Tarek A. Kassim
Editor

Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters

The Handbook of Environmental Chemistry

5 · F

Volume 2
Risk Analysis

Springer

The Handbook of Environmental Chemistry

Volume 5 Water Pollution
Part F, Volume 2

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Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters

Volume 2
Risk Analysis

Volume Editor: Tarek A. Kassim

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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 contaminates 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

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Using Laboratory Experiments and Computer Models for Assessing the Potential Risk of Recycled Waste Materials – Case Studies

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Abstract Experimental methods and models for assessing the risks of recycling waste products are described in this chapter. The basic processes determining the fate of the chemicals in the recycled waste products are also introduced. Two hydrological models are presented: MIKE SHE, which is an integrated groundwater and surface water model, and the MACRO model, which is a relatively simple one-dimensional leaching model. The four case studies included in this chapter give examples on how work on the risk of recycled waste products containing potential hazardous substances (e.g., pesticides, boring chemicals, pesticide residues and antibiotics) has been carried out.

Keywords Model · MIKE SHE · MACRO · Risk assessment · Pesticide · Antibiotics

List of Abbreviations

A	Temperature coefficient describing the temperature dependency of the degradation rate [$°C^{-1}$]
ADI	Acceptable daily intake of the substance [mg/day]
C_L	Concentration in water phase [mg/l]
C_S	Concentration of the chemical bound to the solid matrix or muck [mg/kg]
C_{tot}	Total concentration in muck [mg/kg wet weight]
C_W	Concentration of the chemical in the soil or muck pore water [mg/l]
DI	Daily intake [mg/day]
DOM	Dissolved organic matter [mg/l]
EC_{50}	Concentration at which 50% of the test organisms are affected [mg/l]
f_{OC}	Organic carbon content of the soil [kg/kg]
GUS	Leaching screening index [–]
K_D	Soil partition coefficient [l/kg]
$K_{D,muck}$	Muck-water partition coefficient [l/kg]
K_{OC}	Organic carbon partition coefficient [l/kg]
K_{OW}	Octanol water partition coefficient [l/l]
k_W	Degradation rate constant [day^{-1}]
L	Volume of water [l]
M_{Water}	Amount of chemical from the feeding muck remaining in the water column [mg]
PEC	Predicted environmental concentration [mg/l or mg/kg]
$PEC_{Initial}$	Initial PEC after the first application [mg/kg]
$PEC_{Steady\text{-}state}$	Steady-state PEC [mg/kg]
$PEC_{step\ 1}$	PEC in the first screening
$PEC_{Step\ 2}$	PEC in the second screening
PNEC	Predicted no-effect concentration or the highest acceptable concentration [mg/l or mg/kg]
$PNEC_{soil,\ ecotoxicity}$	Predicted no-effect concentration at which no organisms are expected to be affected [mg/kg]
$PNEC_{soil,\ toxicity\ not}$	Predicted no-effect concentration at which the human intake via soil is expected to exceed the ADI [mg/kg]
QSAR	Quantitative Structure Activity Relationships

RQ	Risk quotient defined by: RQ=PEC/PNEC
S	Amount of solids [kg]
W	Amount of water [l]
T	Temperature (°C)
$T_{1/2}$	Half-life in soil (months)
V	Volume of water from the feeding muck remaining in the water column [m^3]

1 Introduction

Different approaches and tools have been used for assessing the potential risk of recycled waste materials. Despite the fact that general procedures for risk assessment of chemicals and veterinary antibiotics have been developed [1,2], risk assessment for specific waste products will often demand a selective choice of the most appropriate methods for the waste and application concerned.

The purpose of this chapter is to show how risk assessment of different recycled waste products-containing hazardous chemicals has been handled. In the present chapter, four case studies were selected to illustrate some of the general problems connected with the recycling of waste materials, and to describe methods used to assess the potential risk of a broad spectrum of recycled wastes.

To evaluate whether the recycling of waste products causes undesirable effects, the following questions with respect to the contaminants in the waste products should be answered:

- Do the contaminants accumulate in the soil to an unacceptable level? (relevant to the repeated applications of sewage sludge and manure)
- Do the contaminants affect soil-dwelling organisms?
- Can the contaminants be transported to or in the groundwater?
- Can the contaminants be transported to the surface water? and, if so, will they have an unacceptable effect on organisms living in the water?
- Will the contaminants have unacceptable effects on humans?

Thus, the assessment should consider both the risks to humans and the risks to the environment.

The risk characterization in an ecological risk assessment is a simple calculation of the risk quotient (RQ) for all relevant environmental compartments. The risk quotient is defined by: RQ=PEC/PNEC, where PEC is a predicted environmental concentration and PNEC is a predicted no-effect concentration or the highest acceptable concentration. For a number of substances and environmental compartments (e.g. soil and surface water), quality criteria corresponding to PNEC have been derived. If the risk quotient is below one, then the ecological risk is considered negligible. For a complex waste material contain-

ing a large number of chemicals, the risk quotient of the product is often found by summing the risk quotient of each substance, assuming that the chemicals do not interact. This is in some cases a crude assumption.

A common method in the human exposure assessment is to estimate the average daily intake and compare it with the tolerable daily intake. Several models for assessing the human risk of polluted soils exist, for example Risc-Human [3], CalTox [4], CLEA [5], and UMS [6]. These models may also be applied to the assessment of human risk in connection with recycled hazardous waste.

It is thus obvious that a risk assessment of recycled hazardous waste involves both the fate of the chemicals in the environment and the effects on the environment and the human health. The present chapter mainly emphasizes the fate of the chemicals in the environment. However, a short section is included on the assessment of the effects.

2 Effects of Hazardous Chemicals Present in Recycled Waste Materials

There are four primary targets that are of interest in the assessments of recycled hazardous wastes:

- Groundwater – In Denmark, groundwater is used as a drinking water resource. Therefore, the protection of the groundwater against polluting substances has a very high priority. The definition of the highest acceptable concentration in groundwater depends on the substance in question. For pesticides, the highest acceptable concentration is equal to the limit value for pesticides in groundwater, which in Denmark is 0.1 µg/l for each single pesticide and 0.5 µg/l for the total sum of all pesticides [7]. For other substances, for which a drinking water limit exists, the drinking water limit can be used as the critical concentration. If no limit exists, the critical concentration can be derived by assuming a daily intake of groundwater equal to the daily intake of water and using either FAO/WHO values for acceptable daily intake of the substance (ADI) [8] or an estimated ADI. The distribution, fate and transport of the substances to and in the groundwater can be assessed using models such as MIKE SHE, as described in the next section.
- Soil – The risk quotient for a waste product containing several different substances can be estimated in at least two ways. In the first approach, the risk quotient for the entire product can be calculated by summing the estimated risk quotients for each substance. Data on the ecotoxicological effects on soil dwelling organisms (preferably) or toxicity data for aquatic organisms can be used to derive a PNEC for each substance using the principles and the assessment factors proposed by the European Commission [1] or by a statistical method similar to the method suggested by Wagner and Løkke [9]. PNECs for heavy metals can be set to the ecotoxicological soil quality criteria (e.g. as defined by the Danish Ministry of Environment and Energy [10]).

Another approach is to derive a PNEC for the waste product by testing the entire waste product with a number of soil dwelling organisms, for example lettuce seed germination (*Lactuca sativa*) [11], springtail reproduction *Folsomia fimetaria* [12], and inhibition of autotrophic nitrifying bacteria from soil [13]. A PNEC for the tested product may then be derived by using the results for the most sensitive of the test organisms and an assessment factor of 20 according to [14, 15].

- Surface water – As described in the next section, the transport of hazardous substances to surface water can be predicted by models such as MIKE SHE and MACRO. The effects on the organisms living in the surface water can be assessed by the risk quotient, where the PNEC can be estimated by the principles described in [1], if sufficient toxicity data for water dwelling organisms is available.
- Humans – Humans can be exposed to the hazardous substances in waste material via various exposure routes. For example, volatile compounds can be inhaled, polluted soil can be ingested, chemicals can be absorbed through the skin, and chemicals can be ingested via crops, milk or meat originating from polluted farmland. Human risk can be assessed by comparing the estimated average daily intake with the tolerable daily intake for humans. Tolerable daily intakes are often derived from toxicity studies on different mammals, e.g. rats. Further discussion of this topic is outside the scope of this chapter.

