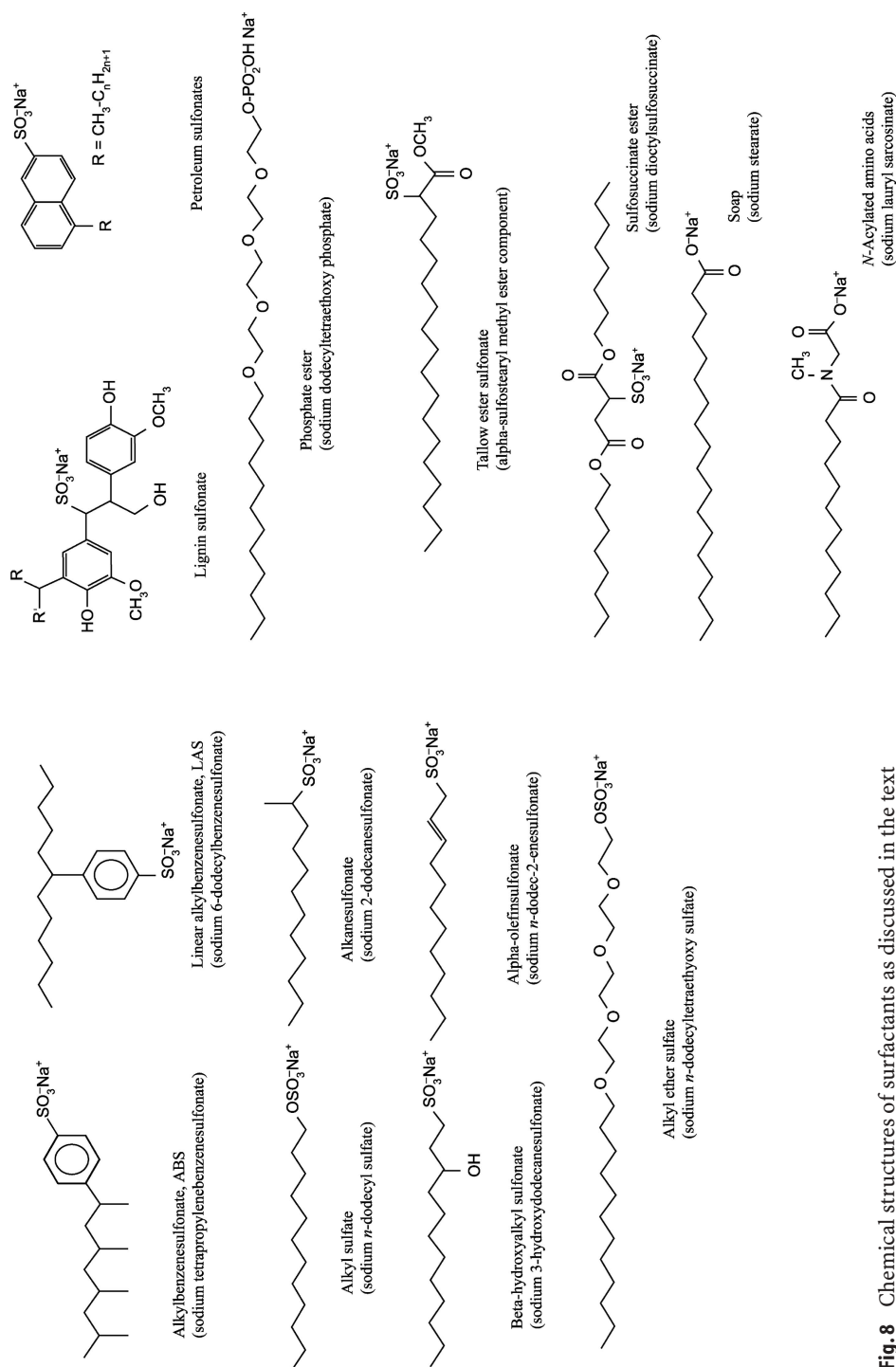
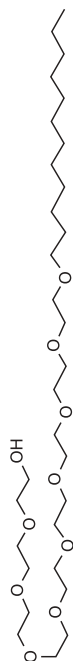
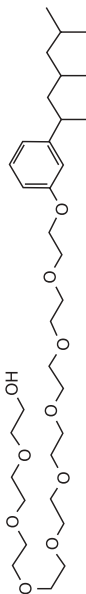


Fig. 7 Structures of various organotin compounds

ANIONICS:**Fig. 8** Chemical structures of surfactants as discussed in the text

NON-IONICS:Ethoxylated alcohol
(dodecanol 9-ethoxylate)

Ethoxylated alkylphenol

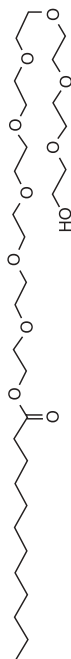
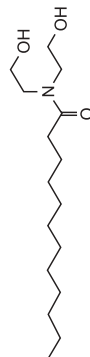
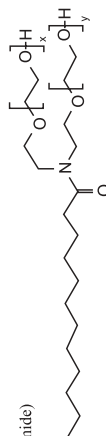
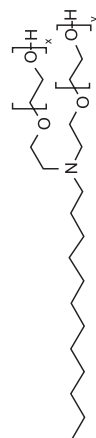
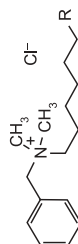
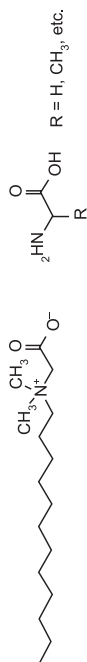
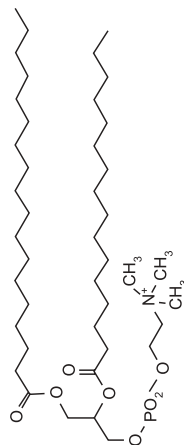
Ethoxylated acids
(dodecanoic acid nonaethyleneglycol ester)Fatty acid alkanolamide
(dodecanoic acid diethanolamide)Ethoxylated alkanolamides
(ethoxylated dodecanoic acid diethanolamide)Ethoxylated amines
(ethoxylated dodecylamine)Amine oxide
(lauryl dimethylamine oxide)

Fig. 8 (continued)

CATIONIC:Fatty acid quaternary ammonium salts
(n-Hexadecyltrimethylammonium chloride)

Benzylalkyl dimethylammonium salts

AMPHOTERICS:Carboxybetaines
(dodecyl dimethylammonium methane carboxylate)

Lecithin

personal care, 17% (soaps, shampoos, and cosmetics). The main groups of surfactants are shown in Fig. 8 and can be summarized as follows:

- *Anionic*: This group has been classified into subgroups, including alkyl benzene sulfonates, linear alkyl benzene sulfonates, alcohol sulfates, alcohol ether sulfates, alkyl phenol ether sulfates, fatty acid amide ether sulfates, alpha-olefin sulfates, paraffin sulfonates, alpha sulfonated fatty acids and esters, sulfonated fatty acids and esters, mono- and di-ester sulfosuccinates, sulfosuccinamates, petroleum sulfonates, phosphate esters, and ligno-sulfonates. Anionic surfactants have been extensively monitored and characterized in various environmental matrices [140–148].
- *Cationic*: The only cationic surfactant found in any quantity in the environment is ditallow dimethylammonium chloride, which is mainly the quaternary ammonium salt distearyldimethylammonium chloride. The organic chemistry and characterization of cationic surfactants has been reported and reviewed [149–153]. The different types of cationic surfactants are fatty acid amides, amidoamine, imidazoline, petroleum feed stock derived surfactants, nitrile-derived surfactants, aromatic and cyclic surfactants, non-nitrogen containing compounds, polymeric cationic surfactants and amine oxides [152–157].
- *Nonionic*: This group contains no ionic functionalities, as their name implies, and includes ethylene oxide adducts of alkylphenols and fatty alcohols. Production of detergent chain-length fatty alcohols from both natural and petrochemical precursors has now increased with the usage of alkylphenol ethoxylates for some applications. This is environmentally less acceptable because of the slower rate of biodegradation and concern regarding the toxicity of phenolic residues [158].
- *Amphoteric (zwitter-ionic)*: They are surface-active agents containing both anionic and cationic functional groups or moieties capable of carrying both ionic charges [139]. However, the term *amphoteric surfactants* or *amphoterics* is used generally to refer to materials that show amphoteric properties. The term *ampholytes* or *ampholytic surfactants*, though synonymous with amphoteric, is used to refer more specifically to surfactants which can accept or donate a proton, such as amino acids. A simple example of this type is 3-dimethyldodecylaminepropane sulfonate. Within this group are also a number of important natural triglycerides (for example lecithin) and alkylbetaines. The latter are obtained by reacting an alkyltrimethylamine with sodium chloroacetate, and because they are compatible with skin, they are used in the cosmetics industry [159].

The presence of some surfactants or their by-products in the aquatic environment has been considered to be a cause of endocrine disruption in the aquatic environment and ultimately in humans. Several workers have extensively reviewed and discussed the analysis, identification, and characterization of as well as the pollution problems associated with surfactants [145–147, 139, 160].

2.4

Experimental Analysis

The power of analytical instrumentation currently available makes it possible to detect organic contaminants leached from solid wastes used as road construction and repair (C&R) materials at extremely low concentrations. Such low detection limits are essential if contaminants are to be measured with the accuracy and precision required to model their environmental chemodynamic behavior. Most of the work on organic analysis and characterization has resulted from the use of gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) [1].

The isolation of the analyte (the contaminant of interest) from the matrix (the SWMs or their leachates) must be fully optimized and highly efficient. Apart from instrumental calibration, the analytical variability of any GC or GC-MS determination of trace organics in leachates might be caused by interference from non-target compounds. Increasing the specificity of the detectors does not necessarily remove the problem, but merely serves to hide the direct evidence of the interference. Varying amounts of extractants, which co-elute with the analyte, will affect the detector signal, giving rise to a reduced or even negative response [161, 162]. Improved reliability and robustness of a method is more likely achieved by efficient sample preparation than by some form of screening by a selective detector [163].

2.4.1

Recovery Measurements

Recovery measurements are one of the most difficult aspects in organic analysis. These measurements are often completed, with the minimum number of replicate determinations over a limited concentration range, to optimistically justify the use of a method. Experiments designed to obtain the efficiency of the analytical method often implicitly assume that this also includes the efficiency of extraction from the matrix [163].

The basic requirement is to estimate how much of the analyte has been removed from the matrix by a given extraction technique. However, the widespread practice of simply adding a known amount of the analyte to the matrix, usually in an organic solvent, prior to extraction and subsequent analysis, does not answer this question. This type of spiked sample analysis determines the accuracy and precision of the subsequent analytical steps, but does not necessarily measure the efficiency of extraction. To determine the efficiency of extraction, it is imperative that the contaminant of interest be bound to the matrix in a similar configuration to how it exists in the environment. The extraction efficiency can then be measured for that analyte in a specific matrix configuration, as follows:

- For *leachates*, water is the only matrix where this can be achieved in a relatively straightforward way. The analytes are added below the surface of the

- sample in a small volume of water-miscible solvent. The water must be completely mixed and allowed to stand at least overnight prior to extraction to allow the contaminants to come into equilibrium with the other organic materials. The spiked water sample must be analyzed in its entirety, including the inner surfaces of the container, either separately or as a single determination.
- *For SWMs*, samples can be doped with known amounts of the analyte by adding the contaminants in a small volume of water-miscible solvent, such as acetone, to the sample. Further mixing in a closed container for not less than 24 hours and then allowing settling for a similar period prior to a final mixing would also be helpful. Samples should be drained of any excess water and extracted wet.

Regular, routine sample recovery measurements can be made by using the method of standard addition. The matrix is spiked with the analytes in a small volume of solvent at a level which is 50%, 100%, 150% and 200% above the estimated level in the sample. A number of independent replicates should be made at each level. Provided that sufficient material is available, the sample can be analyzed prior to spiking. Standard addition to wet samples should be made in a water-miscible solvent (like acetone or methanol). Any convenient solvent can be used to spike waste samples.

Isotope dilution mass spectrometry (IDMS) is another method used to overcome the problem of sample recovery. The ^{13}C -labelled isotope of the analyte is added to the sample at the start of the analysis and the ratio of the labeled to unlabeled compound is measured by MS. This technique eliminates the need for recovery measurements and automatically accounts for any losses in the determination [164]. The two major limitations of this method are the cost and availability of the labeled compounds, and the need to use the MS as a detector.

2.4.2

Pre-extraction/Preservation Treatments

Leachates of solid waste samples used as road C&R materials, when collected, are usually preserved by freezing immediately. Rapid preservation is vital if the integrity of the sample is to be maintained. Samples can be treated in different ways prior to extraction depending on the purpose of the research program. However, this technique is not appropriate if relatively volatile contaminants such as 1-ring aryl hydrocarbons (like alkylbenzenes, chlorobenzenes), PAH (such as naphthalene) are to be determined. In such cases, the leachates should remain frozen prior to analysis and extracted wet.

2.4.3

Extraction Techniques

Although selective extraction of organic compounds appears to be an attractive option, the different types of adsorption sites on solid phases (for instance SWMs) require an exhaustive technique to recover the maximum amount of

the analyte from the substrate. This is particularly true where the compounds to be extracted cover a broad range of polarity, reactivity, and molecular size. Therefore, extraction is primarily a process of separating all of the analytes as completely as possible from the bulk of the matrix. This process will inevitably carry along unwanted co-extracted materials. Selective extraction is only possible when a small number of chemically similar compounds need to be isolated [165–166]. The following is an overview of the most commonly used extraction techniques.

2.4.3.1

Supercritical Fluid Extraction

There have been many reports on the use of supercritical fluid extraction (SFE) to extract PCBs, phenols, PAHs and other organic compounds from various solid wastes [20, 161, 162, 167–175]. The attraction of SFE as an extraction technique is directly related to the unique properties of the supercritical fluid [176, 177]. The supercritical fluids that have been used have low viscosities, high diffusion coefficients and low flammabilities, which are all clearly superior to the organic solvents normally used. Carbon dioxide (CO_2) [89, 90] is the most common supercritical fluid used for SFE, since it is inexpensive and has a low critical temperature (31.3 °C) and pressure (72.2 bar). Other less commonly used fluids include nitrous oxide (N_2O), ammonia, fluoroform, methane, pentane, methanol, ethanol, sulfur hexafluoride (SF_6) and dichlorofluoromethane [89–91]. Most of these fluids are clearly less attractive as solvents in terms of toxicity or as environmentally benign chemicals. Commercial SFE systems are available, but some workers have also made inexpensive modular systems, as follows:

- Levy et al [178] briefly investigated alternative fluids for on-line SFE- capillary GC with CO_2 , N_2O , and SF_6 for the extraction of PAHs and alkanes from solid waste, sediment and shale rock. They initially compared the extraction efficiency of pure fluids and then some fluid mixtures. They found that 20% SF_6 in CO_2 was more effective at 375 bar, and 50 °C for 30 min than each pure fluid for removing both PAHs and alkanes.
- McNally and Wheeler [179, 180] applied SFE to the analysis of sulfonylurea herbicides and their metabolites in soil-solids. Lopez-Avila et al [181] used SFE to extract a series of organochlorine and organophosphorus pesticides from sand using CO_2 and CO_2 modified with acetone.
- Young and Weber [182] presented an equilibrium and rate study of analyte-matrix interactions in SFE in aqueous matrices.