3
Fate of Chemicals: Modelling and Measurement Approach

3.1
Basic Processes

The fate of chemicals in a recycled waste product is determined by several basic processes, the most important being sorption/desorption to the solid particles in the waste product and the soil, abiotic and biotic degradation, evaporation of the volatile compounds, speciation of ionic compounds, and dispersive and advective transport with the percolating water.

Sorption and desorption to the solid matrix is often modelled by assuming equilibrium between the dissolved and bound chemicals. Although, a kinetic approach has been used in some models describing the behaviour of chemicals in the soil (e.g. [16]), normally the dissolved and bound chemicals are assumed to be in equilibrium. The soil partition coefficient (K_D) is often used to describe the partitioning of dissolved and bound chemicals. It is defined as $K_D=C_S/C_W$, where C_S is the concentration of the chemical bound to the solid matrix and C_W is the concentration of the chemical in the soil pore water. K_D for hydrophobic compounds may be estimated by $K_D=f_{OC}\times K_{OC}$, where f_{OC} is the content of organic carbon in the soil, and K_{OC} is the organic carbon partition coefficient. The equation should not be used for hydrophilic or even ionic compounds.

Abiotic degradation includes phototransformations, hydrolysis and oxidation. Abiotic degradation depends on the chemical, as some chemicals do not transform abiotically, while others do so readily. Normally, a pseudo-first-order transformation reaction is assumed. The rate constant is derived either from literature data or from measurements in the laboratory. Care should be taken in the interpretation of rate constants, as the rate constants depend on a number of environmental factors such as, temperature (all abiotic reactions), pH (primarily hydrolysis), redox conditions, light composition and intensity (phototransformation), and also on whether the chemical is bound or dissolved. When no data is available, different Quantitative Structure Activity Relationships (QSAR) approaches may be applicable [17].

Modelling the biotic degradation is difficult. The biotic degradation depends on a number of environmental factors, which can be difficult to control and measure. Important environmental factors include temperature, redox conditions, availability of nutrients, water content in the soil/waste product, and the bioavailability of the chemical in question. In addition, microorganisms may or may not be adapted to the particular chemical, or they can adapt over time. Normally, a first-order degradation reaction is assumed, and the rate of biodegradation is either estimated from literature data or from measurements in the laboratory. As it is not straightforward to extrapolate measured data in the laboratory to the conditions in the environment, a sensitivity analysis of the predicted concentrations is recommended. When no data for the biotic degradation is available, QSAR methods may be used [18, 19].

The speciation of a chemical compound also depends on a number of environmental conditions such as temperature, pH, redox conditions and the presence of other chemicals. Helpful estimation tools have been developed, e.g. the program MINTEQA2 [20].

The transport with percolating water and the dispersion of the chemicals in the pore water are both important for the estimation of the concentration in the pore water and the assessment of the chemicals leachability to the groundwater. Several models can be used to simulate these processes, which to a certain extent also include several of the other processes mentioned above. Two such models, MIKE SHE and MACRO, will be described further in the next sections.

3.2 Potential Risk of Leaching

The leachability of organic chemicals in a hazardous waste to groundwater may be assessed in several ways, for example:

- The GUS screening index may be calculated [21]: $GUS=\log_{10}T_{1/2}\times(4-\log_{10}K_{oc})$, where $T_{1/2}$ is the half-life [months] in soil. For some hydrophilic and ionic substances, where K_{OC} is not appropriate to use, an alternative GUS screening index is used for the assessment: $GUS_{Alternative}=\log_{10}T_{1/2}\times\left(4-\log_{10}\frac{K_D}{0.025}\right)$.

The organic substances are classified into three different groups by the GUS-index: (a) GUS<1.8 "non-leachers", (b) 1.8>GUS>2.8 "borderline substances", (c) GUS>2.8 "leachers". The GUS index can only provide a qualitative assessment of the leachability and does not include the concentration or the applied amount of the substances. It furthermore requires that K_{OC} and $T_{1/2}$ are known.

- The leaching in a column filled with waste material can be measured. This can be relevant if the chemicals in the waste material or the waste material is not well-characterized.
- If it is suspected that the chemical of interest will leach, then its concentration in the soil can be estimated using a more complex model, such as the MACRO model [22] or MIKE SHE [23] according to the recommendation of the Danish EPA [24]. Both of these models will be briefly described in the following sections.

The Danish Environmental Protection Agency (EPA) has drawn up a guidance document on how mathematical models can be used for assessing the potential risk of leaching of pesticides to the groundwater [24]. Presently, no validated regional leaching models are available and the Danish EPA guidelines are only valid until common guidelines within the EU are available. The MACRO [22] and MIKE SHE [23] models have been accepted for the assessment of the potential risk of leaching of pesticides. The two models can also be used to predict the transport of chemicals to surface water. The MACRO model is a relatively simple one-dimensional soil column model, whereas MIKE SHE model is an integrated model on a watershed scale. Although the guidance document was prepared for the assessment of pesticide leaching, the mechanisms governing the leaching of pesticides are similar to the mechanisms governing the leaching of other chemicals in the soil environment.

3.3 Integrated Ground and Surface Water Resources

The efficient management of water resources requires information about all aspects of the land-based hydrologic cycle. Furthermore, it is increasingly necessary to manage water resources on a watershed or even river basin scale, for which integrated, distributed hydrological models are important tools.

The complexity of a natural hydrologic system must be reduced to those features that effectively control system behaviour. In many hydrologic systems this includes both surface water and groundwater processes [25]. Detailed modelling of such integrated systems is both computationally intensive and data demanding. However, recent advances in computer processing power, the widespread use of GIS and the availability of remotely sensed data, has made the modelling of integrated systems easier.

In a fully integrated groundwater and surface water system, rainfall will either infiltrate into the ground or pond on the ground surface. Ponded water

will either evaporate or flow downhill to a nearby stream. Infiltrating water will either reach the groundwater table or be removed by plant roots and transpired. Stream flow must be routed through the stream network taking into account base flow to and from the groundwater. Both stream and groundwater flow must also account for anthropogenic 'uses', such as diversions for irrigation and drinking water extraction.

The term 'integrated' is often loosely used in the literature to refer to model codes that describe and link two or more hydrologic processes. However, a true integrated model is one that couples and simultaneously simulates all of the relevant hydrologic processes for a model site including precipitation, overland flow, channel flow, unsaturated flow, and saturated groundwater flow [23]. Many codes include some or all of these processes, but differ in the detail of the process descriptions. In a distributed code, the state variables, such as hydraulic conductivity, can vary spatially across the model domain. The alternative is a 'lumped' model, such as HSPF [26], where the domain is divided into subbasins, within which the state variables are constant.

A physically based code can be defined as one that solves the full set of partial differential equations describing flow and mass conservation for each of the relevant processes in the hydrologic cycle [27].

Although MIKE SHE [23] is the most widely used code for integrated ground and surface water modelling [28], many other codes have been developed to simulate such systems. Most frequently, these codes are based on MODFLOW [29]. However, in the sense outlined above, MODFLOW alone cannot be considered an integrated code, since it is strictly a saturated groundwater code with limited ability to exchange water with surface water bodies. Additional packages have been developed for MODFLOW that increase its effectiveness at coupling it to surface water bodies, but this does not make it an integrated code. For example, the Stream Package [30] does not model surface water flow but it is rather an accounting program for keeping track of the water budget in a stream.