2.4.3.2

Soxhlet

Soxhlet extraction is commonly used to extract non-polar and semi-polar trace organics from a wide variety of solid phases [20, 163, 183–184]. The size of the systems can vary, but the more common configurations use between 100 and

500 ml of solvent to extract between 20–200 g of sample. Larger systems can be used, but require proportionally more solvent. It is essential to match the solvent polarity to the solute solubility and to thoroughly wet the matrix with the solvent when extraction commences.

SWMs or C&R materials need to be thoroughly wetted with solvent to obtain an efficient extraction. Non-polar solvents do not readily wet the surface of dry samples and are too immiscible with water to be able to penetrate water-wet material. This problem can largely be overcome by: (a) dampening the sample with an electrolyte (like 1% ammonium chloride, overnight); (b) using azeotropes or binary mixtures such as acetone or methanol with hexane or dichloromethane which have sufficient polarities and water solubilities to wet the particle surfaces. If there is a need to remove waxes and lipids of a sample, it can be saponified prior to extraction [1–4, 163]. In some cases, this technique can result in an even higher recovery. On the other hand, Garcia-Ayuso et al [185] introduced the microwave-assisted Soxhlet extraction technique and reported its advantages over other regular Soxhlet and/or different extraction procedures.

2.4.3.3

Blending and Ultrasonic

The simplest extraction technique is to blend or ultrasonically agitate a sample with an appropriate organic solvent at room temperature. Apart from the polarity of the solvent, the efficiency of the extraction is dependent upon the homogeneity of the sample and the mixing/ultrasonication/blending/soaking time. The mixture of sample and organic solvent are separated from each other by centrifugation or filtration and washing with solvent. Blending has been used for solid phase samples [105, 163, 185], as follows:

- Schwab et al [186] found that *n*-hexane or cyclohexane and iso-propanol recovered <1% of the tri- and tetra-catechols in the solid sample.
- Remberger et al [187] attempted to extract both the “free” and the “bound” fractions with an acetonitrile/hexane/methyl *tert*-butyl ether solvent mixture. However, a higher recovery (25–100%) was obtained by using methanolic potassium hydroxide.
- Wells et al [188] reported the same improvement with saponification for the recovery of some PCBs from sewage sludge during an intercomparison exercise.
- Brezny and Joyce [189] made a comparative study of the recovery of ten chlorophenol contaminated soils using conventional solvent extraction and in situ acetylation.

2.4.3.4

Liquid-Liquid

Liquid-liquid extraction (LLE) is based on the partition of organic compounds between the aqueous sample (the leachate) and an immiscible organic solvent.

The efficiency of an extracting solvent depends on the affinity of the compound for this solvent, as measured by the partition coefficient (in other words it depends on the ratio of volumes of each phase and on the number of extraction steps). Solvent selection for the extraction of leachates is described and reported in many reviews and recent articles [163, 190–191] and is related to the nature of the analyte. Non-polar or slightly polar solvents are generally chosen. Hexane and cyclohexane are typical solvents for extracting aliphatic hydrocarbons and other non-polar contaminants such as organochlorine or organophosphorus pesticides. Dichloromethane and chloroform are certainly the most common solvents for extracting non-polar to medium polarity organic contaminants [1–4].

LLE can be performed simply using separatory funnels. The partition coefficient should therefore be large because there is a practical limit to the phase-volume ratio and the number of extractions. When the partition coefficient is small and the sample very dilute, a large volume must be handled and continuous liquid-liquid extractors should be used. The extractions then take several hours. Such extractors have been described in the literature [187]. The partition coefficient may be increased by adjusting the pH to prevent ionization of acids or bases or by forming ion pairs or hydrophobic complexes with metal ions, for example. The solubility of analytes in the aqueous phase can be reduced by adding salts. Fractionation of samples into acidic, basic and neutral fractions can be attained by successive extractions at different pH [1].

LLE of relatively polar and water-soluble organic compounds is, in general, difficult. The recovery obtained from 1 L of water with dichloromethane is 90% for Atrazine, but lower for its more polar, degradation products, such as de-isopropyl- (16%) de-ethyl (46%) and hydroxy-atrazine (46%). By carrying out LLE with a mixture of dichloromethane and ethyl acetate with 0.2 M ammonium formate, the extraction recoveries for the three degradation products were increased to 62, 87, and 65%, respectively [1].

LLE results in the extraction of the analyte into a relatively large volume of solvent which can be concentrated using a rotary evaporator to a few milliliters. Further concentration to a few hundred microliters can be carried out by passing a gentle stream of pure gas (usually dry N₂) over the surface of the extract contained in a small conical vial. The solvent-evaporation method is slow and has a risk of contamination. Micro-extractors have been described, and have the advantage of avoiding the further concentration of organic solvents [179, 180, 190, 192].

The main advantages of LLE are its simplicity and the use of simple and inexpensive equipment. However, it is not free from practical problems such as the formation of emulsions, which are sometimes difficult to break up [165]. The evaporation of large solvent volumes, and the disposal of toxic and often flammable solvents, are also inherent to the method. LLE requires several sample-handling steps and contamination and loss must be avoided at every step. The glassware must be carefully washed or annealed and stored under rigorous conditions. The organic solvents used must be pure pesticide-grade when extracting traces of pesticides from aqueous samples.

2.4.3.5

Solid-Phase

Solid-phase extraction (SPE) or liquid-solid extraction is a sample preparation method, which is especially well adapted to the handling of water samples. SPE has been widely used and reported in several research articles [101, 193–197]. Trace organics are trapped by a suitable sorbent packed in a so-called extraction column through which the water passes and are later recovered by elution with a small volume of organic solvent. Extraction and concentration are therefore performed at the same time. This technique appears less straightforward than LLE, because there is a large choice of sorbents and because the recoveries depend on the sample volume. In fact, SPE is simple when one considers that it is based on the well-established separation principles of liquid chromatography. SPE can be used: (a) *off-line*, the sample preparation being completely separated from the subsequent chromatographic analysis, or (b) *on-line*, by direct connection to the chromatographic system (typically GC).

2.4.4

Clean-Up Techniques

Normally, an extraction technique is selected to give the highest recovery for a wide range of contaminants. Therefore the extract will most likely contain a high proportion of co-extracted material. Many of the clean-up techniques have been tailored into a series of multi-residue schemes in order to maximize the use of each sample [105, 184, 197]. This is of particular value when the maximum amount of chemical information is required for each sample.

The main requirement for any clean-up and group separation scheme is that it effectively removes not only the bulk of the co-extractants, such as lipids, sulfur, carotenoids and other pigments, but also those compounds that may potentially interfere in the final determination. There are three main ways in which co-extracted material may interfere in the final determination if not removed:

- Gross contamination can overload the HPLC or GC columns with obvious and usually rapid deterioration of chromatographic performance. This can occur with so called “rapid” techniques where the detector is used as a filter, such as selected ion monitoring (SIM) MS, or where the clean-up method has been overloaded (like with an excess of lipid). This problem can be overcome by using and monitoring more selective clean-up techniques.
- Interferences caused by inadequate chromatographic separation during the final determination. This can be improved by multi-dimensional GC or multi-dimensional preparative LC.
- Interference occurs when compounds co-elute with the analytes and are not detected directly by a specific detector. The effect is to create negative peaks or an erratic response for the analyte. This problem can be identified by using a non-specific detector such as an ion trap MS detector, MS in the electron impact ionization mode or a flame ionization GC detector.

These problems are overcome by applying a tailored LC separation prior to the final determination and having a built-in feedback to monitor the success of the separation or to give a warning of any failure. Table 1 summarizes the most commonly used clean-up techniques in the organic analysis of environmental contaminants [1–4, 102, 105, 163, 184, 197–202].

2.4.5

Fractionation

Before using state-of-the-art analysis and characterization techniques, most sample extracts are separated or fractionated prior to analysis [1–4, 163]. There are many fractionation schemes reported in the literature, and isolation of organic fractions generally incorporates thin layer chromatography (TLC) or column chromatography using alumina, silica gel or a combination of both. A simple scheme that can be used to obtain various lipid fractions was developed by eluting them from the chromatographic column with solvent mixtures of increasing polarity as *n*-hexane, dichloromethane and methanol [1–4]. Once the fractions containing the compounds of interest have been separated, further fractionation can be made by urea adduction or molecular sieving to separate linear compounds from branched and cyclic compounds.

2.4.6

Automation

Automation does not always remove the problems of time and effort associated with manual methods. A critical evaluation of both the manual methods to be replaced and the automated alternative should be made before embarking on a new scheme. New, improved and rapid methods described in the literature may not always be appropriate [163]. The following is a summary of the most common automation techniques.

2.4.6.1

Robotics

Regardless of the pretreatment method, simple manipulations in sample preparation remain one of the most labor-intensive areas of analytical work [204]. There are many applications of auto-injection, multi-dimensional chromatographic separations and data analysis, but sample preparation has not had the same level of automation in most laboratories. The key advantages of automation are unattended repetitive tasks (time saving); greater accuracy, consistency, reliability, the removal of the analyst fatigue factor, and continuous operation with toxic solvents (dichloromethane) and corrosive materials (SiO₂/sulfuric acid, also fine powder adsorbents) (safety). Automated systems may require isolation but not fume exhaust hoods (saving space and cost).

Robotic systems in a small analytical laboratory have the greatest application to the intermediate sample manipulation steps. The removal of excess sol-

Table 1 Clean-up techniques in the organic analysis of environmental contaminants

Methods	Advantages	Disadvantages	References
Saponification	Removal of triglycerides and wax esters by extraction with 5% potassium hydroxide in methanol	Suitable only for the most chemically resistant contaminants	1–4, 198
	Hydrolysis of most organophosphorus pesticides		1–4, 198
	Determination of some PCBs	Susceptibility of the more chlorinated PCBs to loss of chlorine (at high temperature <70 °C for <1 h)	199
Sulfuric acid	Suitable for the most robust chemical groups such as organohalogens without an oxygen bridge	Not suitable for Dieldrin, Endrin and Aldrin	1, 105
	Involving shaking the analyte extract in an alkane solvent with the concentrated acid	This reaction is more manageable if the acid is adsorbed onto silica gel	1, 105
Solid phase clean-up	Used in an “off-line” mode, primarily to remove the bulk of co-extracted materials prior to a more refined clean-up prior to the final determination		105, 195
	Preparation of columns in the laboratory or using commercial solid phase extraction (SPE) cartridges	Disposability of the normal phase cartridges and column materials since many of polar co-extractants bind firmly to the substrate surface	200, 203
	Regeneration of columns and cartridges in some circumstances by flushing with methanol	Gross contamination from the co-extractants precludes their re-use	1, 200
Gel permeation chromatography (GPC)	Use of similar LC clean-up and separations “on-line” for less contaminated samples		163
	Separation between lipid material <500 Å which is the first to elute from such columns followed by the smaller molecules (including most of the organic contaminants that accumulate in sample matrices)		102, 163, 197

Table 1 (continued)

Methods	Advantages	Disadvantages	References
Gel permeation chromatography (GPC)	Non-destructive and can be used to isolate less robust contaminants (like organophosphorus pesticides)		181, 197, 201
	Isolation of unknown contaminants or alteration products where there is little information on the polarity/chemical functionality of the molecule		
Supercritical fluid extraction (SFE) clean-up	More tolerant of handling a large mass of lipid in each sample, where columns (50 cm×25 mm i.d) can cope with up to 500 mg of lipid	The difficulty of completely removing all traces of lipids	1
	Possibility of increasing the size of the adsorption column to remove 250 mg of lipid	Requirement to use larger volumes of solvent to elute the more polar organics	1, 197
	Complete separation between the bulk matrix and the small organic contaminants (<500 Da) <i>in situ</i> .	Limitation and difficulties in selecting the optimum SFE parameters to obtain a lipid free sample	1, 202
	Removal (with a few exceptions) of all soluble lipophilic material along with the trace organic contaminants		
Sulfur removal	The use of adsorbents such as Tenax, Carbowack C, Spherosil XOA200, florisil and reverse phase C ₁₈ sorbent to trap organics and subsequently desorb them using SFE with CO ₂	Instability of Carbowack when used with supercritical fluids and high molecular weight artifacts were extracted from Tenax	1, 199
	Elemental sulfur removal prior to analysis by ECD-GC or GC-MS by the reaction with: (a) mercury or a mercury amalgam to form mercury sulfide, (b) copper to form copper sulfide, or (c) sodium sulfite in tetrabutyl ammonium hydroxide (Jensen's reagent)	Removal of sulfur with mercury or copper requires the metal surface to be clean and reactive The need to clean with dilute HNO ₃ if the metal surface becomes covered with sulfide	1

vent with the Zymark evaporator [1], for example, can be closely controlled, fully automated and can be operated in parallel (up to six samples per instrument). This technique has considerable advantages over rotary evaporation, which is prone to lose volatile organic compounds (like chlorobenzenes) under vacuum and rapid vaporization. Automated repetitive manipulations are well served by a robotic system [1].

2.4.6.2

On-Line Automation

Although on-line automation systems offer considerable attractions, such techniques need to be fully investigated before applying them to an analytical manipulation. The transition from a manual to an automatic method is more easily made if each step in the existing method is readily amenable to such a change. For example, column extraction or SFE are good candidates for automation, but combining them would only be suitable with extensive robotics. Most LC methods, whether gravity columns, SPE or HPLC can be automated and connected on-line to the final GC or GC-MS stage. However, there are two main unresolved problems with the on-line LC-GC approach for multi-residue analysis, which can be summarized as follows:

- Although the separation between some unwanted co-extractants and the analytes is well suited to an on-line system, high lipid or elemental sulfur loading is more effectively removed off-line. Most on-line systems at present work most effectively with low lipid content [204], although some applications have overcome the problem of lipid removal.
- The LC-GC is used to isolate analytes in a separate fraction from other interferences, usually by heart cutting, and then to chromatograph that fraction by GC. However, difficulties arise when multiple fractions must be isolated from each sample by the LC. The sample should also be separated into fractions when similar compounds are present at considerably different concentrations or where chromatographic overlap is to be avoided. Under such conditions, the multiple fractions produced by the on-line LC cannot be analyzed directly by linking a single GC. This difficulty may, however, be overcome by using an on-line heart cut into the GC autosampler, so that each fraction can be taken sequentially into the GC.

Despite the difficulties of “on-line” automation, the need to develop such systems is considerable. The increase in the number of different compounds that must be determined and the number of samples required for a meaningful survey or laboratory study make it essential to improve the quality and through-put of samples. There are a number of stages needed to fully automate trace organic analysis. Autosampler LC or GC-Data Systems as GC-MS, GC-ion trap detector (ITD) are well established and require no further elaboration here [204].

2.4.7

Identification and Characterization

In the past few years, the number of organic contaminants that have been identified from various sources has increased dramatically due to extensive analytical research by numerous scientists [2–16]. The major reason for this marked increase is a result of analytical development in the detection and identification of organic markers, in particular by GC-MS and associated data systems. The development of high-resolution capillary columns has led to their routine usage in most GC-MS systems. The improved separation of complex organic mixtures (COMs) through the use of high-resolution capillary columns has led to the identification of additional molecular markers. Along with the increase in gas chromatographic resolution, fast-scanning mass spectrometers, both quadrupole and magnetic sector instruments, are able to obtain spectra on relatively small and narrow chromatographic peaks. The present situation is completely different than before, when it was necessary to isolate compounds in pure crystalline form in order to enable structural determinations to be made by classical chemical techniques.