There have been a number of attempts to couple MODFLOW more rigorously to one-dimensional, unsteady channel flow models such as MODBRANCH [31] and MODNET [32]. This type of coupling may be sufficient for strict groundwater and channel flow interactions but ignores the important dynamic recharge and overland flow processes. Other attempts have been made to link MODFLOW more rigorously to watershed models, such as HSPF [26, 33]. However, such watershed models typically include simplified process descriptions. More importantly, the dynamics are often poorly represented since the outflow from one code is often input into the other code as a source/sink term in the following time period.

More recently, advanced variably saturated groundwater/surface water models have been developed that solve the exchange flows implicitly among all of the processes (e.g. [34] and [35]). These codes are promising, but at the moment are very computationally intensive and have been used little outside of the research community.

3.4 The MIKE SHE Hydrological Modelling System

MIKE SHE is an extension of the original the Système Hydrologique Européen (SHE) code [36]. Since then, MIKE SHE has been further developed and distributed by DHI Water and Environment (www.mikeshe.com). Since its initial development, MIKE SHE has been successfully applied in hundreds of applications around the world.

Each module in MIKE SHE describes one of the major hydrological processes in the hydrological cycle and, together, they provide a complete integrated description of the land-phase of the hydrological cycle (Fig. 1). Each component can be run separately or coupled to one or more of the other components. Furthermore, each process includes both complete and simplified process descriptions to decrease the computational burden when possible. The flow processes represented in MIKE SHE include: snow melt, rainfall interception and evapotranspiration, overland flow and channel flow, vertical flow in the unsaturated zone, and groundwater flow. In MIKE SHE, each of these processes operates spatially and at time steps consistent with the spatial and temporal scale of the process.

Unsaturated flow is a critical process in MIKE SHE, as the unsaturated zone plays a central part in most model applications. Only vertical unsaturated flow is simulated in MIKE SHE, since unsaturated flow is primarily vertical due to

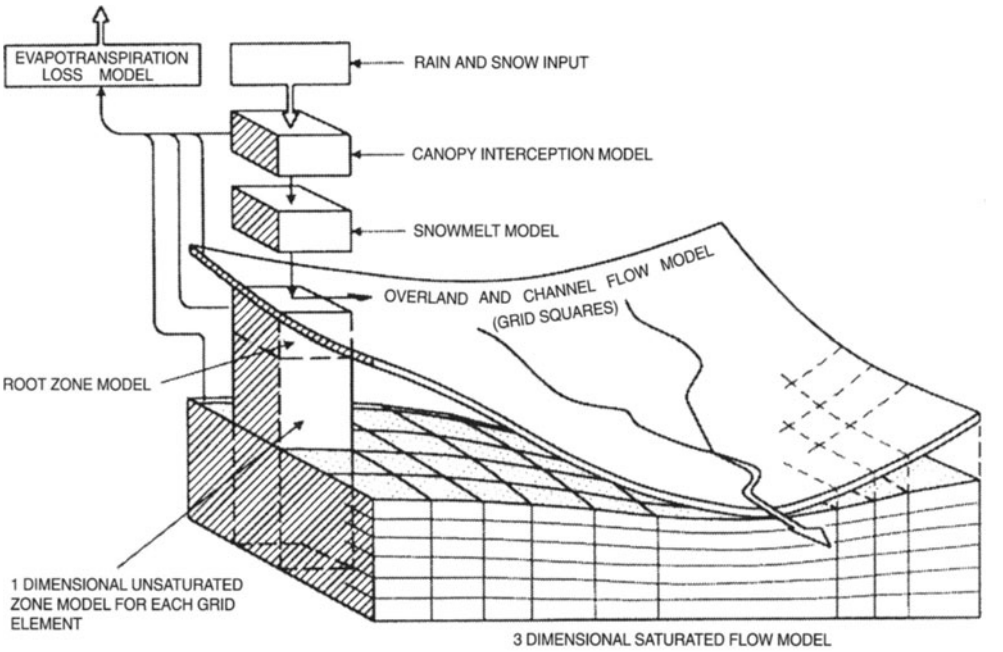


Fig. 1 Pathways for transport of pesticides to surface water

gravity. MIKE SHE includes a coupling procedure between the unsaturated zone and the saturated zone to compute the correct soil moisture and water table dynamics in the lower part of the soil profile. There are two options in MIKE SHE for calculating flow in the unsaturated zone: the Richard's equation or a simplified gravity flow procedure. The full Richard's equation requires input for the moisture-retention curve and the effective conductivity. The simplified gravity flow procedure assumes a uniform vertical gradient in the soil column and the infiltration and percolation processes are described in terms of gravity flow. Each cell in the model is assigned to a soil zone. Each soil zone has a defined soil profile. In this way, the unsaturated zone can be nominally 'lumped', in so far as the unsaturated flow can be solved once for each soil zone or, alternatively for each individual cell.

Evapotranspiration is an integral part of the unsaturated zone process, as it determines the timing and magnitude of groundwater recharge and overland flow generation. Evapotranspiration is the sum of evaporation (from soil, water and plant surfaces) and transpiration (water removed by plant roots and transpired from the leafy parts of the plant). In MIKE SHE, actual evapotranspiration is calculated from a reference evaporation based on the Kristensen-Jensen model [37]. Alternatively, the net rainfall can be calculated by a simple water balance approach. Both methods use the calculated soil moisture in the root zone to determine the actual evapotranspiration.

Overland sheet flow is generated in MIKE SHE when the top layer of the unsaturated zone becomes saturated. Net rainfall, evaporation and infiltration are introduced as source/sinks allowing the surface to dry out in areas where the soil is more permeable. Local depressions in the topography, as well as barriers, such as roads and levies, are conceptually modelled as detention storage.

Channel flow is simulated with DHI's widely used MIKE 11 river hydraulic model, where floodplains and river structures can be included. MIKE 11 can be applied to branched and looped stream networks and quasi two-dimensional flow on flood plains. The flow over a wide variety of structures can also be simulated, such as broad-crested weirs, culverts, and other regulating and control structures.

Groundwater flow is calculated using a regular three-dimensional finite-difference grid based on the given boundary conditions and the interaction with the other components included in the model.

The fate and transport of solutes is simulated using specialized modules. As well, the solute transport mechanisms modelled in MIKE SHE allow the solutes to be transferred between surface and sub-surface water and back again. MIKE SHE also contains tools for calculating soil-plant-atmosphere interactions, using DAISY [38]. DAISY can be used for simulating such things as changes in crop yield under various agricultural practices, irrigation optimisation, and pesticide and nitrate leaching from agricultural areas.

3.5 MACRO

The Swedish MACRO model was originally developed for the simulation of the fate of pesticides in the soil environment. However, the transport mechanisms in the soil for chemicals applied to soil with waste products and pesticides sprayed directly on the field are basically the same. The main difference, which has to be considered, is how the chemicals enter the soil environment.

Like many other leaching models, MACRO is a one-dimensional model, in which horizontal movements – besides drainage – are neglected. The MACRO model includes – in contrast to many other leaching models – a description of the water and solute transport in both micropores and macropores. The very rapid transport in macropores may be of particular significance in clay soils. MACRO is composed of three modules:

- A module describing the water balance and transport in the soil column on the basis of soil data, precipitation and global radiation data
- A module estimating the temperature profile through the soil column on the basis of air temperature data
- A module describing the transport and degradation of the solute

MACRO applies a first-order kinetics for the degradation in each of four "pools" of chemicals in the soil (micro- and macropores, solid/liquid phases), together with an instantaneous sorption equilibrium and a Freundlich sorption isotherm. The MACRO model describes the following solute transport mechanisms in the soil column: advection, dispersion, diffusion and colloidal transport. Transport with dissolved organic matter (DOM) is not included. The chemicals, which are adsorbed to soil colloids, may be rapidly transported through the soil column during strong rain events.

The differential equations that describe the transport and mass balance of water and solute together with the heat balance are solved numerically by defining the soil column as a number of superjacent boxes, each box assumed homogenous with respect to properties and solute concentration. Detailed description of the MACRO model can be found in the literature [22, 39]. Links to a number of documents describing the MACRO model can be found via the homepage: http://www.slu.se/bgf.

Different computer versions of MACRO model exist. The basic equations describing the transport of water and solute (besides the colloidal transport) are, however, the same in the different versions. MACRO can be downloaded from the internet (http://www.mv.slu.se/bgf/).

4
Case Studies

The following four case studies show how to assess the risk of recycled waste products containing potential hazardous substances. The first example is not directly a case study of recycled waste material. Rather, it describes the modelling of pesticide transport to and within streams, after pesticides have been applied to farm fields within a watershed. However, the study process is generally applicable to the modelling of solute transport to and within surface water, and a similar method could be developed for other applications where organic chemicals are applied to the land surface via waste material. The second example is based on a case, where underground material (muck) from the establishment of the Copenhagen Metro was planned to be used as landfill material. The muck contained remnants of chemicals used in the boring process. The chemicals in the waste material were relatively well known, as information on the composition of the boring chemicals and the consumption volumes was available. The third case is an example of recycled sludge from a pesticide factory in the agricultural soil. The fourth case describes the assessment of recycled manure. Besides standard chemicals used in agriculture, such as cleaning agents [40], manure may also contain pharmaceutical residuals, which is the focus of the fourth case study.

4.1
A Modelling Tool for Predicting Pesticide Concentrations in Streams

In 1998, the Danish Environmental Protection Agency initiated the development of a modelling tool that could be used during the pesticide registration process to assess the concentration likely to occur in streams and ponds after normal, legal agricultural use of the pesticide. This tool can estimate the impact in two 'typical' watersheds, based on chemical data provided by the manufacturer. The organizations involved in the development were DHI-Water and Environment, the National Environmental Research Institute (Denmark), the Danish Institute of Agricultural Science (Flakkebjerg), and the Danish counties of Funen and Northern Jutland.

Although this tool was specifically developed for estimating the concentration of pesticides in streams, the study process is generally applicable. That is, the pathways for transport to nearby streams were systematically analysed, representative watersheds were selected, and then the chemicals applied in typical scenarios. Following this process, a similar tool could be developed for other applications where organic chemicals are applied to the land surface, such as land farming of treated organic waste.

4.1.1 Pathway Analysis

Pesticides (or any chemical) sprayed on the land surface may reach a surface water body via (Fig. 2): direct spray drift, rain (wet deposition), dust (dry deposition), surface runoff (dissolved in runoff, or bound to colloids or eroded particles), groundwater, and drain flow (dissolved in drain flow, or bound to colloids or eroded particles).

Of these pathways, spray drift has traditionally been considered the most important route for pesticide transport to surface water. However, local weather, topography and vegetation are important determinants of the actual exposure. Even though the potential for pollution is considerable, particularly during low-flow situations in the summer, few measurements exist that demonstrate its occurrence [41].

Although rainfall may contain measurable amounts of contamination, in general, wet deposition is not relevant as a source of local surface water contamination due to nearby pesticide spraying. Little data on dry deposition is available, but most of the volatilised fraction seems to be re-deposited within a few kilometers of the source [42]. The total air-related transport to a stream (drift plus deposition) may contribute 5–10% of the total stream load [43].

Surface runoff related pesticide losses, including erosion, have been reported in a few studies [44, 45]. However, in Denmark, significant soil erosion is a relatively local phenomenon that is often triggered by particular weather conditions [46]. Thus, although surface runoff related pesticide impacts might be of local importance, in Denmark they are not particularly widespread. Furthermore, erosion and surface runoff typically occur in locations where drains are not present or when the drains are not functioning.

Subsurface transport is characterized by infiltration through the unsaturated zone, followed by discharge to surface water bodies via drains or groundwater base flow. Infiltration through the unsaturated zone occurs either through the soil matrix or through macropores. In sandy soils, infiltration and solute transport respect Darcy's law and the advection/dispersion equations. However, in sandy loams macropore flow can allow water and solutes to move quickly through the unsaturated zone when local saturation occurs in the upper part of the profile. Both adsorption and degradation of organic compounds occur in the unsaturated zone, particularly when transported through the matrix. These two processes can result in nearly 100% removal rates.

Transport through groundwater may be an important background source of contamination in small streams on sandy areas, where the baseflow component can be large. However, adsorption and degradation may continue to limit the movement of organic solutes through the soil matrix.

Concentrations of pesticides can be much higher in drain flow. The common picture for drained moraine soils is that shortly after the pesticide application a high concentration peak of short duration occurs, due to macropore flow [47, 48]. Furthermore, after a heavy rainfall, drains can contribute large amounts

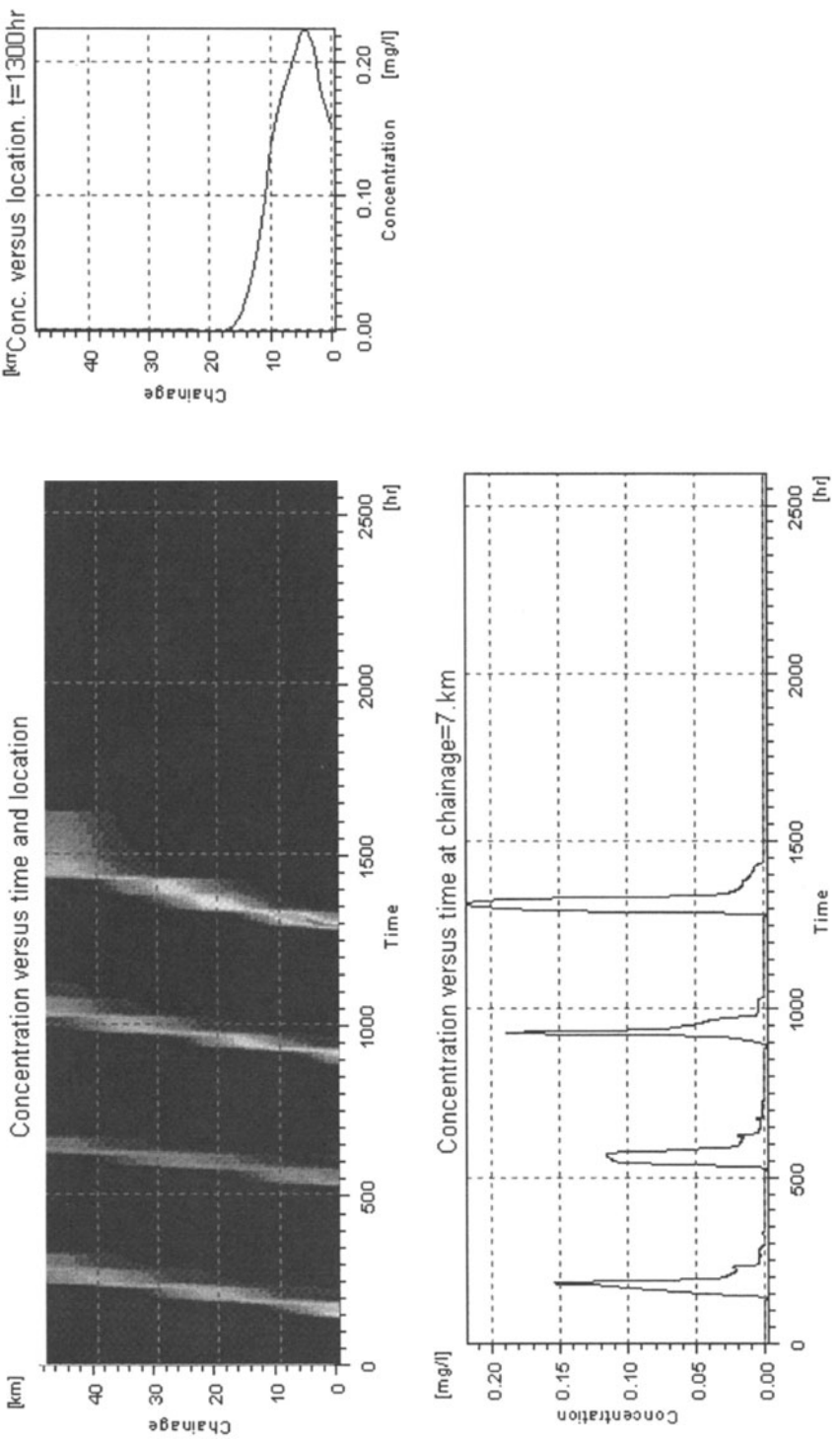


Fig. 2 Pesticide concentrations moving through the stream. 'Chainage' refers to the distance along the stream

of sediment to a stream that can be significantly contaminated with hydrophobic pesticide residue [49].