A dramatic change in instrumental development for environmental chemical analysis and specifically for molecular contaminants has occurred over recent years [205–218]. The following sections will review the different techniques and instrumental development currently used for the characterization of organic contaminants.

2.4.7.1

Gas Chromatography

In 1975, gas chromatography (GC) with glass capillary columns provided the best means for resolving complex organic mixtures of contaminants [219–221]. Currently, the available capillary columns are made of flexible fused silica with low activity, which eliminates many of the problems previously associated with glass capillary columns [163, 222, 223]. The latest development is columns with the liquid phase actually bonded to the fused silica. These columns have a much longer life and can be washed with solvents if peak shapes degenerate as a result of the accumulation of polar compounds on the column [224, 225]. Furthermore, the columns can be taken to a much higher final temperature with low levels of column bleed. Therefore, the number of organic compounds currently resolvable on capillary columns is much greater than those resolved in the 1970s [220–230].

2.4.7.2

Gas Chromatography-Mass Spectrometry

Mass spectrometers use differences in mass-to-charge ratio (m/z) between ionized atoms, molecular fragments, or whole molecules to differentiate among each other. Mass spectrometry is therefore useful for quantitation of atoms or

molecules and also for determining chemical and structural information about them [231–235]. Molecules have distinctive fragmentation patterns that provide information used to identify structural components. The general operation of a mass spectrometer is to: (a) create gas-phase ions, (b) separate the ions in space or time based on their mass-to-charge ratio, and (c) measure the quantity of ions of each mass-to-charge ratio.

In general a mass spectrometer consists of an ion source, a mass-selective analyzer, and an ion detector. Since mass spectrometers create and manipulate gas-phase ions, they operate in a high vacuum system. The magnetic-sector, quadrupole, and time-of-flight designs also require extraction and acceleration ion optics to transfer ions from the source region into the mass analyzer. Tables 2 and 3 provide brief descriptions of the most commonly used ionization techniques and the different types of mass spectrometers available, respectively [163, 232–235, 241, 242, 244–246].

Table 2 The commonly used ionization techniques in mass spectrometry

Methods	Description	References
Electron impact (EI)	An EI ion source uses an electron beam, usually generated from a rhenium filament, to ionize gas-phase atoms or molecules Electrons from the beam (usually 70 eV) knock an electron from a bond of the atoms or molecules creating fragments and molecular ions EI ionization is popular in environmental analyses because of its stability, ease of operation, simple construction, precise beam intensity control, relatively high efficiency of ionization and narrow kinetic energy spread of the ions formed	163, 234, 235
Chemical ionization (CI)	CI has proven to be a useful technique for the MS analysis of many contaminants CI uses a reagent ion to react with the analyte molecules to form ions by either a proton or hydride transfer: $MH + C_2H_5^+ \rightarrow MH_2^+ + C_2H_4$ $MH + C_2H_5^+ \rightarrow M^+ + C_2H_6$ The reagent ions are produced by introducing a large excess of reagent gas (like methane) relative to the analyte into an electron impact (EI) ion source. Electron collisions produce CH_4^+ and CH_3^+ which further react with methane to form CH_5^+ and $C_2H_5^+$: $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	232, 234, 235

Table 2 (continued)

Methods	Description	References
Negative ion chemical ionization (NICI)	NICI is a sensitive and selective mass spectrometric ionization technique for the analyses of a wide range of organic compounds The NICI mode usually requires that the analyte be derivatized so that it contains highly electron-capturing moieties (like fluorine atoms or nitrobenzyl groups). Such moieties are generally inserted onto the target analyte after isolation and before mass spectrometric analysis The sensitivity of NICI analyses is generally two to three orders of magnitude greater than that of EI analyses. Little fragmentation occurs during NICI, and this mode of ionization is generally employed for quantitative analyses of trace amounts of compounds of known structure in conjunction with the use of heavy isotope-labeled internal standards. Negative ionization may occur, in general, by two mechanisms: – <i>Electron-molecule reactions</i>: This process is also referred to as electron capture detection mass spectrometry (ECD-MS), and is amenable to compounds containing electrophilic moieties (such as compounds with positive electron affinities). ECD-MS has been investigated and used extensively for analyses of many classes of environmental contaminants and for forensic toxicological applications. – <i>Ion-molecule reactions</i>: Ion-molecule reactions, such as proton abstraction, depend on the analyte and the NICI reagent gas used. Irrespective of the mechanism of ionization, NICI is characterized as a soft ionization technique, whereby NICI spectra exhibit prominent molecular anions, and therefore molecular weight information.	1, 242
Electro-spray ionization (ESI)	The ESI technique is widely used in environmental analysis, where the source consists of a fine needle and a series of skimmers A sample solution is sprayed into the source chamber to form droplets. The droplets carry a charge when they exit the capillary, and as the solvent evaporates, the droplets disappear leaving highly charged analyte molecules	27, 35, 42, 234, 235, 244–246
Fast-atom bombardment (FAB)	In FAB, a high-energy beam of neutral atoms, typically Xe or Ar, strikes a solid sample causing desorption and ionization FAB is used for large organic molecules that are difficult to mobilize into the gas phase	163, 235–243

Table 2 (continued)

Methods	Description	References
Fast-atom bombardment (FAB)	FAB causes little fragmentation and usually gives a large molecular ion peak, making it useful for molecular weight determination The atomic beam is produced by accelerating ions from an ion source through a charge-exchange cell The ions pick up an electron in collisions with neutral atoms to form a beam of high-energy atoms	163, 235–243
Plasma and glow discharge	A plasma is a hot, partially-ionized gas that effectively excites and ionizes atoms A glow discharge is low-pressure plasma maintained between two electrodes It is particularly effective at sputtering and ionizing material from solid surfaces	234, 235, 243
Field ionization (FI)	Molecules can lose an electron when subjected to a high electric potential resulting in FI High fields can be created in an ion source by applying a high voltage between a cathode and an anode called a field emitter A field emitter consists of a wire covered with microscopic carbon dendrites, which greatly amplify the effective field at the carbon points	1, 163
Laser ionization mass spectrometry (LIMS)	A laser pulse can ablate material from the surface of a sample, and create a microplasma which ionizes some of the sample components The laser pulse accomplishes both vaporization and ionization of the sample	1, 30, 63, 234, 235
Time-of-flight mass spectrometry (TOF-MS)	A TOF-MS uses the differences in transit time through a drift region to separate ions of different masses It operates in a pulsed mode so ions must be produced or extracted in pulses An electric field accelerates all ions into a field-free drift region with a kinetic energy of qV, where q is the ion charge and V is the applied voltage. Since the ion kinetic energy is $0.5 mv^2$, lighter ions have a higher velocity than heavier ions and reach the detector at the end of the drift region sooner TOF-MS has been used widely for different environmental applications	31, 32, 234, 235
Fourier-transform mass spectrometry	Fourier-transform mass spectrometry takes advantage of ion-cyclotron resonance to select and detect ions	163, 234, 235

Table 3 The different types of mass spectrometers available

Type	Description	References
Quadrupole mass spectrometry and MS/MS	It consists of a mass filter with four parallel metal polarity rods Opposing rods have an applied potential of $(U+V\cos(wt))$ and the other two rods have a potential of $-(U+V\cos(wt))$, where U is a direct current voltage and $V\cos(wt)$ is an alternating current voltage The applied voltages affect the trajectories of the ions traveling down the flight path centered between the four rods For given direct and alternating current voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all others are deflected from their original path A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied	163, 234–241
Magnetic-sector mass spectrometry	The ion optics in the ion-source chamber of a mass spectrometer extract and accelerate ions to a kinetic energy of 70 eV In the flight tube, they are separated between the poles of the magnetic field according to mass Only ions of mass-to-charge ratio that have equal centrifugal and centripetal forces pass through the flight tube The accuracy is adequate to utilize this method mainly for high-resolution mass spectrometry	234, 235
Ion-trap mass spectrometry	The ion-trap mass spectrometer uses three electrodes to trap ions in a small volume The mass analyzer consists of a ring electrode separating two hemispherical electrodes A mass spectrum is obtained by changing the electrode voltages to eject the ions from the trap The advantages of the ion-trap mass spectrometer include compact size, and the ability to trap and accumulate ions thus increases the signal-to-noise ratio of a measurement	39, 234, 235

The combination of high-resolution capillary columns with fast scanning quadrupole or magnetic sector mass spectrometers provides an excellent method for the identification of a large proportion of the compounds in complex organic materials. It is worth mentioning that GC-MS analysis has the added advantage over GC of providing structural information on many unknown components responsible for the chromatographic peaks, as well as components that appear to be hidden in the baseline of the chromatogram [217]. The basis for GC-MS detection of molecular markers is the fact that in the ion source of the mass spectrometer many molecular markers fragment in a systematic manner to produce one or more characteristic (key) ions that can be used to detect the particular organic marker in question.

The best example to explain the fragmentation pattern and data interpretation in GC-MS is provided by the ubiquitous molecular markers with the hopane-type structure (Fig. 1; Structures VII and VIII). The molecular weight varies according to the substituent R at C-21, which has been shown to range from H to $C_{13}H_{27}$. Generally, hopanes are a very important class of biomarkers in petroleum-contaminated samples [11–16]. Hopanes fragment in the mass spectrometer producing two major ions as shown in Fig. 9. The first is at m/z 191 from the A/B ring fragment and the second at m/z 148+R from the D/E ring fragment where the mass will vary depending on the substituent R. The relative intensities of the ions at m/z 191 and m/z 148+R vary depending on the stereochemistry at the C-17 and C-21 positions. However, by monitoring only the variations in intensity of these characteristic ions (SIM), rather than acquiring a complete mass spectrum at each scan, the sensitivity of the mass spectrometer for detecting hopanes is increased by several orders of magnitude.

GC-MS using high-resolution capillary columns and low-resolution mass spectrometers has been a popular analytical technique in environmental analysis [1]. However, additional analytical techniques have been used very recently to extend the capabilities available for the determination of molecular mark-

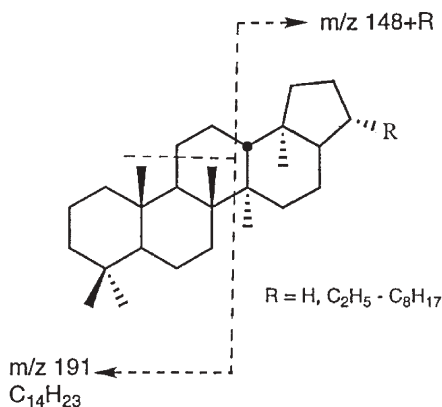


Fig. 9 MS fragmentation pattern of a hopane-type structure

ers. One example is the use of tandem mass spectrometry (MS-MS), which is another technique used for the direct analysis of individual molecular markers in complex organic mixtures [39, 206, 209, 236–240]. This technique provides a rapid method for the direct analysis of specific classes of molecular markers in whole sample extracts. In this approach, the system is set up to monitor the parent ions responsible for a specific daughter ion as described above, and the distribution of parent ions obtained under these conditions should provide the same information as previously obtained by GC-MS [207, 240]. Even greater specificity can be achieved by a combination of GC-MS-MS [241, 243]. In view of the complexity of SWM samples and the need to detect the presence of individual organic compounds or classes of compounds, it would seem that MS-MS, especially coupled with GC, would be extremely valuable in future environmental organic geochemistry studies.

2.4.7.3

Liquid Chromatography-MS

Other combinations of chromatography techniques with MS which may be useful in organic analysis are the coupling of high-performance liquid chromatography (HPLC) with MS [36, 170, 206, 207, 247–254], LC with MS-MS [255–261], LC with atmospheric pressure chemical ionization MS (LC-APCI-MS) [262], and Fourier transform infrared spectroscopy-fast atom bombardment coupled to LC-MS (FTIR-FAB-LC-MS) [263].

LC-MS has been used to study various aromatic fractions from coal derived liquids, and there are also a number of reports on its use in the analysis of porphyrin mixtures [264]. The early work by Dark et al [265] using LC-MS for coal-derived liquids was mainly concerned with the separation and identification of polycyclic aromatic components. However, it is interesting to note that developments in the field of fused silica capillary columns for GC has been so rapid that most of the aromatic compounds with six or seven aromatic rings can now be passed through a GC, eliminating the need for LC [266]. Nevertheless, the role for LC in the future of petroleum and environmental geochemistry may again be directed at examining higher molecular weight and more polar molecules.

2.4.7.4

Future Developments

Most of the development work on organic contaminants has resulted from the use of GC-MS and synthesis of authentic standards or surrogate standards. However, with advances in other techniques it is clear that this field will benefit by making greater use of alternative identification and characterization methods. The following is a summary of some advances and instrument combinations:

- Fourier transform infrared spectroscopy (FTIR) can now be combined with GC to provide IR spectra on peaks eluting from a capillary column [263, 267–269].

- A combination of GC-FT-NMR-MS is also being developed to provide an extremely powerful tool for identifying molecular markers [270, 271]. If sufficient quantities of individual molecular markers can be isolated, then there are various ^1H [270, 272] and ^{13}C nuclear magnetic resonance techniques [231, 271–273] available to assist in their structural identification.
- High-performance liquid chromatography was combined with electrospray ionization mass spectrometry (HPLC-ESI-MS) to quantitatively differentiate crude natural extracts of various environmental samples [244, 246] and to NMR (HPLC-MS-NMR) for quantitation measurement [274].
- Microwave-assisted extraction coupled with gas chromatography-electron capture negative chemical ionization mass spectrometry (MAE-GC-EC-NCI-MS) was described for the simplified determination of imidazolinone herbicide-contaminated soils at the ppb level [275].
- Liquid chromatography was developed to analyze carbonyl (2,4-dinitrophenyl)hydrazones with detection by diode array ultraviolet spectroscopy (DA-UV) and by atmospheric pressure negative chemical ionization (APNCI) mass spectrometry [276]. In addition, LC can be combined with electrospray ionization coupled on-line to a photolysis reactor for better detection and confirmation of photodegradation products [245].
- High-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry (HRGC-EC-NI-HRMS) has been used for quantifying chloroalkanes in environmental samples [277].
- Flash pyrolysis-GC-MS has been applied recently to identify and determine various principal groups of pyrolysed organic matter as well as other organic compounds [213, 278, 279].

3 Genetic Source Modeling

Although a major element of an environmental forensics investigation involves chemical fingerprinting to identify contaminants, fingerprinting alone is not always sufficient to provide answers to questions of source and responsibility. Environmental forensics has recently evolved beyond the chemical domain and now routinely incorporates an evaluation of site-specific geologic components such as hydrogeology, stratigraphy, and solid phase properties. Chemometrics, the numerical analysis of chemical data, synthesizes all of this complex information to visualize it. Forensic investigations are further strengthened through access to equally important contaminated-site historical records. These often contain information useful for identifying candidate contamination source areas, chemical parent product types from which contaminants have originated, as well as release and spill histories.

In the early stages of a leaching process or a release, it is a more straightforward task to identify the contaminant at a certain site. However, after weathering (chemical, physical and biological signature-altering processes) and

mixing with pre-existing background contaminants, the obvious initial signature of the released contaminant begins to lose its identity.

The first step in distinguishing differences or similarities between contaminants in source samples (end members or original sources) and those of released products has always been pattern recognition of target contaminant distributions. Historically, these identifications have relied on visual interpretation of subtle differences or similarities in gas chromatograms of samples. Because these analyses do not relate to specific compounds, such techniques are often difficult to explain and defend [1]. In modern environmental forensic investigations, such methods have been supplanted by a number of powerful data interpretative tools. These tools include graphical techniques that examine relationships among marker compounds, as well as more advanced statistical multivariate techniques for examining these relationships. The following sections provide a summary of the most commonly applied statistical and mathematical modeling techniques used for genetic source confirmation of environmental contaminants.

3.1

Discriminant Analysis

The main use of discriminant analysis (DA) is to predict group membership (the association of contaminants that represent a certain source) from a set of predictors. Discriminant function analysis consists of finding a transform that gives the maximum ratio of difference between a pair of group multivariate means to the multivariate variance within the two groups [280]. Accordingly, an attempt is made to delineate contaminant associations based on maximizing between group variance while minimizing within group variance. The predictors' characteristics are related to form groups based on similarities of distributions in *n*-dimensional space, which are then compared to groups input by the user. This enables the environmental chemist to test the validity of groups based upon actual data, to test groups that have been created, or to put objects into groups. DA may act as a univariate regression and is also related to analysis of variance (ANOVA, [281]). The relationship to ANOVA is such that DA may be considered to be a multivariate version of ANOVA. The underlying assumptions of DA are: (a) the observations are a random sample, (b) each group is normally distributed, DA is relatively robust to departures from normality, (c) the variance/covariance matrix for each group is the same, and (d) each of the observations in the initial classification is correctly classified (training data) [282–285].

3.2

Cluster Analysis

Cluster analysis is an exploratory data analysis tool for solving classification problems of contaminants and identifying their original sources. Its object is to sort cases (various organic contaminants) into groups or clusters (aliphatics,

aromatics, aldehydes, esters, acids, and so on) so that the degree of association is strong between members of the same cluster and weak between members of different clusters [1, 4]. Each cluster therefore describes, in terms of the data collected, the class to which its members belong; and this description may be abstracted through use from the particular to the general class or type.

Cluster analysis is therefore a tool of discovery. It may reveal associations and structure in data which, though not previously evident, nevertheless are sensible and useful once found. The results of cluster analysis may contribute to the definition of a formal classification scheme, such as molecular marker source confirmation, or indicate rules for assigning new cases (samples) to classes (groups) for identification and diagnostic purposes.

In other words, cluster analysis is simply a method to group contaminants by similarity, for which a number of properties or parameters exist [286-290]. Various distance measurements are used, and the analysis is performed in a sequential manner, reducing the number of clusters at each step. Such a procedure has been described for pollution research as a way to group contaminants that have the most similarity between each other, indicating a common source.

3.3

Principal Components Analysis

Principal Components Analysis (PCA) is probably the oldest and best known of the techniques of multivariate analysis [1-4, 291]. PCA involves a mathematical procedure that transforms a number of possibly correlated variables (contaminants) into a smaller number of uncorrelated variables called *Principal Components* (PCs). The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

Both PCA and factor analysis (see Sect. 3.4) aim to reduce the dimensionality of a set of data, but the approaches to do so are different for the two techniques. Each technique gives a different insight into the data structure, with principal component analysis concentrating on explaining the diagonal elements of the covariance matrix, while factor analysis explains the off-diagonal elements [1, 291-294].

Principal components are linear combinations of random or statistical variables, which have special properties in terms of variances. The central idea of PCA is to reduce the dimensionality of a data set that may consist of a large number of interrelated variables while retaining as much as possible of the variation present in the data set. This is achieved by transforming the PCs which are uncorrelated into a new set of variables which are ordered so that the first few retain most of the variation present in all of the original variables [292-295].

One of the statistical concerns in PCA is cross correlation between independent variables under consideration. This can simply be assessed by examination of the correlation matrix of the parameters responsible for variations of such data. Further manipulations can be performed on this matrix or on the

variance-covariance matrix including the dependent variable. By methods of linear algebra, such a matrix may be transformed by prescribed methods into one containing non-zero elements only on the diagonal. These are called Eigenvalues of the matrix, and associated with each of these is an Eigenvector that is a linear combination of the original set of variables. Eigenvectors, unlike the original set of variables, have the property of being exactly orthogonal; that is, the correlation coefficient between any two of them is zero.

If a set of variables has substantial covariance, it will turn out that most of the total variance will be accounted for by a number of Eigen vectors equal to a fraction of the original number of variables. A reduced set containing only the major Eigen vectors or principal components may then be examined or used in various ways. This method is often used as a preprocessing tool. If only the principal components are considered, new orthogonal variables can be constructed from the Eigen vectors and hence the dimensionality of the parameter space can be reduced while most of the information in the original variable set is retained.

3.4

Factor Analysis and Linear Programming Techniques

3.4.1

Q-mode Factor Analysis

Factor analysis has recently been used in source partitioning modeling of molecular marker investigations [1–4, 296–300]. Q-mode factor analysis is based on grouping a multivariate data set based on the data structure defined by the similarity between samples. It is devoted exclusively to the interpretation of the inter-object relationships in a data set, rather than to the inter-variable (or covariance) relationships explored with R-mode factor analysis.

The objective of Q-mode factor analysis is analogous to geochemical partitioning models that seek to determine the absolute abundance of the dominant components (molecular markers, MMs) of samples such as SWMs and/or their leachates [2, 3, 301]. It provides a description of the multivariate data set in terms of a few end members (associations or factors, usually orthogonal) that account for the variance within the data set. A factor score represents the importance of each variable in each end member. The set of scores for all factors makes up the factor score matrix [302, 303]. The importance of each variable in each end member is represented by a factor score, which is a unit vector in n (number of variables) dimensional space, with each element having a value between -1 and 1 , and the sum of the squared elements equal to 1.00 [2, 4]. The relative importance of each end member factor in each SWM and/or its leachate sample is its factor loading value. The complete set of factor loadings describing each SWM and/or its leachate sample in terms of its end members is the factor-loading matrix.

Q-mode factor analysis defines the similarity of objects by considering the component proportions. The method searches elements in the **A** matrix for the most divergent objects, represented by the pure component concentrations or

those constituted by a significant proportion of these components, which can be represented as vertices of a concentration simplex. The other data set objects are linear combinations of the divergent ones. The contribution of each object is obtained by an eigen-analysis of a real symmetric matrix obtained from the data matrix. The measure of similarity used is the cosine theta ($\cos\theta$) matrix (the matrix whose elements are the cosine of the angles between all sample pairs) [1–4, 303]. For two objects, n and m , $\cos\theta$ is calculated by:

$$\cos\theta_{nm} = \frac{\sum_{j=1}^q a_{nj}a_{mj}}{\sqrt{\sum_{j=1}^q a_{nj}^2 \sum_{j=1}^q a_{mj}^2}} \quad (1)$$

For positive a elements, this index varies from zero (no similarity), to one (identical).

The mathematical procedure starts by calculating $\cos\theta$ for all pairs of objects in the data set of matrix A . The first step normalizes the A matrix rows, pre-multiplying A by an $n \times n$ diagonal matrix D^{-1} , the inverse of the D matrix. The principal diagonal of matrix D is composed of square roots of the sum of squares of the row vector elements of A ,

$$W_{(n \times p)} = D^{-1}A \quad (2)$$

The similarity or association matrix is defined by

$$H = WW^tA = D^{-1}AA^tD^{-1} \quad (3)$$

and can be approximately expressed as the product of the score, $T_{(n \times q)}$, and the loading matrix, $P^t_{(p \times q)}$, with q being the approximate rank of the matrix W . The T matrix, determined by Imbrie and Purdy [303], does not furnish a set of compositionally distinct objects. One way of resolving this problem is by means of “Varimax” and oblique rotations.

Simple Q-mode factor analysis fails to provide a direct solution to the partitioning problem. This is because: (1) the vectors generated by factor analysis are not composition vectors and therefore cannot be used to indicate the absolute composition of the end-members; (2) the factor scores only give a relative measure of the importance of each variable in each end-member and also reflect any scaling done on the data set prior to the analysis (such as transforming variable values to percent of range or normalizing variables to equal means); (3) the factor score matrix can contain negative values (for compositions of geochemical/environmental end-members this is an unreasonable condition); (4) the factor loading matrix indicates only the relative importance of each end-member and not an absolute abundance, and; (5) the factor loading matrix also commonly contains negative values.

An extension of Q-mode factor analysis [1, 303–306] provides a solution to the first, second and fourth problems listed above, those associated with obtaining absolute compositions of the end-members themselves. Normally when

factor analysis is used there is no restriction placed on the sum of the variables within a sample. For example, with geochemical/ environmental data, if the data are expressed in wt% or in ppm there is no requirement that the sum of the variables simply equal 100% or 1,000,000 parts to do the analysis, because the analysis is based on ratios. If the data are closed by summing the variables in each sample to a constant value, the factor scores can be converted into actual compositions of the original variables. Also, with a closed data set, the absolute abundance of each end-member factor in each sample can be calculated.

The problem of negative values in the factor loading matrix can be eliminated if a "Varimax" rotation is used in the factor analysis [305]. This rotation of the factor vectors ensures that the absolute abundance of each end-member factor in each sample is greater than or equal to zero. The reason for this can be seen by a two-dimensional illustration of the "Varimax" rotation (Fig. 10b). The first operation in a Q-mode factor analysis points a vector in the direction of maximum variability of the data set (Fig. 10a). This direction usually correlates with the vector representing the mean value for all variables. A second vector points in the direction of the next greatest variability and is restricted to be orthogonal to the first vector. The addition of principal axes is continued until the desired amount of the variability of the data set is described. As can be seen in the two dimensional example in Fig. 10a, the second axis is constrained to point in an extreme direction compared to the sample compositions and is usually a chemically unreasonable composition (in this case, an end-member with a negative concentration of BeP, see Fig. 10). The "Varimax" rotation rotates the principal component axes so that the variability within the data set explained by each axis is maximized (with the restriction that the axes remain orthogonal). This rotation brings the end-member axes closer to real simple compositions [1, 4, 305]. Therefore, "Varimax" rotation rigidly rotates the vectors of the T matrix until they coincide with the most divergent vectors in space. The order of the T matrix for rotation is equal to the number of simplex vertices, which is determined from the number of significant eigen values. The T matrix is then rotated to produce a new matrix, F, where

$$F = TR \quad (4)$$

with $R_{(qxq)}$ being the transformation matrix and $F_{(nxq)}$ being the "Varimax" weights. Each row of F corresponds to an object or a linear combination of objects and each column represents a factor. Also, as can be seen in Fig. 10b, all samples can now be described in terms of positive or zero contributions of the end-member factors.

Therefore, the combination of using a data set in which the sum of the variables in each sample is constant and of using a "Varimax" rotation results in a factor analysis which describes each sample in terms of the absolute abundance of end-member factors whose compositions are given in terms of concentrations of the original data variables. Unfortunately, as can be seen from Fig. 10b, the compositions of these "Varimax" end-members can and usually do contain large negative values for some variables (which may reflect inverse relation-

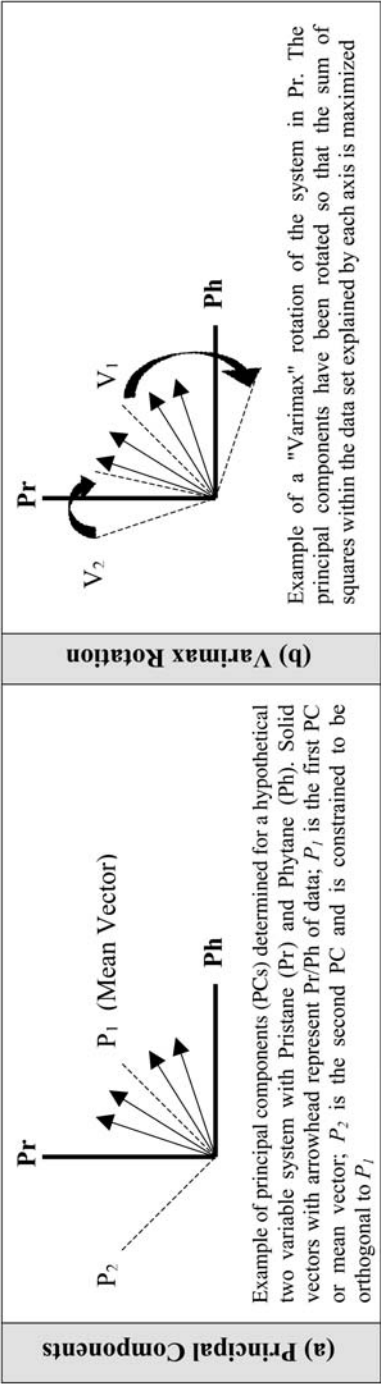


Fig. 10 Different vector rotation techniques

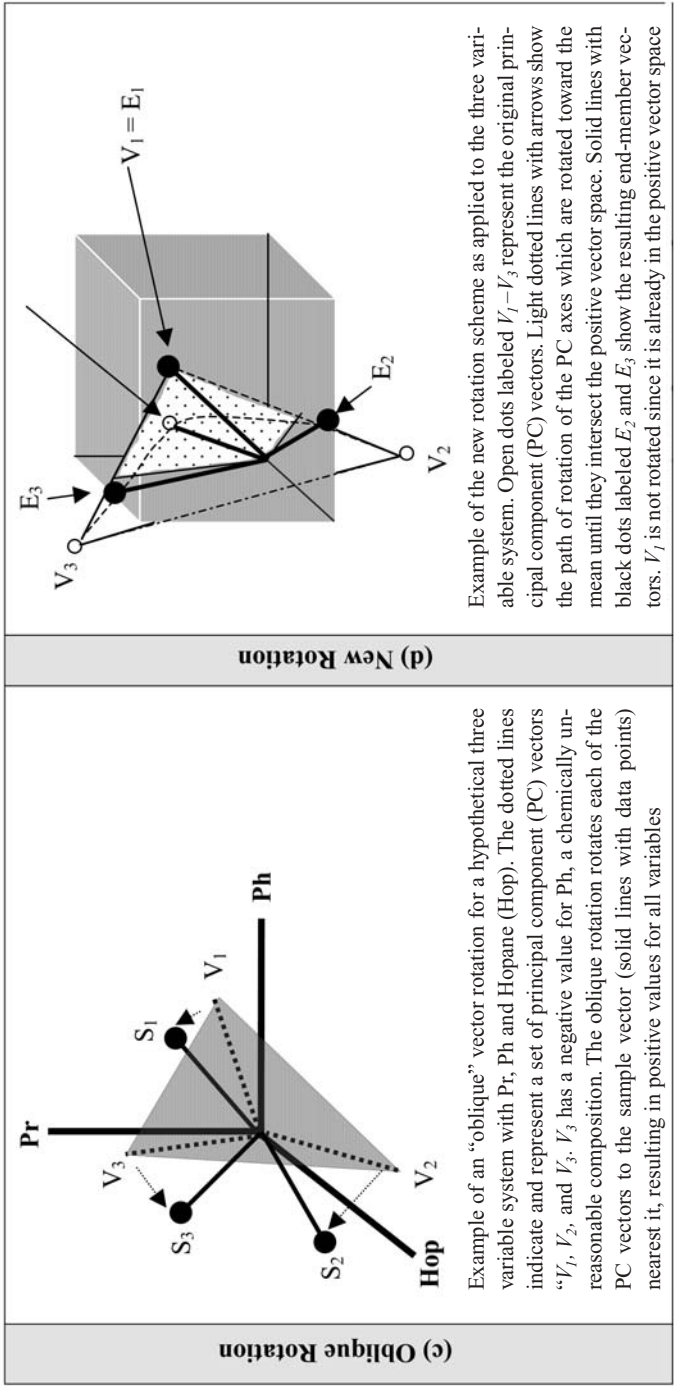


Fig. 10 (continued)

ships) and therefore cannot represent real geochemical/environmental end-member compositions.