4.1.2 The Modelling Tool

4.1.2.1 Model Scale

These pathways and processes act at different spatial and temporal scales. Dynamic groundwater/surface water interactions, as well as erosion, act at the catchment scale. Wind drift and drain flow act locally but can be simulated at a catchment scale. Thus, the catchment scale is used for the modelling tool. The time scale for peak concentrations in the stream due to drift and drain flow is of the order of minutes, whereas the trend in baseflow contribution to the stream is of the order of months. Ideally, the scenarios should be run with short time steps (to catch the peaks) over a long period (to simulate the trend). However, restrictions on computational capacity and the size of the output files necessitate some compromises. The modelling tool is based on the integrated groundwater/surface water modelling system, MIKE SHE as described previously.

4.1.2.2 Model Catchments

Two Danish catchments belonging to the Danish National Monitoring Program were selected as the basis for the scenarios. The first catchment is covered primarily by moraine clay soils, while sandy soils predominate in the other. Together these two texture types make up nearly 60% of the Danish arable area. Both catchments are representative of intensively farmed areas in Denmark and contain first-order streams of the type in which high concentrations of pesticides are found. The sandy catchment is slightly less populated, with 98% of the land area being farmed, while the moraine catchment is 89% farmed. More detailed descriptions of the catchments can be found in [50]. An integrated groundwater/surface water model was developed for each catchment and calibrated and validated on monitoring data from the two catchments.

4.1.2.3 Scenarios

The purpose of the modelling tool is to help assess the concentration likely to occur in typical streams and ponds after normal, legal agricultural use of a pesticide. The models for the two catchments were calibrated and validated against existing data to ensure that the simulated processes are modelled correctly. However, the modelling tool required by the Danish EPA must ensure that the

calculated concentrations are representative for typical streams and ponds. Thus, the site-specific models were slightly modified to more closely reflect typical conditions in Denmark.

In both models, the size and topography of the catchment, as well as the stream hydraulics and the overall land use distribution remains unchanged in the scenarios. For the scenarios, the changes to the models include the removal of tree barriers along the stream length, the opening of culverted sections, and the 100% spraying of all cropland. In the scenarios, the pesticide is applied every year during the simulation period, with several applications per year. Furthermore, since the time between application and rainfall is important, different simulations must be run with different application dates.

4.1.2.4 User Interface

The typical users of the modelling tool are regulators, rather than full time modellers. Thus, special consideration has been given to tailoring the modelling system to the user group. The user interface allows the regulator to select a hydrological scenario and then specify crop, buffer zone width, and pesticide properties, as well as one metabolite and its properties. The user is also allowed to run a limited number of Monte Carlo simulations on the most sensitive parameters, to obtain an estimate of the uncertainty. However, the user cannot change the hydrological simulations, as they are pre-run and used as input to the transport simulations.

The structure of the output for the tool also required special consideration. Typically, the biological effects of pesticide exposure have been reported based on lethal concentrations in standing water over a time period. This does not reflect the mechanisms of repeated spikes of contamination that is typical in streams. Nor, does it reflect the observed dilution of peak concentrations as they move downstream. Therefore, the output tools have been created to relate the dynamic and spatially variable stream concentrations in the model to the static toxicity levels typically reported in the literature (see Fig. 2).

4.1.3 Summary of Findings

The project is non-traditional in several ways. It works with catchments instead of "edge-of-field" scenarios, and all the scenarios are hydrologically consistent. Further, it deals with ponds and streams rather than just ponds, which is more traditional. "Worst-case" scenarios have not been defined, as the complex interaction between climate, soil texture, pesticide characteristics and time is such that a single worst-case scenario cannot exist. The initial results can be summarized as follows:

- Very little data exists on the toxicity associated with the dynamic concentrations seen in streams. The Danish EPA has initiated a number of projects

to study the effects of these shorter exposures. Furthermore, the relevance of dissolved concentrations versus concentrations in macrophytes and bed sediments is under debate and has not been addressed in this study.
- The initial results show that the major events measured in the streams must be related to point-source pesticide inputs rather than non-point source agricultural inputs. This has demonstrated to the Danish EPA that more attention should be directed at the handling of pesticides on the farms to reduce the likelihood of point sources being created.

4.2 Recycling Waste Materials-Containing Boring Chemicals in a Landfill Deposit

A tunnel for the new Copenhagen Metro is being built and the excavated material (i.e. muck) is being landfilled. Before the contractor was permitted to landfill the muck, they had to assess the risk associated with the boring chemicals (e.g. foams, foam polymers, greases, vegetable oils, etc.) contained in the muck. Further, they were required to investigate whether the landfill could be considered 'clean' after a certain period due to natural biodegradation processes. The approximate consumption rate of each of the borings chemicals, together with the composition of the boring chemicals, was known. The assessment was carried out in three steps: (a) prescreening, where the potential hazardous substances were identified, (b) chemical analysis of the muck samples with respect to the potential hazardous substances, and (c) modelling the fate of the hazardous substances in the deposit. The following is a summary.

4.2.1 Step 1: Prescreening

The composition and the expected consumption volume per meter drilled tunnel for all boring chemicals were known. Thus, it was possible to estimate a conservative $PEC_{step\ 1}$ for all substances in question, by assuming that all chemicals used would end up in the muck.

The highest acceptable concentration of the substances were derived by both estimating a PNEC with respect to soil dwelling organisms ($PNEC_{soil,\ ecotoxicity}$) and with respect to human intake ($PNEC_{soil,\ toxicity}$). The $PNEC_{soil,\ ecotoxicity}$ was mainly derived from effect data for water dwelling organisms using the principles described in [1]. The $PNEC_{soil,\ toxicity}$ was derived by estimating the human daily intake via inhalation of air and dust, dermal contact and ingestion of the muck by both an adult and a child. It ($PNEC_{soil,toxicity}$) was for the different substances set equal to the concentration in soil, at which the average daily intake was equal to the estimated ADI.

The $PNEC_{soil,\ ecotoxicity}$ was less than the $PNEC_{soil,\ toxicity}$ for all substances. Thus, the soil dwelling organisms were considered more sensitive to the boring chemicals than humans were. Therefore, the PNEC was set equal to the $PNEC_{soil,\ ecotoxicity}$ for all substances.

For a number of chemicals the $PEC_{step\ 1}$ was less than the PNEC, which meant that these substances were not of concern. However, for some glycols, as well as non-ionic and anionic tensides, the $PEC_{step\ 1}$ exceeded the PNEC, which meant that these chemicals might be hazardous to the soil organisms.

4.2.2 Step 2: Chemical Analysis

$PEC_{step\ 1}$ was considered very conservative, as all chemicals were assumed to end up in the muck. To make a better estimate of the PEC, samples of muck from the drilling process was analysed, with respect to the identified potentially hazardous substances (e.g., glycols, non-ionic and anionic tensides).

Some of the substances were assumed to adsorb relatively strongly to the muck, so the analysis was carried out by mixing the muck with water in three solid (S) to water (W) ratios, and the water phase was then analysed with respect to the substances of potential concern (glycols, non-ionic and anionic tensides). It was assumed that equilibrium between dissolved and bound chemical was established in each of the three solid to water ratios. It was also assumed that the equilibrium between dissolved and bound chemical could be described by a linear isotherm. That is, $C_S=K_{D,muck}\cdot C_L$, where C_S is the concentration of the substance bound to the muck (mg/kg), $K_{D,muck}$ is the muck-water partition coefficient, and C_L is the concentration in water phase. $K_{D,muck}$ was then determined as the value, where the variation of the estimated initial concentration in the muck $PEC_{Step\ 2}=C_{tot}=(K_{D,muck}+W/S)\cdot C_L$ for the three S:W ratios was lowest.