To eliminate the problem of end-members with negative, variable values, non-orthogonal rotations have been used [305, 306]. The “oblique” rotation used by Imbrie and Van Andel [305] involves the rotation of each “Varimax” end-member to the one “nearest” to it in composition (Fig. 10c). Since each “Varimax” axis is rotated to a sample contained in the data set, the end-member factors are obviously constrained to have realistic compositions. However, in order for this technique to adequately describe the data, some samples in the data set must be pure end-members. For fine-grained bottom sediment this is generally not the case. The use of an oblique projection can rotate orthogonal “Varimax” factors until they coincide with the most divergent vectors. In this way, the others are defined as proportions of these objects. This is accomplished by constructing a $V_{(qxq)}$ matrix that contains the highest absolute values of the “Varimax” weights in each object column. The oblique projection matrix is given by

$$C = FV^{-1} \quad (5)$$

where V^{-1} is the inverse of V . The row vectors of the C matrix furnishes the proportional contributions of all the objects in terms of the reference objects. To recalculate these values in terms of the original data, it is necessary to divide each column vector of matrix C by the vector length of the corresponding object. This denormalizes the column vectors of the C matrix. If the number of analytes in the contaminant mixtures is unknown, oblique rotation permits its determination. The use of too many factors (or columns in V) results in physically meaningless concentration values in matrix C . In fact, many of these values are negative.

Factor analysis has not often been used to determine the actual composition of end-member sources in complex mixtures [304], because transformations of the original data variables during the statistical analysis result in negative factor scores for some variables and negative concentrations of some variables in the end-member. Therefore, in the present chapter a new rotation technique (Fig. 10d) combined with an extended Q-mode factor analysis is proposed and used to determine chemically reasonable end-member compositions from the aliphatic hydrocarbon MM data set. This rotation scheme does not require the hypothesis of having sampled pure end-members, but does assume that true end-member compositions lie between the composition identified by Q-mode factor analysis (which forms a set of orthogonal axes) and the best known statistical parameter within a data set (the vector of mean composition) [1–4, 304]. Generally, the end-member compositions can be found by rotating, one at a time, each “Varimax” axis toward the mean vector until the composition of the rotated axis is chemically reasonable (all variable concentrations are greater than or equal to zero, Fig. 10d). These relations are accomplished by the following steps:

- 1) Determine the “Varimax” representation of the mean composition of the data. Let M denote the “Varimax” vector of the mean composition.

- 2) Set a tolerance value defining “zero concentration” for each variable. This tolerance value is equal to the precision of the analysis or measurement of the variables. Any negative variable concentration within its tolerance value of zero will be considered equal to zero. For the application of this technique to the present Abu Darag sediment data set, the tolerances were set equal to the precision with which the contaminants were determined.
- 3) For each “Varimax” axis, determine whether the variable concentrations are chemically acceptable (non-negative). If not, rotate the “Varimax” vector toward the mean vector in steps scaled such that 100 steps are required to rotate the vector in question to the mean vector (Fig. 10d).

Algebraically, this can be expressed as:

$$(1 - a)V_i + aM = E_i \quad (6)$$

where $a=0.01, 0.02, \dots, 1.0$; V_i is the i th “Varimax” axis and E_i is the i th end-member. After each step, the composition of E_i is tested to determine whether this new vector is within the acceptance region. After the rotation is complete, all negative concentrations smaller than the tolerance values are set to zero. The “Varimax” representation and mean composition is determined from the total amount of information contained in the data set.

The criteria for choosing the number of end-members [1, 3] used to model the MM data of SWMs and/or their leachates are: (1) at least 90% of the variance in the data set must be explained by the sums of squares of the end-members, (2) all end-member factors that explained less than 2% of the total variance were rejected, and (3) all end-members which did not have a coherent distribution when mapped or plotted were rejected.

3.4.2

Linear Programming Technique

After identifying the end-member composition using this objective approach (Fig. 10d), a linear programming technique (LPT) can be used to determine the abundance of each end-member in each SWM and/or its leachate sample [1–4]. This LPT utilizes the inverse technique to provide a better fit of the observed MM data set with respect to the end-member compositions [304].

Once the number and compositions of end-members are determined, the next step is to obtain a quantitative estimate of the relative amount of each end-member in each sample. Because SWMs and/or their leachates are considered to be mixtures of complex organic compounds, the bulk composition of each sample is assumed to consist of some linear combination of end-member compositions, so each sample can be represented mathematically as a system of n equations (n =the number of individual contaminant variables used to identify the compositional end-members for a SWM and/or its leachate sample) in m unknowns (m =the number of major compositional end-members that are present), of the form:

$$\begin{aligned}
S_{P_1} &= K_1 E_{1P_1} + K_2 E_{2P_1} + \dots K_m E_{mP_1} + R_{P_1} \\
S_{P_2} &= K_1 E_{1P_2} + K_2 E_{2P_2} + \dots K_m E_{mP_2} + R_{P_2} \\
&\vdots \\
S_{P_n} &= K_1 E_{1P_n} + K_2 E_{2P_n} + \dots K_m E_{mP_n} + R_{P_n}
\end{aligned} \tag{7}$$

Where $S_{P_1}, S_{P_2}, \dots, S_{P_n}$ are the measured concentrations of MM contaminant variables $P_1, \dots, P_n$ in the sample; $E_{1P_1}, \dots, E_{mP_n}$ are the concentrations of MM contaminant variables $P_1, \dots, P_n$ in the compositional end-members $E_1, \dots, E_m$ determined by factor analysis; $K_1, K_2, \dots, K_n$ are unknowns whose magnitude for each sediment sample reflect the relative contributions of each compositional end-member in that sediment sample; and, $R_{P_1}, R_{P_2}, \dots, R_{P_n}$ are residual terms reflecting the fact that each equation is in exact due to sampling and/or analytical error. These systems of equations are usually over-determined ($n > m$) in organic geochemical/environmental partitioning models, so optimum solutions can be obtained using linear programming methods [1–4]. The major advantage of obtaining a linear programming solution is that certain physical constraints can be incorporated into the mathematical calculations. For example, the linear programming solution specifies that no compositional end-member can have a negative contribution to the total composition of SWMs and/or their leachates [1–4].

The residual terms associated with each system of equations represent the difference between the linear programming estimate and the actual concentration of each organic contaminant in the sample. The optimum solution for each system of equations is that for which the residual terms are minimized. Since a perfect modeling solution would account for 100% of the measured concentration for each organic contaminant, the validity of the present environmental forensic MM model can be evaluated by calculating a mean residual percent of each contaminant (the mean residual for each contaminant divided by the mean contaminant concentration) [1]. Therefore, the use of linear programming technique partitioning helps correct the initial end-member compositions of SWMs and/or their leachates, and their abundances, to better fit the observed multivariate data set, as well as to specify and select the compositions of the end-members.

3.5

Artificial Neural Networks

Artificial neural networks (ANNs) are programs designed to simulate the way a simple biological nervous system is believed to operate. They are based on simulated nerve cells or neurons that are joined together in a variety of ways to form networks. These networks have the capacity to learn, memorize and create relationships amongst data [307–313] or chemical characteristics [314–319]. There are many different types of ANNs that can be used in environmental forensic investigations, but some are more popular than others. The most widely used ANN is known as the Back Propagation ANN. This type of ANN is excellent at prediction and classification tasks. Another is the Kohonen or Self

Organizing Map, which is excellent at finding relationships amongst complex sets of contaminant data.

Over the last decade there has been a growing interest in using ANNs for source confirmation modeling of environmental contaminants. ANNs are able to map the non-linear relationships between variables that are characteristic of a common pollution source. ANNs require no a priori assumptions about the model in terms of mathematical relationships or distribution of data. Therefore ANNs have the potential to discover useful models where domain knowledge of original sources is limited.

4

NCHRP Project: A Case Study

The viability and integrity of the USA highway systems depend mainly on the continual rehabilitation and maintenance of the existing network. In such activities, a wide variety of materials are used, including Portland cement concrete, asphalt cement concrete, petroleum-base sealants, various solid wastes, wood preservatives, and additives [1, 17, 320–326]. During the wet season, there is potential for leaching some of the chemical constituents in these materials and the possibility of transport to adjacent surface and subsurface water bodies. Toxic chemicals, organic and/or inorganic, from these materials could result in adverse environmental effects on the ecological health of streams, ponds, wetlands, and groundwater systems [321, 322, 327]. If such water bodies are used as a source of potable water, adverse human health effects could occur as well.

Accordingly, the Department of Civil, Construction and Environmental Engineering at Oregon State University has conducted a study commissioned by the US-National Academy of Sciences, Transportation Research Board, National Cooperative Highway Research Program (NCHRP) in order to identify the possible impact of highway C&R materials on the quality of surface and ground waters [328, 329]. The scope of the study has been discussed thoroughly by Kassim et al [320], which included the development of a validated toxicity-based methodology to assess such impacts and to apply the methodology to a spectrum of materials in representative highway environments (see other chapters in the present book). The present sections provide an overview of the application of environmental forensic and genetic source modeling approaches to a group of solid waste materials (SWMs) of complex organic mixtures (COMs) that are used as road construction and repair materials.

4.1

Goals

The main objectives here are to analyze and characterize various leachates from SWMs commonly used as road construction and repair (C&R) materials, collected from several sites in the United States, in terms of their organic com-

pound contents, as represented by their molecular marker (MM) signatures (in other words, to construct an environmental forensic investigation). In addition, the distributions, chemical structures, and applicability of such MMs in determining characteristic group(s) representative for each individual and/or a group of SWMs (sources) were also conducted to develop a genetic source model specific for those SWMs.

4.2

Materials and Methods

The following sections describe the various waste materials, the analyses and characterization of the different multi-tracer molecular markers (MMs), as well as the statistical data analysis technique performed for the present project.

4.2.1

Waste Materials

Waste materials of complex organic mixtures (COMs), used as road C&R materials, were extensively examined and represent the most common wastes currently generated in large quantities in the United States (see the “Recycling Solid Wastes as Road Construction Materials” chapter of the present book). They include the following: crumb rubber, roofing shingles, coal combustion by-products, municipal solid waste incinerator combustion ash, concrete sealer (methyl methacrylate, MMA), foundry sand, plastics, and pressure treated wood (with ammonical copper zinc arsenate “ACZA”, copper chromated arsenate “CCA”, and creosote).

4.2.2

Leachate Preparation

Recent studies have compiled information about leaching tests to evaluate the use of solid wastes in highway construction [320, 330–333]. In general, these studies have shown that leaching behavior within and between materials is controlled by geochemical characteristics. Because of the slow kinetics of such leaching, several projects have focused on the development of accelerated leaching tests to predict long term leaching behavior [332–334].

Leaching of C&R materials is a complex phenomenon in which many factors influence the release of specific constituents from a construction material. These factors include major element chemistry, pH, redox (reduction/oxidation) conditions, chemical complexation, liquid-to-solid ratios, contact time, and biological activity. Leaching using a variety of elutriates has been used for characterization of C&R material, regulatory compliance, and simulation of on-site effects [335].

A fundamental understanding of factors that govern the leaching of inorganic and organic contaminants and standard leaching tests has been developed for a

Table 4 Leaching tests

Tests	Description [1, 17, 320–322]
Batch leaching	The short-term (24-h) batch leaching test is conducted to provide leachate (source term) for fate and transport studies It consists of 1,000 g of solids (crushed and sieved to ≤ 14 in.) with 4 L distilled water (1:4 solid:liquid mass ratio) placed in a sealed 2-L bottle, tumbled for 24 h at room temperature, and filtered to remove solids The leachate is analyzed during the screening process and is used in tests to determine the Fate and Transport model coefficients Analysis of the leachate during the toxicological and chemical screening process provides the chemical composition and toxicity data needed for initial evaluation of the test material
Flat plate leaching	The flat plate test determines the leaching rates from a defined surface where mass transfer across a solid/liquid boundary controls the leaching or flux rate (expressed in $\text{mg}/\text{cm}^2\text{-h}$) It focuses on release by diffusion or dissolution from the granular construction materials in a simulated on-site experiment The test material is formed into a flat plate and submerged in the bottom of a Pyrex glass reactor of 1 L volume distilled water The material is leached into the water phase, which is mixed above the flat plate with a paddle stirrer to avoid diffusional limitations in the liquid phase Increasing concentrations of the contaminant are measured chemically with time, normally 7 days. The flux rate of the compound of interest across the diffusion-controlled surface can then be determined This flux will represent the transport of chemicals from an in-place, flat, and compacted material surface, such as a highway surface
Column leaching	It is used to simulate the reference environment where the crushed test material (by itself or mixed with an aggregate) is used as a fill material The laboratory column is filled (loose packed) with the test material and distilled water is pumped through the column to simulate rain or runoff percolation through the highway subsurface (flow rates of 5–50 cm/day) The contaminants are leached from the test material into the water under laminar flow conditions The concentration of the contaminant of concern is at a peak at the beginning of the test and decreases with time. Hence, sampling should occur more frequently at the beginning of the experiment. The faster the flow rate, the more quickly the contaminants will be leached from the fill material. Therefore, the frequency of sampling also depends on the flow rate

variety of solid wastes. Specifically, a number of research efforts have documented the fundamental leaching behavior for a wide variety of construction materials and debris [332, 333]. Important factors identified in these studies are pH and liquid-to-solid (L/S) ratios. Knowing the pH of the leachate allows for the analysis of solution-phase speciation for ionizable metals and organic compounds.

Systematic leaching behavior of highway C&R materials involves a differentiation of whether the leaching process is controlled by dissolution or diffusion kinetics or by surface wash-off [1–4, 321, 322]. Surface wash-off will occur rapidly, whereas dissolution and diffusion are slow processes. Such information will determine the time frame under which leaching processes should be observed (hours, days, weeks, or years).

The use of serial batch and column tests can provide cumulative release data which describe leaching rates (release versus time). Additional leaching tests can be employed to determine the role of solution phase ligands (like organic acids, chelators, chloride, and so on), redox conditions, and sorption to solid phases in altering leaching and toxicity. Geochemical models can be used to estimate chemical speciation in leachates from selected highway C&R materials [1, 17, 321, 322].

In the present study, batch leaching tests were designed to determine rates of leaching and equilibrium leachate concentrations under conditions of high mixing, high surface areas of the construction material, and continuous surface renewal. Column leaching tests are designed to determine the rates of leaching under conditions of low mixing, high surface areas, and continuous surface renewal. Flat plate tests are designed to determine rates of leaching under conditions of low mixing, low surface areas, and diffusion-limited surface transport. Table 4 describes and summarizes these tests in detail.

4.2.3

Molecular Marker Analysis

The following sections summarize the extraction, analysis, instrumental detection, identification, and quantification of MM.

4.2.3.1

Extraction and Fractionation

To minimize contamination, all glassware was cleaned with soap and water, rinsed with distilled water, heated in an oven at 550 °C for 8 h to combust any traces of surficial organic matter, and finally rinsed twice each with ultra-pure methanol and methylene chloride. The KOH used for saponification was extracted three times with *n*-hexane and once with methylene chloride in a separatory funnel to remove organic interference.

An extraction protocol was designed for qualitative and quantitative analyses of the MMs from waste samples and their leachates. All of the extraction and analytical steps are shown in Fig. 11. For SWM leachates, liquid/liquid

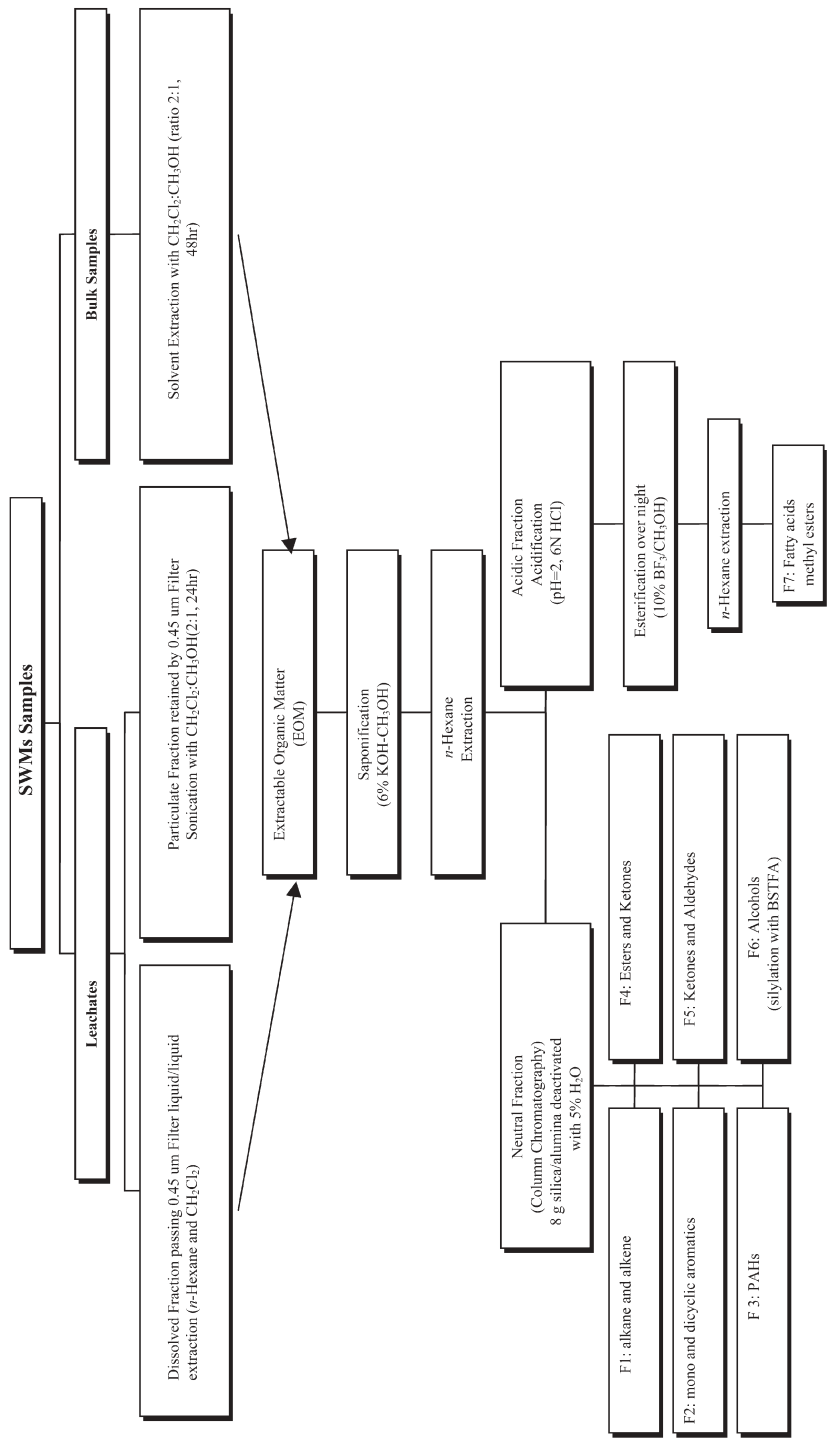


Fig. 11 Schematic of experimental protocol for analysis of organic contaminants

extractions were performed in separatory funnels using *n*-hexane followed by chloroform (CHCl_3). The bulk waste materials were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1v/v). These extracts are a measure of the amount of extractable organic matter (EOM) present in any sample. All of the extracts (EOM) were concentrated to 2 ml and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4×30 ml), the latter after acidification (pH 2) with 6N HCl (Fig. 11).

The acidic fractions, previously reduced to 0.5 ml, were esterified by refluxing overnight with 15 ml of 10% BF_3 /methanol. The BF_3 /methanol complex was destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4×30 ml of *n*-hexane.

The neutrals were fractionated by long column chromatography. A column (50×1.2 cm) filled with 8 g each of alumina (top) and silica (bottom), both deactivated with 5% water, was used. The following fractions were collected: (I) 45 ml of *n*-hexane (aliphatic hydrocarbons, F1), (II) 25 ml of 10% methylene chloride in *n*-hexane (monoaromatic hydrocarbons, F2), (III) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons "PAHs", F3), (IV) 25 ml of 50% methylene chloride in *n*-hexane (esters and ketones, F4), (V) 25 ml of methylene chloride (ketones and aldehydes, F5), and (VI) 50 ml of 10% methanol in methylene chloride (alcohols, F6). The last fraction was derivatized prior to GC or GC-MS analysis for further qualitative molecular examination by silylation with bis(trimethylsilyl)trifluoroacetamide (BSTFA).

A recovery experiment for the long column chromatography was carried out using several standards such as *n*- $\text{C}_{32}\text{D}_{66}$, a series of 35 *n*-alkane compounds; and d_{10} -pyrene, d_{10} -chrysene and a series of 37 PAH compounds.

4.2.3.2

Instrumental Analyses

High-resolution gas chromatography (GC) was conducted on a Hewlett-Packard (HP) 5890A gas chromatograph, equipped with a split/splitless capillary injection system and a flame ionization detector (FID). The samples were analyzed in the splitless mode using a fused silica capillary column (30 m × 0.25 mm i.d., DB-5, 0.25 μm film thickness, J&W Scientific) and helium as carrier gas. The analog signal was monitored and/or integrated with a HP 3393A integrator. The GC conditions were: FID 300 °C, injector 300 °C, oven temperature initially 65 °C, programmed to 290 °C at 4 °C/min, isothermal at 290 °C (60 min). The GC-MS analyses were performed with an HP GC (identical column with initial temperature 50 °C, isothermal 6 min, programmed at 4 °C/min to 310 °C, isothermal 60 min) interfaced directly to an HP-MSD quadrupole mass spectrometer (electron impact, emission current 0.45 mA, electron energy 70 eV, scanned from 50–650 Daltons). Data acquisition and processing were performed with an HP-Chemstation.

4.2.3.3

Identification and Quantification

Contaminant identification was based on comparison with the GC retention times and mass fragmentation patterns of standard reference materials, and with the help of the Wiley standard library incorporated in the Chemstation data system. Molecular marker identification was achieved using various standard mixtures injected in both GC and GC-MS.

Quantification was based on the application of perdeuterated compounds (like $n\text{-C}_{32}\text{D}_{66}$ and $\text{d}_{10}\text{-pyrene}$) as internal standards. In order to correct for detector response, sets of relative response factors were determined for every fraction from multiple injections. Normal and isoprenoid alkanes were quantified on the GC, while the rest of the molecular markers were determined by GC-MS.

4.2.3.4

Organic Carbon Analysis

Organic carbon analyses were carried out for all waste bulk samples and their leachates using a Carlo Erba NA-1500 CNS analyzer. Waste samples were combusted at 1000 °C in an oxygen-rich medium to CO_2 . The CO_2 gas was separated chromatographically, detected with a thermal conductivity detector, and the resulting signals were digitized, integrated, and mathematically processed along with results based on standards. For leachate samples, dissolved organic carbon (DOC) was determined using a Hitachi DOC analyzer and calculated by the difference between the measured total carbon (TC) and inorganic carbon (IC) content of the samples. Concentrations of MMs in all samples were calculated relative to the organic carbon content (TOC or DOC).

4.3

Statistical/Mathematical Modeling

Data for MM compositions of different SWMs and their leachates were examined statistically in order to determine any significant compositional variations among samples. Most statistical analyses were performed using the SAS Statistical Package V 6.12 [335]. In this report, the results of Q-mode factor analysis and linear programming techniques will be presented. The objectives of the statistical analyses were to define the MM characteristics for the different SWMs and their leachates, and to determine their original sources.

4.4

Findings

4.4.1

Forensic Investigation

Molecular markers (MMs) – organic compounds detected in the environment with structures suggesting an unambiguous link with known natural products – are specific indicator compounds that can be utilized for genetic source correlation [14, 58, 59, 68]. Such molecules are characterized by their restricted occurrence, source specificity, molecular stability, and suitable concentration for analytical detection [59]. MMs have widespread applications in organic compound characterizations and source identifications [55, 57, 336, 337].

The molecular marker compositions of different SWM leachates studied in the present case, along with their chemical structures and molecular weights, are summarized and described in detail in Table 5. Chemical structures for all compounds are shown in Figs. 1–8. Because of the unique composition and environmental toxicity of aliphatic (of petroleum and petrochemical origin) and aromatic hydrocarbons, full descriptions of various suites of molecular markers detected in SWM leachates and their possible sources are summarized comprehensively in Table 6.

In brief, important remarks for such MM compositions are as follows:

Aliphatic hydrocarbon MM suites (Fig. 1), typically of petroleum/petrochemical origin, consist of:

- Homologous long chain *n*-alkane series ranging from $<C_{15}$ to $>C_{38}$ with no carbon number predominance.
- Unresolved complex mixtures (UCM) of branched and cyclic hydrocarbons eluting between $n-C_{16}$ and $n-C_{33}$.
- Isoprenoid hydrocarbons such as norpristane (2,6,10-trimethylpentadecane), pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) (Structures I–III).
- Tricyclic terpanes (Structure IV), usually ranging from $C_{19}H_{34}$ to $C_{30}H_{56}$, and in some cases to $C_{45}H_{86}$.
- Tetracyclic terpanes such as 17,21- and 8,14-*seco*-hopanes (Structures V–VI).
- Pentacyclic triterpanes, such as the 17 α (H),21 β (H)-hopane series (Structures VII–VIII), consisting of 17 α (H)-22,29,30-trisnorhopane (T_m), 17 α (H),21 β (H)-29-norhopane, 17 α (H),21 β (H)-hopane and the extended 17 α (H),21 β (H)-homohopanes ($>C_{31}$) with subordinate amounts of the 17 β (H),21 α (H)-hopane series and 18 α (H)-22,29,30-trisnorneohopane (T_s).
- Steranes with the 5 α ,14 α ,17 α -configuration (Structure IX), 5 α ,14 β ,17 β -configuration (Structure X), and the 13 α ,17 β -diasteranes (Structure XI).

Table 5 Molecular markers, chemical compositions and molecular weights of SWM leachates

#	Name	Chemical composition	MW
(I) Aliphatic hydrocarbons			
<i>n</i> -Alkanes			
1	<i>n</i> -hexadecane	C ₁₆ H ₃₄	226
2	<i>n</i> -heptadecane	C ₁₇ H ₃₆	240
3	<i>n</i> -octadecane	C ₁₈ H ₃₈	254
4	<i>n</i> -nonadecane	C ₁₉ H ₄₀	268
5	<i>n</i> -eicosane	C ₂₀ H ₄₂	282
6	<i>n</i> -heneicosane	C ₂₁ H ₄₄	296
7	<i>n</i> -docosane	C ₂₂ H ₄₆	310
8	<i>n</i> -tricosane	C ₂₃ H ₄₈	324
9	<i>n</i> -tetracosane	C ₂₄ H ₅₀	338
10	<i>n</i> -pentacosane	C ₂₅ H ₅₂	352
11	<i>n</i> -hexacosane	C ₂₆ H ₅₄	366
12	<i>n</i> -heptacosane	C ₂₇ H ₅₆	380
13	<i>n</i> -octacosane	C ₂₈ H ₅₈	394
14	<i>n</i> -nonacosane	C ₂₉ H ₆₀	408
15	<i>n</i> -triacontane	C ₃₀ H ₆₂	422
16	<i>n</i> -hentriacontane	C ₃₁ H ₆₄	436
17	<i>n</i> -dotriacontane	C ₃₂ H ₆₆	450
18	<i>n</i> -tritriacontane	C ₃₃ H ₆₈	464
19	<i>n</i> -tetratriacontane	C ₃₄ H ₇₀	478
20	<i>n</i> -pentatriacontane	C ₃₅ H ₇₂	492
21	<i>n</i> -hexatriacontane	C ₃₆ H ₇₄	506
22	<i>n</i> -heptatriacontane	C ₃₇ H ₇₆	520
23	<i>n</i> -octatriacontane	C ₃₈ H ₇₈	534
24	2,6,10-trimethylpentadecane (norpristane)	C ₁₈ H ₃₈	254
25	2,6,10,14-tetramethylpentadecane (pristane)	C ₁₉ H ₄₀	268
26	2,6,10,14-tetramethylhexadecane (phytane)	C ₂₀ H ₄₂	282
27	Unresolved Complex Mixture (UCM)		
Tricyclic terpanes			
28	C ₁₉ -tricyclic	C ₁₉ H ₃₄	262
29	C ₂₀ -tricyclic	C ₂₀ H ₃₆	276
30	C ₂₁ -tricyclic	C ₂₁ H ₃₈	290
31	C ₂₃ -tricyclic	C ₂₃ H ₄₂	318
32	C ₂₄ -tricyclic	C ₂₄ H ₄₄	332
33	C ₂₅ -tricyclic	C ₂₅ H ₄₆	346
34	C ₂₆ -tricyclic (<i>S</i>)	C ₂₆ H ₄₈	360
35	C ₂₆ -tricyclic (<i>R</i>)	C ₂₆ H ₄₈	360
36	C ₂₈ -tricyclic	C ₂₈ H ₅₀	388
37	C ₂₉ -tricyclic	C ₂₉ H ₅₂	402

Table 5 (continued)