The results of the chemical analysis showed that the concentration estimated in step 1 ($PEC_{Step\ 1}$) was larger than the analytically determined concentration ($PEC_{Step\ 2}$) for all cases. However, the analytically determined concentration ($PEC_{Step\ 2}$) was still greater than the PNEC for each of the substances of concern. The question then became, how long will it take for the concentration in the landfill to fall below the PNEC.

4.2.3 Step 3: Modelling the Fate of Substances in the Deposit

4.2.3.1 Model Formulation

A relatively simple model was formulated to assess the fate of the substances in the deposit and to estimate the time needed for the concentrations of the substances of concern to fall to the PNEC. The deposit was modelled as a number of adjacent boxes (both horizontally and vertically). Advective transport, sorption/desorption and biodegradation were considered. The muck is initially pumped into the landfill as slurry and the solids were allowed to settle. After a period of time, the water in the pit was replaced by solids, creating a 'dry' deposit. In the model, it was assumed that sedimentation of the solids occurs immediately, that

the initial water content in the slurry was 60% (volume, measured), and the water content in the sediment was 30% (volume, based on experience). It was assumed that the dissolved and bound chemicals were at equilibrium. Thus, a certain amount of chemical was assumed to be released to the free water, as follow:

$$M_{Water} = V \cdot C_W$$

where V is the volume of water from the feeding muck remaining in the water column, and C_W is the concentration of chemical dissolved in the water phase.

It was assumed that the biodegradation rate of the substances of concern followed first order kinetics (both aerobic and anaerobic). The rate constants were determined from laboratory studies (see next section).

Both aerobic and anaerobic conditions are likely in the deposit, and a model for the oxygen content in the deposit was formulated. Reaeration, diffusion of oxygen within the deposit, and consumption of oxygen due to biodegradation were considered. It was assumed that the surface of the deposit was oxygen saturated. The oxygen consumption rate due to biodegradation was assumed to be constant and was determined from laboratory studies (see next section).

The temperature in the deposit varied throughout the year, with temperatures below freezing in the winter and above 20 °C in the summer. The average temperature was assumed to be 10 °C.

4.2.3.2 Biodegradation Studies

The aerobic and anaerobic biodegradation rates of the substances of concern were measured in a muck suspension at 17 °C in a laboratory study. Samples taken from the water phase were submitted to chemical analysis. The oxygen consumption rate of both muck with boring chemicals and muck without boring chemicals was measured as well.

Both temperature and solid:water ratio in the biodegradation studies differed from the assumed conditions in the deposit. Extrapolation of the biodegradation results in the laboratory study to realistic environmental conditions was carried out. It was assumed that:

- The biodegradation rate of the substances followed first order kinetics
- Only biodegradation of the dissolved components takes place, which leads to the first laboratory biodegradation rate constant k_W(17 °C). The fraction of dissolved chemical was estimated from the muck-water partition coefficients ($K_{D,muck}$) determined in step 2
- The rate of biodegradation is doubled for every 10 °C increase in temperature. The rate of biodegradation at a temperature T was, therefore, estimated from the measured rate in the laboratory by

$$k_W(T\ °C) = k_W(17\ °C) \cdot e_A(T-17);\ A = 0.08\ °C^{-1}$$

The measured oxygen consumption rate of both muck with boring chemicals and muck without boring chemicals was found to be very similar. This means

Table 1 Biodegradation studies of Comet muck

Compound (group)	K_D [l/kg]	k_W(aerob) [day^{-1}]	k_W(anaerob) [day^{-1}]
Anionic tensides	2.6 (2.0–3.8)	0.39	0.020
Non-ionic tensides	0.0	0.39[a]	0.020
Glycol 1	4.6	0.078	>0.078
Other glycols	4.6	0.078	>0.078

[a] Assumed equal to the degradation rate for anionic tensides.

that the additional oxygen consumption due to the boring chemicals is small relative to the natural oxygen consumption. It was furthermore found that oxygen consumption rate was almost constant after an initial very rapid oxygen consumption. Thus, the oxygen consumption rate was assumed constant with time in the model. The oxygen consumption rate found in the laboratory was then extrapolated to the conditions in the deposit. A pseudo muck-water partitioning coefficient was determined for the organic material in the muck and used for the extrapolation. The results of these biodegradations studies are given in Table 1.

4.2.3.3 Model Validation

The column model was validated by comparing the model predictions with results from two column experiments carried out on muck samples. The columns were 20 cm in diameter and 40 cm in height. Each column was filled with approximately 18.5 kg dry mass of muck and flushed with water for 61 days until a L/S ratio of 0.9 l/kg (L: volume of water flushed through the column, S: mass of muck in the column). The chemical concentrations in the flushing water were measured at different L/S ratios and the muck in the column was analysed after the experiment. The experiments took place at a temperature of 20 °C.

Table 2 Predicted and measured mass balance of a column experiment. Number in brackets are measured values

	Anionic tensid.	Non-ionic tensid.	Glycol 1 k_W=0.078 day^{-1}	Glycol 1[a] k_W=0.4 day^{-1}
Leached (%)	16 (16)	23 (<72)	15 (<10)	12 (<10)
Degraded (%)	55 (56)	77 (-)	10 (>39)	40 (>39)
Remain. (%)	28 (28)	0,0 (-)	75 (<51)	48 (<51)

[a] k_W for glycol 1 was modified in order to get better agreement between measured and calculated mass balance.

Table 2 shows a comparison between the measured and the predicted mass balance of the column experiments. A good correspondence between the measured and predicted mass balance for the anionic tensides can be seen. The detection limits for the other substances of concern are relatively high, so it is not possible to make a proper validation for these substances. However, there is no contradiction between the measured and calculated values.

4.2.3.4 Model Calculations

Deposits of varying sizes were simulated. The depth of the deposit varied between 3.6 and 5.2 m and the area between 30,000 and 82,000 m^2. The initial con-

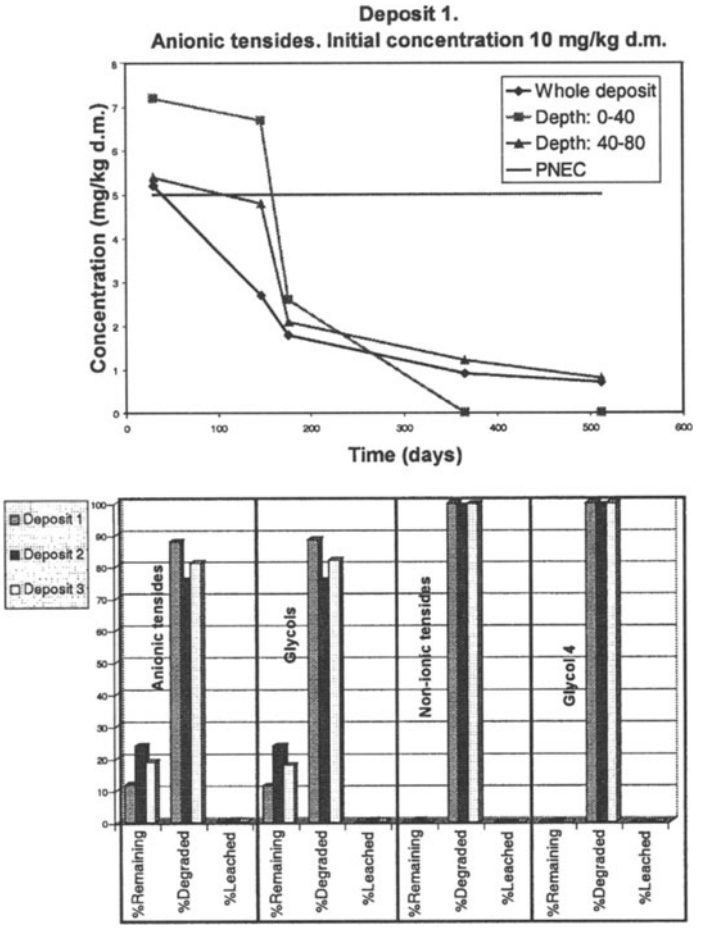


Fig. 3 Predicted mass balance of the deposits. Predicted concentration of anionic tensides as a function of depth and time

centration of the substances of concern varied between a realistic concentration and a worst case concentration (anionic tensides: 3–10 mg/kg; non-ionic tensides: 0.3–1.0 mg/kg; "glycol 4": 30–100 mg/kg and "other glycols" 10.5–35 mg/kg).