#	Name	Chemical composition	MW
Tetracyclic terpanes			
38	C ₂₄ -tetracyclic (17,21-seco-hopane)	C ₂₄ H ₄₂	330
39	C ₂₈ -tetracyclic (18,14-seco-hopane)	C ₂₈ H ₅₀	386
40	C ₂₉ -tetracyclic (18,14-seco-hopane)	C ₂₉ H ₅₂	400
Pentacyclic triterpanes			
41	18 α (H)-22,29,30-trisnorneohopane (Ts)	C ₂₇ H ₄₆	370
42	17 α (H)-22,29,30-trisnorhopane (Tm)	C ₂₇ H ₄₆	370
43	17 α (H),21 β (H)-29-norhopane	C ₂₉ H ₅₀	398
44	17 α (H),21 β (H)-hopane	C ₃₀ H ₅₂	412
45	17 α (H),21 β (H)-homohopane (22S)	C ₃₁ H ₅₄	426
46	17 α (H),21 β (H)-homohopane (22R)	C ₃₁ H ₅₄	426
47	17 α (H),21 β (H)-bishomohopane (22S)	C ₃₂ H ₅₆	440
48	17 α (H),21 β (H)-bishomohopane (22R)	C ₃₂ H ₅₆	440
49	17 α (H),21 β (H)-trishomohopane (22S)	C ₃₃ H ₅₈	454
50	17 α (H),21 β (H)-trishomohopane (22R)	C ₃₃ H ₅₈	454
51	17 α (H),21 β (H)-tetrakishomohopane (22S)	C ₃₄ H ₆₀	468
52	17 α (H),21 β (H)-tetrakishomohopane (22R)	C ₃₄ H ₆₀	468
53	17 α (H),21 β (H)-pentakishomohopane (22S)	C ₃₅ H ₆₂	482
54	17 α (H),21 β (H)-pentakishomohopane (22R)	C ₃₅ H ₆₂	482
Diasteranes			
55	13 α ,17 β -diacholestane (20S)	C ₂₇ H ₄₈	372
56	13 α ,17 β -diacholestane (20R)	C ₂₇ H ₄₈	372
Steranes			
57	5 α ,14 α ,17 α -cholestane (20S)	C ₂₇ H ₄₈	372
58	5 α ,14 β ,17 β -cholestane (20R)	C ₂₇ H ₄₈	372
59	5 α ,14 β ,17 β -cholestane (20S)	C ₂₇ H ₄₈	372
60	5 α ,14 α ,17 α -cholestane (20R)	C ₂₇ H ₄₈	372
61	5 α ,14 α ,17 α -ergostane (20S)	C ₂₈ H ₅₀	386
62	5 α ,14 β ,17 β -ergostane (20R)	C ₂₈ H ₅₀	386
63	5 α ,14 β ,17 β -ergostane (20S)	C ₂₈ H ₅₀	386
64	5 α ,14 α ,17 α -ergostane (20R)	C ₂₈ H ₅₀	386
65	5 α ,14 α ,17 α -sitostane (20S)	C ₂₉ H ₅₂	400
66	5 α ,14 β ,17 β -sitostane (20R)	C ₂₉ H ₅₂	400
67	5 α ,14 β ,17 β -sitostane (20S)	C ₂₉ H ₅₂	400
68	5 α ,14 α ,17 α -sitostane (20R)	C ₂₉ H ₅₂	400

Table 5 (continued)

#	Name	Chemical composition	MW
(II) Polycyclic aromatic hydrocarbons			
Neutral PAHs			
69	Quinoline “benzo[<i>b</i>]pyridine”	C ₉ H ₇ N	129
70	2,3-Dimethylquinoline	C ₁₁ H ₁₁ N	157
71	Phenanthrene	C ₁₄ H ₁₀	178
72	Anthracene	C ₁₄ H ₁₀	178
73	Fluoranthene	C ₁₆ H ₁₀	202
74	Pyrene	C ₁₆ H ₁₀	202
75	11H-Benzo[<i>a</i>]fluorene	C ₁₇ H ₁₂	216
76	Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂	228
77	Chrysene/triphenylene	C ₁₈ H ₁₂	228
78	Benzo[<i>b+k</i>]fluoranthenes	C ₂₀ H ₁₂	252
79	Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	252
80	Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252
81	Perylene	C ₂₀ H ₁₂	252
82	Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276
83	Dibenz[<i>ah</i>]anthracene	C ₂₂ H ₁₄	278
84	Benzo[<i>ghi</i>]perylene	C ₂₂ H ₁₂	276
85	Anthanthrene	C ₂₂ H ₁₂	276
86	Coronene	C ₂₄ H ₁₂	300
87	Dibenzo[<i>ae</i>]pyrene	C ₂₄ H ₁₄	302
Alkyl-substituted PAHs			
<i>(Alkyl phenanthrene series)</i>			
88	3-Methylphenanthrene (3MP)	C ₁₅ H ₁₂	192
90	2-Methylphenanthrene (2MP)	C ₁₅ H ₁₂	192
91	9-Methylphenanthrene (9MP)	C ₁₅ H ₁₂	192
92	1-Methylphenanthrene (1MP)	C ₁₅ H ₁₂	192
93	Dimethylphenanthrenes	C ₁₆ H ₁₄	206
94	Trimethylphenanthrenes	C ₁₇ H ₁₆	220
95	Tetramethylphenanthrenes	C ₁₈ H ₁₈	234
<i>(Alkyl pyrene/fluoranthene series)</i>			
96	Methylpyrenes/fluoranthenes	C ₁₇ H ₁₂	216
97	Dimethylpyrenes/fluoranthenes	C ₁₈ H ₁₄	230
98	Trimethylpyrenes/fluoranthenes	C ₁₉ H ₁₆	244
<i>(Alkyl 228 series)</i>			
99	Methyl-228	C ₁₉ H ₁₄	242
100	Dimethyl-228	C ₂₀ H ₁₆	256
<i>(Alkyl 252 series)</i>			
101	Methyl-252	C ₂₁ H ₁₄	266
102	Dimethyl-252	C ₂₂ H ₁₆	280
103	Trimethyl-252	C ₂₃ H ₁₈	294
104	Tetramethyl-252	C ₂₄ H ₂₀	308

Table 5 (continued)

#	Name	Chemical composition	MW
(III) Non-hydrocarbons			
Phthalates			
105	Phthalic anhydride	C ₈ H ₄ O ₃	148
106	Dimethyl phthalate	C ₁₀ H ₁₀ O ₄	194
107	Diethyl phthalate	C ₁₂ H ₁₄ O ₄	222
108	Dibutyl phthalate	C ₁₆ H ₂₂ O ₄	278
109	Bis(2-ethylhexyl) phthalate	C ₂₄ H ₃₈ O ₄	390
Thiazoles			
110	Benzothiazole	C ₇ H ₅ NS	135
111	2(3H)-Benzothiazolone	C ₇ H ₅ NOS	151
Amines			
112	N,4-Dimethylbenzenamine	C ₈ H ₁₁ N	121
113	N,N,3-Trimethylbenzenamine	C ₉ H ₁₃ N	134
Amides			
114	N-(2,4-Dimethylphenyl)formamide	C ₉ H ₁₁ NO	149
Various alcohols			
115	Dicyclopentadienol	C ₁₀ H ₁₃ O	149
116	[1,1'-Biphenyl]-2-ol	C ₁₂ H ₁₀ O	170
Acids			
117	Benzoic acid	C ₇ H ₆ O ₂	122
118	Nonanoic acid	C ₉ H ₁₈ O ₂	158
119	Decanoic acid	C ₁₀ H ₂₀ O ₂	172
120	Dodecanoic Acid	C ₁₂ H ₂₄ O ₂	200
121	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	228
122	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	256
123	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	284
Phenol and substituted phenols			
124	Phenol	C ₆ H ₆ O	94
125	2,3,4,5,6-Pentachlorophenol	C ₆ Cl ₅ OH	266

Table 6 Description of various molecular markers and their probable sources

MMs	Description	Possible source	Reference	
Aliphatic hydrocarbons	Normal alkanes	- <i>n</i>-alkanes are present in all solid wastes and their leachates - They range in carbon chain length from C₁₆-C₃₈ - Their concentrations in different SWMs vary between 9.2-25 mg/g OC for SWMs and between 9.8-34.6 mg/g OC for leachates	- Without calculating the CPI ratio (ratio no. 1, Table 7), the source might be terrestrial biomass or petroleum	1-4, 16, 55-60
	Isoprenoids	- Present as pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) - Total isoprenoid concentrations relative to organic carbon for all solid wastes and their leachates average 0.57 mg/g OC and 0.66 mg/g OC, respectively	- Petroleum and petrochemical products	1-4, 11, 13, 66-69
Tricyclic terpanes	- The tricyclic terpane series (key ion <i>m/z</i> 191) is present in all waste materials and ranges from C₁₉H₄₂ to C₂₉H₅₂, with no C₂₂ or C₂₇ and a C₂₃ predominance - Concentrations in SWMs range between 1.3-4.3 µg/g OC - Concentrations in SWM leachates range between 3.0-2.2 µg/g OC	- Petroleum and petrochemical products	1, 11, 70-72	
Tetracyclic terpanes	- Tetracyclanes are derivatives of the hopanes. Both 17,21- and 8,14-<i>seco</i>-hopanes are found in fossil fuels. The 17,21-<i>seco</i>-hopanes have ring-E opened hopane structure, and the 8,14-<i>seco</i>-hopanes have ring-C opened hopane structures - The tetracyclic terpanes found in the SWMs are comprised of a C₂₄-17,21-<i>seco</i>-hopane (in other words <i>E</i>-norhopane) and C₂₈ and C₂₉-8,14-<i>seco</i>-hopanes - The total concentrations for the SWMs ranged from 1.0-1.7 mg/g OC and 0.07-0.33 µg/g OC for their leachates, respectively	- Petroleum and petrochemical products	1, 71-73	

Table 6 (continued)

MMs	Description	Possible source	Reference
Aliphatic hydrocarbons	- The major pentacyclic hydrocarbons from petroleum are the 17α(H),21β(H)-hopanes, generally ranging from C₂₇ to C₃₅. The identification of these compounds is based primarily on their mass spectra and GC retention time in the <i>m/z</i> 191 key ion fragmentogram - The predominant analog in the SWM samples is 17α(H),21β(H)-hopane, with subordinate amounts of 18α(H)-22,29,30-trisnorhopane (T_s), 17α(H)-22,29,30-trisnorhopane (T_m), 17α(H),21β(H)-29-norhopane, and minor concentrations of the 17β(H), 21α(H)-hopanes and the extended 17α(H),21β(H) homohopanes (>C₃₁) with the fully mature epimer conformation at C-22 - The total hopane concentrations for different SWMs ranged from 27.0–89.0 μg/g OC, while for the leachates between 5.5–17.5 μg/g OC	- Petroleum and petrochemical products (including lube oils)	1–4, 60
Steranes and diasteranes	- The sterane series have mainly the 5α,14β,17β-configuration, and a lesser amount of the 5α,14α,17α-configuration, with a small amount of 13α,17β-diasteranes - The total sterane concentrations ranged between 0.9–7.2 μg/g OC for SWMs and 0.2–2.1 μg/g OC for leachates	- The homolog distributions (C₂₇ vs. C₂₉) are of utility in determining the reservoir origin of petroleum	1–4, 50–54
UCM	- A UCM of branched and cyclic hydrocarbons eluting between <i>n</i>-C₁₆ and <i>n</i>-C₃₃ is present in extracts of the SWMs and but various lower concentrations among leachates because of the different leachability properties of SWM - The UCMs maximize between <i>n</i>-C₂₇ and <i>n</i>-C₃₁ retention times	- Petroleum and petrochemical products (like lube oils) - Bacterial biodegradation of hydrocarbon compounds	1–4, 11, 13, 59–62

Table 6 (continued)

MMs	Description	Possible source	Reference
Polycyclic aromatic hydrocarbons (PAHs)	- Regardless of solid waste materials, the PAH compositions are similar with the presence of minor alkylated homologs mainly for phenanthrene, pyrene, perylene and benz[<i>a</i>]anthracene - The PAHs show a predominance of fluoranthene, pyrene, benz[<i>a</i>]anthracene, chrysene/triphenylene, benzo[<i>b+k</i>]fluoranthenes, benzo[<i>e</i>]pyrene and benzo[<i>a</i>]pyrene for SWMs - Low molecular weight PAHs are the dominant PAHs in leachate samples - The total PAH concentrations vary between 9.9–36.8 µg/g OC for SWMs and 2.2–11.8 mg/g OC for their leachates - For the different SWMs and their leachates, the alkylated PAHs of the phenanthrene, fluoranthene/pyrene, <i>m/z</i> 228 and <i>m/z</i> 252 series maximize at C₂, C₂, C₁₋₂ and C₂, respectively - Relatively high concentrations of 2- and 3-methylphenanthrene (MP) compared to 1- and 9-MP were observed for the SWMs and their leachates indicating thermal alteration. This can be explained in terms of the rearrangement of the alkyl-MP, favoring the thermodynamically more stable 2- and 3-positions at high temperatures	- Anthropogenic sources, such as vehicular exhaust, emissions from combustion processes, refining, and other activities involving high temperature pyrolytic reactions and incineration	1–4

Table 7 Genetic source confirmation ratios and parameters for molecular markers

#	Molecular marker ratios and parameters	Mean values	Description	Reference
1	$CPI = \frac{1}{2} \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{31} + C_{33}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right)$	1.09	The CPI, a measure of biologically synthesized <i>n</i> -alkanes, indicates the relative contributions of <i>n</i> -alkanes from natural (CPI>1) compared to anthropogenic (petroleum and industrial pollution, CPI≤1) sources	1, 57-69
2	$\left(\frac{U}{R} \right) = \left(\frac{\text{Concentration of unresolved complex mixture (UCM)}}{\text{Concentration of } \sum \text{ resolved hydrocarbon peaks (mostly } n\text{-alkanes)}} \right)$	1.76	The UCMs maximize between <i>n</i> -C ₂₇ and <i>n</i> -C ₃₁ retention times, supporting a petroleum impact The UCM/resolved hydrocarbon ratio is higher for SWMs than their leachates because of the lower leaching rate of the UCM compared to the resolved aliphatic hydrocarbons	1, 63
3	$\left(\frac{Pr}{Ph} \right) = \left(\frac{2,6,10,14\text{-tetramethylpentadecane (pristane)}}{2,6,10,14\text{-tetramethylhexadecane (phytane)}} \right)$	0.50	A biodegradation rate index	1-4, 65-68, 338
4	$\left(\frac{Pr}{C_{17}} \right) = \left(\frac{\text{Pristane}}{C_{17}} \right)$	0.40	The ratio of >1 indicates a high biodegradation rate of a petrochemical source	1-4, 65-68

Table 7 (continued)

#	Molecular marker ratios and parameters	Mean values	Description	Reference
5	$\left(\frac{\text{Ph}}{\text{C}_{18}}\right) = \left(\frac{\text{Phytane}}{\text{C}_{18}}\right)$	1.33	The ratio of >1 indicates a high biodegradation rate of a petro-chemical source	1-4, 65-68
6	C_{max} = The highest <i>n</i> -alkane peak	27	The C_{max} gives an indication of the relative source input. A $C_{\text{max}} \geq 27$ for <i>n</i> -alkanes reflects the incorporation of higher plant wax and C_{max} at lower carbon numbers indicates a major input from petrochemical sources. The average dominant C_{max} determined for the <i>n</i> -alkanes in the present study is <C ₂₇ , which indicates a petrochemical source for most SWMs.	22, 28, 63, 65-68
7	$\left(\frac{\text{Ts}}{\text{Tm}}\right) = \left(\frac{18\alpha(\text{H})-22,29,30\text{-trisorneohopane}}{17\alpha(\text{H})-22,29,30\text{-trisnorhopane}}\right)$	0.73	Petroleum biodegradation and maturity indices	1-4, 57, 65-68
8	$\text{Triplet Ratio} = \left[\frac{(C_{26}\text{-Tricyclic S}) + (C_{26}\text{-Tricyclic R})}{(C_{24}\text{-Tricyclic})}\right]$	0.53		
9	$\left(\frac{C_{23}\text{Tri}}{C_{30}\beta}\right) = \left(\frac{C_{23}\text{-Tricyclic}}{17\alpha(\text{H}),21\beta(\text{H})\text{-hopane}}\right)$	0.05		