Figure 3 shows a predicted mass balance of the four substances of concern and the predicted concentration for the anionic tensides as a function of time together with the PNEC for the anionic tensides. It is seen that the biodegradation is the most important removal process and that the chemicals only leach to a minor degree (<1%). The non-ionic tensides and "glycol 4" are almost completely removed within one year of depositing. With respect to the other group of glycols, around 80% is removed within the first year of depositing. The concentration of the anionic tensides is expected to be below the PNEC within the first half a year after the depositing is begun.

4.2.4 Summary of Findings

A model for the estimation of the chemicals fate in a deposit was formulated, where the biodegradation rate constants and sorption coefficients were based on laboratory data. The model was partly validated on basis of column experiments.

The model showed that biodegradation of the investigated compounds is the most important removal process in the deposit, and that the leaching of the chemicals only contributes to a minor degree (<1%) to the total mass loss. The contractor was allowed to deposit the muck on a site in Copenhagen, as long as the content of the substances of concern muck did not exceed certain concentrations. The contractor was obliged to have muck samples analysed for anionic and non-ionic tensides regularly during the construction period.

4.3 Agricultural Usage of a Solid Waste Product From a Pesticide Factory

Cheminova phosphate is a waste product due to the production of pesticides at Cheminova Agro A/S in Denmark. The waste is a dried calcium-stabilized sludge product from the biological wastewater treatment plant (WWTP) of the factory. The dry product (95% dry matter) is applied as a phosphatic fertilizer to agricultural soil. Besides a content of inorganic macronutrients (approx. 6% phosphate, 1% nitrogen, 20% sulfate and 30% carbonate), the product contains small residues of heavy metals, pesticides, degradation products, and other organic substances from the production. The total content of organic matter is approximately 10% [51].

The product is regularly analysed by the company, and the variations of the concentrations of the different substances are well known. A worst case realistic scenario was set up for the composition of the Cheminova phosphate based on the measured maximum concentrations and the knowledge of the production conditions at the factory (Table 3). Several of the substances were not detectable, and in those cases, the detection limit was used as the maxi-

mum concentration. Due to the amount of macronutrients in the product, Danish regulations allows it to be applied to agricultural soil at a rate of either 0.5 tons/ha every year or 2 tons/ha every three years [10].

An environmental risk assessment was carried out to predict the risk associated with applying the product to agricultural soils. It was assumed that the application of the waste product was in accordance with the regulation of the Danish Ministry of Environment and Energy [10], i.e. the product would be applied under circumstances ensuring no risk for run-off to surface water. This section presents the results of the different approaches used for the risk assessment.

Table 3 Concentration of evaluated substances in the Cheminova phosphate for the worst case scenario used for estimation of PEC in the soil compartment

Substances	Concentration [mg/kg product]
Thiophosphates (4 subst.)	0.05
P2-acids (7 subst.)	<0.71
Triesters (2 subst.)	0.74
Pyrimidines (3 subst.)	2.60
Alkyl sulphides (4 subst.)	<0.02
Heavy metals	
Zinc	460
Nickel	14.0
Copper	430
Cadmium	0.33
Lead	4.6
Mercury	1.7[a]
Chromium	17.0
Pesticides[b]	
Chlormephos	0.003
Chlorpyrifos	0.020
Dimethoate	0.002
Ethion	0.002
Formothion	<0.002
Mecarbam	0.005
Glyphosate	<5 (<30)[c]
Malathion	0.030
Methyl parathion	0.030
Ethyl parathion	0.005
E-sulfotepp	0.030

[a] The concentration will normally be approx. 0.2 mg/kg.

[b] A total of 13 pesticides were evaluated. The concentrations of two more pesticides were <0.005 mg/kg of product.

[c] 30 mg/kg was used in the MACRO modelling.

4.3.1 Applied Methods

4.3.1.1 Ecotoxicological Effects

The ecotoxicological effects of the Cheminova phosphate in soil were evaluated using two methods. In the first method, the estimated risk quotients for each substance were summed to obtain the risk quotient for the total product. PNEC for the substances were mainly derived from aquatic ecotoxicity data, which were extrapolated to soil ecotoxicity by assuming that only the dissolved part of the substances contributes to the effects. In the second method, the entire product was tested against three soil-dwelling organisms deriving the PNEC of the product and the risk quotient for the total product was estimated. The calculations of the risk quotient were carried out using application rates of 0.5 tons and 2 tons product per ha.

Profiles of the risk quotient estimated from the risk quotient for each substance were also calculated as a function of time, by modelling the leaching and biodegradation of the substance as a function of time.

4.3.1.2 The Assessment of Uptake in Plants

Following the principles described by Tørløv et al. [15], the concentrations in the soil of 13 pesticides, including e-sulfotepp (an impurity), were estimated using an application rate of the Cheminova phosphate of 2 tons/ha every three years. The uptake concentrations in plants were estimated for cereals, root crops, and leafy vegetables. The potential human intake of the substances were calculated assuming that a person only eats plant products from fields treated with Cheminova phosphate. The daily intake (DI) of each substance was calculated using statistical data for the intake of vegetables from the Danish Veterinary and Food Administration [52], and the DI values were compared with the FAO/WHO values for acceptable daily intake (ADI) [8].

4.3.1.3 Leaching to Groundwater

The leachability to groundwater was assessed in three steps, as follows:

- Calculation of the screening index GUS
- The concentration in the percolate 10 cm below the soil surface was estimated using a simplified leaching box model
- The concentration 1 m below the soil surface was estimated using the MACRO model (version 4.0) [22] following the recommendations of the Danish EPA [24]. The concentration of glyphosate was assumed to be 30 mg/kg of the waste product in the MACRO modelling.

4.3.2 Results and Discussion

The ecotoxicological assessment, based on PEC/PNEC values over time for the individual components, indicates that Cheminova phosphate will lead to toxic effects in the soil immediately after the application, and that the effects will persist for periods exceeding the possible application intervals of one year and three years, respectively. The pesticides are expected to be the major contributor to the toxicity, followed by the P2-acids. Except for the pesticides, neither the P2-acids nor the other constituents will cause any serious toxic effects. An individual assessment of each substance within the pesticides revealed that e-sulfotepp was the dominating toxicant with a PEC/PNEC of 3.9 for an application of 2 tons product/ha. Number two in a ranked row of the most toxic substances was ethyl parathion (PEC/PNEC=1.4) followed by malathion (PEC/PNEC=0.37). Glyphosate gave the lowest PEC/PNEC value of 4×10^{-5}.

The ecotoxicological test of the entire Cheminova phosphate product and a similar phosphate fertilizer without the organic compounds and the heavy metals using soil-dwelling organisms showed that there were no significant differences between the two products. The results indicate that the differences observed were due to the inorganic salts in the Cheminova phosphate and not to the minor concentrations of the organic xenobiotic.

Calculation of the concentrations of heavy metals in the upper 10 cm soil layer after application of 2 tons product/ha resulted in concentrations that were lower than the recommended soil quality criteria (a factor between 70 and 6550).