Table 7 (continued)

#	Molecular marker ratios and parameters	Mean values	Description	Reference
10	$\left(\frac{C_{29}\alpha}{C_{30}\beta}\right) = \left(\frac{17\alpha(H),21\beta(H)\text{-norhopane}}{17\alpha(H),21\beta(H)\text{-hopane}}\right)$	0.80	Petroleum biodegradation and maturity indices	
	HHI is the ratio between the S and R epimer at C-22 for the 17α(H)-homohopane series $(C_{31}-C_{31}) = \left[\frac{22S}{(22S + 22R)}\right]$, as follows:		In typical petroleum and their products, the extended 17α(H),21β(H)-hopane homologs >C ₃₁ have the epimers at C-22 at an equilibrium ratio {S/(S+R)} of 0.6 (homohopane index). The homohopane index for SWMs and their leachates varies from 0.6–0.8 (essentially the same as crude oils)	1–4, 57–71
11		C ₃₁ 0.71		
12		C ₃₂ 0.67		
13		C ₃₃ 0.57		
14		C ₃₄ 0.61		
15		C ₃₅ 0.72		
	Sterane epimerization parameter at C-20 is calculated for C ₂₉ for 5α,14α,17α-C ₂₉ -sterane and 5α,14β,17β-C ₂₉ -sterane as:		The epimerization ratio at C-20 of the C ₂₉ sterane is characteristic of petroleum thus confirming such residues in the SWMs and their leachates	1–4, 57–71
16	$\alpha\alpha C_{29} \left[\frac{20S}{(20S + 20R)} \right]$	0.61		

Table 7 (continued)

#	Molecular marker ratios and parameters	Mean values	Description	Reference
17	$\alpha\beta C_{29} \left[\frac{20S}{(20S + 20R)} \right]$	0.70		
18	$\left(\frac{\% \text{Alkyl PAHs}}{\sum \text{PAHs}} \right) = \left(\frac{\sum \text{concentrations of all alkyl PAHs}}{\sum \text{concentrations of all PAHs}} \right) \cdot 100$	48.9	Generally the proportion of alkylated to parent PAH depends on the combustion temperature. Thus, coal and wood smoke particulate matter contain a phenanthrene mixture maximizing at the parent PAH with an exponential drop to the C ₄ -homologs. In contrast, vehicular emissions exhibit a pattern of low amounts of phenanthrene and maximum at the C ₁ -homologs, and petroleum input is characterized by a distribution increasing uniformly from less to more alkylated homologs up to C ₅ and greater.	1-4, 57, 66-68, 74-78
19	$\left(\frac{P}{P + An} \right) = \left(\frac{\text{phenanthrene}}{\text{phenanthrene} + \text{anthracene}} \right)$	1.00		
20	$\left(\frac{B(a)An}{B(a)An + Chr/Triph} \right) = \left[\frac{\text{benz[a]anthracene}}{\text{benz[a]anthracene} + \text{chrysene/triphenylene}} \right]$	0.12		
21	$\left(\frac{B[e]P}{B[e]P + B[a]P} \right) = \left[\frac{\text{benzo[e]pyrene}}{\text{benzo[e]pyrene} + \text{benzo[a]pyrene}} \right]$	0.70		
22	$\left(\frac{Inpy}{Inpy + Bper} \right) = \left[\frac{\text{indeno[1,2,3-cd]pyrene}}{\text{indeno[1,2,3-cd]pyrene} + \text{benzo[ghi]perylene}} \right]$	0.65		

Polycyclic aromatic hydrocarbons (Fig. 2) consist of:

- The PAH compositions are similar, regardless of the SWMs and their leachates, with minor alkylated homologs mainly for phenanthrene, fluoranthene/pyrene, m/z 228 (including benz[*a*]anthracene), and m/z 252 (including perylene).
- There are significant PAH concentration differences between solid waste materials and their leachates due to PAH solubilities.
- The PAHs for SWMs show a predominance of fluoranthene, pyrene, benz[*a*]anthracene, chrysene/triphenylene, benzo[*b+k*]fluoranthenes, benzo[*e*]pyrene and benzo[*a*]pyrene.
- Low molecular weight PAHs are the dominant analogs in leachate samples.

Further forensic analysis for all MMs has been conducted using various genetic source ratios or parameters among aliphatic and aromatic compounds. As examples, a few ratios are detailed below, while a complete list of ratios is shown in Table 7.

- The identification of the homologous *n*-alkanes in the aliphatic hydrocarbon fractions for most leachates allowed the determination of the carbon preference index (CPI, ratio no. 1), which provides supportive evidence for the relative incorporation of different aliphatic hydrocarbon sources.
- The determination of the C_{max} (parameter no. 6) for every sample also gives an indication of the relative source input, where a $C_{max} \geq C_{27}$ for *n*-alkanes reflects the incorporation of higher plant wax, and C_{max} at lower carbon numbers indicates a major input from petrochemical sources.
The presence of pristane, phytane and their ratios (ratios no. 3–5) indicate a petrochemical input.
- The distribution of the 17 α (H)-hopane series is characteristic of and specific to petroleum and petrochemical products (like lube oils). In typical petroleum and their products, the extended 17 α (H),21 β (H)-homohopane homologs $>C_{31}$ have the epimers at C-22 at an equilibrium ratio $S/(S+R)$ of 0.6 (homohopane index). The homohopane index (ratios no. 11–15) for all samples varies from 0.6–0.8, essentially the same as for crude oil.
- Sterane hydrocarbons present in fossil fuels are additional useful molecular marker indicators for petroleum impact. Their homolog distributions (C_{27} versus C_{29}) are useful for determining the reservoir origin of petroleum. The epimerization ratio at C-20 of the C_{29} sterane (ratio nos. 16 and 17) is characteristic of petroleum, confirming such residues in the SWMs and their leachates.
- Generally, the proportion of alkylated to parent PAH depends on the combustion temperature (ratio nos. 18–22). Therefore, coal and wood smoke particulate matter contain a phenanthrene mixture maximizing at the parent PAH with an exponential drop to the C_4 -homologs. In contrast, vehicular emissions exhibit a pattern of low amounts of phenanthrene and a maximum

at the $>C_1$ -homologs, and petroleum input is characterized by a distribution increasing uniformly from less to more alkylated homologs up to C_5 and greater.

- Relatively high concentrations of 2- and 3-methylphenanthrene (MP) compared to 1- and 9-MP are indicative of thermal alteration. This can be explained in terms of the rearrangement of the alkyl-MP, favoring the thermodynamically more stable 2- and 3-positions at high temperatures.

Therefore, coupling various ratios (for instance CPI, U/R, and so on), quantitation of molecular markers, organic geochemical parameters (like C_{max} , UCM), and PAHs allows the determination of the main sources of the aliphatic and aromatic hydrocarbon compounds (petrochemical versus thermogenic/pyrolytic) characteristic of the SWMs and their leachates under study. However, these analyses presented only the *assessments* of the different sources of the MMs in most samples, not their *source strengths* (see Sect. 4.4.2).

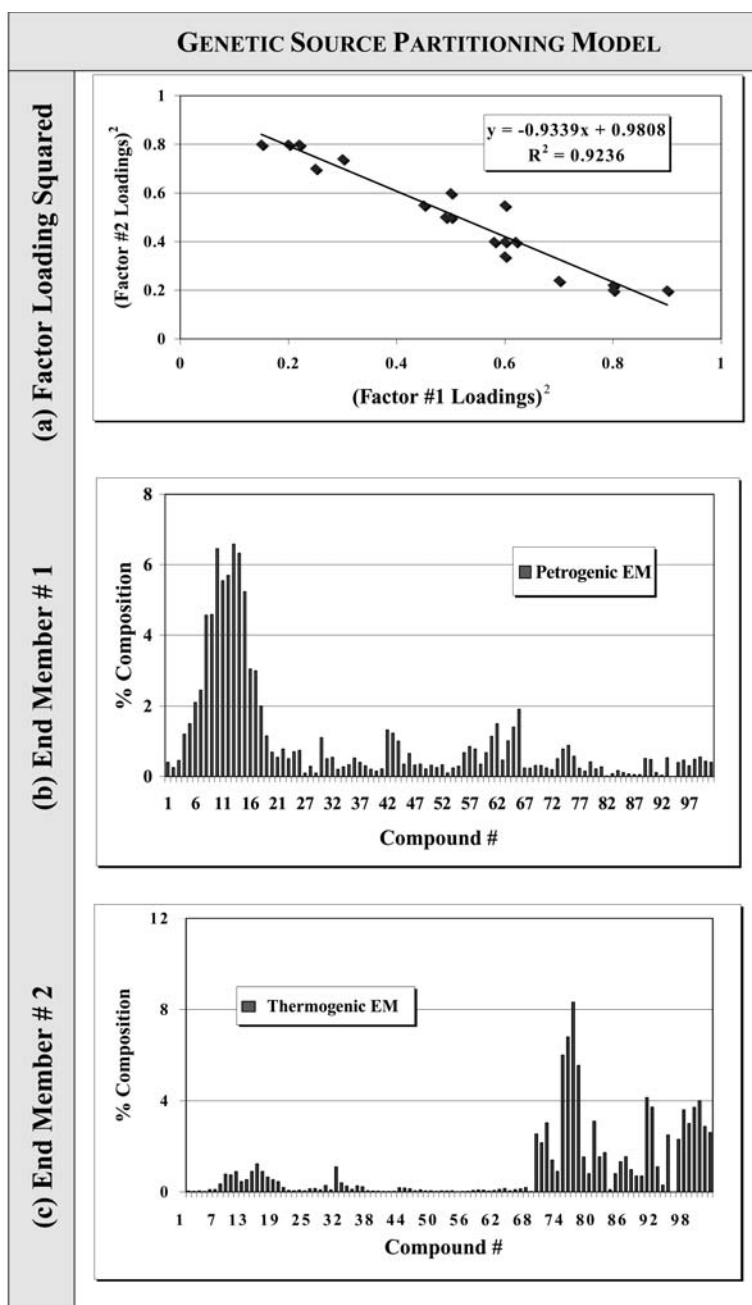
4.4.2

Source Partitioning Model

The present multi-tracer forensic model for various wastes used as road C&R materials, and their leachates, generated a large amount of data, necessitating the use of statistical techniques to cluster the data into significant groups and reduce it to a number of factors (end members or original sources), which represent, in an organic geochemical partitioning sense, the combined effects of several chemical processes or factors.

Both Q-mode factor analysis and liner programming techniques (Sect. 3.4) were used in the present study, yielding the following results (Fig. 12):

- Two significant principal factor loading scores, providing information about sample variation of about 63.4% and 28.2%, respectively (maximum cumulative information 91.6%).
- The distribution of the various factors in each SWM sample was obtained by squaring individual molecular marker compounds of the factor loading matrix, where the sum of the squared loadings for all factors of a particular waste sample equals 1.00 (communality; which is the proportion of the total variance in a particular sample that is explained by those factors). The individual squared loading of one factor represents the fraction that factor contributes to the solid waste sample (if a sample has a factor 1 loading of 0.4 then $(0.4)^2=0.16$, or 16% of the sample is from factor 1).
- To observe associations between SWM samples (groupings), the graph showing factor 1 versus factor 2 indicated that most samples plot near the binary mixing line (a line from factor 1=1.00, factor 2=0 to factor 1=0, factor 2=1.00). This indicated that two main factors can explain the majority of the contaminant composition of the SWM samples.
- Squaring individual elements of the factor score matrix yielded the sum for a particular factor equal to 1.00. The proportion which an individual MM



contributes to the total MM composition of an end member was determined by dividing the absolute value of the MM score for that factor by the sum of the absolute values of all the MM scores for that factor.

- In order to assign the origin (source) and interpret the observed factor data, the rotation proposed by Leinen and Pisias [304] and linear programming techniques yielded two end member (EM I and EM II) compositions, as follows:
 - *End member 1*: Dominated mainly by *n*-alkanes (63.8%), regular isoprenoid hydrocarbons (pristane and phytane, 1.5%), tri- and tetracyclic MM series (5.0%), the hopane series (7.4%) with a predominance of 17 α (H),21 β (H)-hopane and both C-22 *S/R* configurations for the homologs >C₃₁, and the diasterane/sterane series (0.6%). In addition, a minor contributions from different unsubstituted and substituted PAHs recorded 4.09% and 3.03%, respectively.
 - *End member 2*: Dominated mainly by a group of unsubstituted and substituted PAHs ($\leq 84\%$) with a minor contribution of aliphatic hydrocarbon molecular markers ($\leq 16\%$). Fluoranthene, pyrene, chrysene/triphenylene, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene were the most dominant unsubstituted PAHs in the second end member.

Based on the statistical findings (Sect. 4.4.2, Fig. 12) and the molecular marker compositions specific to SWMs and their leachates (Sect. 4.2.3), two main sources could be assigned: (a) *a petrochemical source*, represented by EM 1 (63.4%); (b) *a thermogenic/pyrolytic source*, represented by EM 2 (28.2%).

5

Conclusion

Organic contaminants leached from various solid waste materials (SWMs) used in road construction and repair, discussed in the present chapter, included petroleum hydrocarbons, pesticides, phthalates, phenols, PCBs, organotin compounds, and surfactants. In order to conduct a forensic investigation of these contaminants, it is important that: (a) suitable pre-extraction and preservation treatments are implemented for the samples, and (b) specific extraction and/or cleanup techniques for each organic contaminant are carried out prior to the identification and characterization steps.

Most of the development work on molecular markers (MMs) has resulted from the use of GC-MS, but with advances in other techniques it is clear that this field will benefit from making greater use of alternative identification methods, such as Fourier transform infrared spectroscopy and nuclear magnetic resonance techniques. Isotopic measurements can now be used to obtain complimentary information on the history and origin of a sample. It is now possible to perform a forensic investigation using stable carbon isotopic analyses on individual MMs by GC-Isotope Ratio MS without prior isolation of com-

ponents from a mixture, and determine the natural carbon-13 abundances and therefore sources of the compounds.

In general, genetic source assignment modeling for MMs specific for SWMs and their leachates was important in the present research because the environmental toxicity and chemodynamics (the behavior, fate, transport) of these wastes and their leachates can only easily be predicted by studying these "statistically and experimentally" assigned fractions and their molecular compositions. This is a cost-effective approach to hazardous waste management, decision-making, and environmental impact assessment (EIA) of solid waste materials before disposing or reusing them without certain treatments. Therefore, multivariate statistical analyses using both extended Q-mode factor analysis and the linear programming technique proved to be useful in partitioning SWMs and their leachates into two main end members (sources) of molecular markers, explaining 92.9% of the variation among the samples.

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