The comparison of the estimated maximum potential daily intake (DI) and the acceptable daily intake (ADI) of the pesticides showed that the potential DI was at least a factor 10^4 lower than the ADI. There was no ADI available for sulfotepp and chlormephos. However, the estimated DI for these substances is much lower (4×10^{-3}–4×10^{-5}) than the lowest of the ADIs for the other substances. Thus, it was concluded that the Cheminova phosphate is not expected to create any significance exposure to humans via the intake of agricultural products.

Based on GUS indices, thiophosphates, P2-acids, triesters, alkyl sulphides, hydroxypyrimidine, chlormephos, dimethoate, malathion, and mecarbam were categorised as either "borderline substances" or "leachers". The estimated concentrations in the percolate at a depth of 10 cm in the soil column were above 0.1 µg/l for application of 2 tons Cheminova phosphate/ha for the P2-acids, the triester *O,O,O*-trimethylthiophosphate, the pyrimidine hydroxypyrimidine, and glyphosate. The leaching behaviour of these substances, including dimethoate and e-sulfotepp, was studied in more detail using the more complex MACRO model.

The simulations with the MACRO model showed that none of the substances are expected to occur in concentrations above the limit for pesticides in groundwater (0.1 µg/l), neither for a sandy soil (Karup) nor a loamy area (Langvad).

4.3.3 Summary of Findings

The two different approaches used to evaluate the ecotoxicological effects of Cheminova phosphate gave quite different results. When the components were evaluated individually using mainly aquatic ecotoxicity data, the Cheminova phosphate appeared to be persistently toxic to soil organisms. However, when soil organisms were exposed to Cheminova phosphate, there were no significantly different ecotoxicological effects between the Cheminova phosphate and a reference phosphate fertilizer without heavy metals and organic xenobiotics. Thus, the single substance approach may be valuable for ranking specific substances according to their toxicity but it should be supplemented by tests with the entire complex product for a risk assessment using organisms from the target compartment. Furthermore, the application of the GUS index and a simplified mathematical model is a suitable first step to evaluate the leaching potential of chemicals applied to soil.

4.4 Recycled Manure-Containing Antibiotics

Antibiotics are used to fight bacterial infections in both humans and animals. Despite the relative high usage of some antibiotics, very little information on the environmental release of this group of substances is available ([53, 54]). Antibiotics for humans are mostly given therapeutically, whereas in veterinary use antibiotics are also given as a precautionary measure as feed additives. Antibiotics are primarily used in the husbandry of pigs, calves and poultry, but they are also used therapeutically to treat horses, sheep and cows. All new veterinary medicinal products launched in the EU after January 1, 1998, must undergo an environmental risk assessment before they can be marketed. This will help to include ecological considerations in the cost benefit of the use of antibiotics [2].

In the literature, attention has also been drawn to the possibility that antibiotics in the environment could contribute to the overall development of antibiotic resistance. Selection of resistant bacteria in the presence of antibiotics is already a recognized problem, which may be threatening the future effectiveness of such treatment for livestock and humans. A number of authors have studied the transfer of genes between bacteria in both sediment, soil, water and waste water [55–57]. Despite its great importance, this item will not be discussed further in this section.

Compared to many other industrial chemicals, the exposure routes for veterinary antibiotics in the environment are relative easy to identify. The two main exposure routes are excretion of drugs via faeces and urine from grazing animals and the spreading on arable soil of drug via manure from stabled animals. In the field, urine and faeces are dispersed separately, whereas in stables the urine and faeces are collected, mixed and stockpiled before being spread on

the fields. The use of manure or slurry as a fertilizer on arable land may involve a risk for the environment, as residues of antibiotics are spread on land or pastures as a constituent of the manure or slurry. This case study presents several methods for the environmental risk assessment of antibiotics on a screening level. The focus is on the effects on the soil ecosystem and the leachability of the antibiotics. The antibiotics sulfadiazine, chlortetracycline, oxytetracycline and tylosin were selected to illustrate the methods used. Often the molecular structure of antibiotics includes several functional groups enabling different degradation processes to occur, which generally tends to reduce the environmental potency of the compounds. One exception is the tetracyclines, which form several potent degradation products [58, 59]. Furthermore, some antibiotics are not only excreted as parent compounds, but also as conjugated metabolites, whose stability and potency in the environment is unknown [53]. Therefore, the metabolites of the antibiotics should also be considered in the assessment, but this is not presented here.

4.4.1 Applied Methods

4.4.1.1 Estimation of PEC – Concentrations of the Drugs in Soils

Several issues have to be considered when estimating the PEC of antibiotics. These include the use pattern of the drug, treatment frequency, the physiological characteristics of the target animals, existing regulations for the use of manure, husbandry practices, and the kinetics of the antibiotics in the animal (i.e. pharmacokinetics), in the stored manure and in the soil [60]. Very little is known about the fate ((micro) biological and chemical degradation) of antibiotics during the storage of manure prior to spreading [54]. Therefore, the uncertainty in the predicted environmental concentration (PEC) of antibiotics due to manure spreading will be larger than the uncertainty in the PEC related to grazing animals, where pharmacokinetic parameters determine the time-related exposure via urine and faeces.

Most antibiotics are water-soluble and excreted with the urine as parent compounds or metabolites. However, some antibiotics are less water-soluble and these are also excreted with faeces. Several model approaches have been developed for the determination of PEC [60, 61]. Table 4 gives an overview of the model used for estimating the PEC on a screening level. This method is further described by Halling-Sørensen [60]. Both an initial PEC after the first application ($PEC_{Initial}$) and a steady-state PEC ($PEC_{Steady\text{-}state}$) after an infinite number of repeated applications were estimated. The antibiotics were assumed to degrade by first-order kinetics both in the slurry and in the soil. Table 5 gives data on the doses, $\log K_{OW}$, excretion fractions for urine and faeces, and assumed degradation rates both in manure and in the soil environment for the four selected antibiotics.

Table 4 Estimation of PEC

Item	Grazing animals	Application in a slurry
Assumptions	Excretion of antibiotics within one day. No pharmokinetics needed to be considered	Excretion of antibiotics within one day. No pharmokinetics needed to be considered
	Mixing in soil: Urine is assumed to be mixed in the top layer of the soil the fraction of the antibiotics in the water fraction of the dung is assumed to be mixed in the top layer of the soil	Mixing in soil: The manure is assumed to be mixed in the top layer of the soil
	Application frequency: The soil is assumed to receive dung/urine with a constant time interval	Application frequency: The soil is assumed to receive manure/slurry with a constant time interval (T_i)
Determination of $PEC_{Initial}$	$PEC_{Initial} = \frac{D \cdot m_{Animal} \cdot N_{Animal} \cdot T \cdot (F_{Urine} + F_{Dung} \cdot F_{Leached})}{\rho_{Soil} \cdot F_{spreading} \cdot H_{Mix}}$	$PEC_{Initial} = \frac{C_N \cdot Q_N}{\rho_{Soil} \cdot H_{Mix}}$ $C_N = \frac{D \cdot m_{Animal} \cdot T \cdot (F_{Urine} + F_{Dung})}{T_{Storage} \cdot P_N} \cdot \sum_{i=0}^{Time_i = i} e^{-k_{slurry} \cdot T_i}$
Parameters	D: daily dosage. See Table 6 for data on this m_{Animal}: animal weight (kg): 100 (pig), 220 (beef cattle) N_{Animal}: number of animals in the field per hectare: 15 (pigs), 10 (beef cattle) T: days of treatment F_{Urine}: fraction of antibiotics excreted with urine. See Table 6 for data on this.	Q_N: the area based load of manure (kg N/ha) = 170 (pigs); 210 (cattle) ρ_{Soil}: the soil density (kg/m^3)=1500 H_{Mix}=Mixing depth (m)=0.05 D: daily dosage. See Table 6 for data on this m_{Animal}: animal weight (kg): 100 (pig), 220 (beef cattle), 20 (piglets)

Table 4 (continued)

Item	Grazing animals	Application in a slurry
	F_{Dung}: fraction of antibiotics excreted with dung. See Table 6 for data on this $F_{Leached}$: fraction antibiotics in the dung leached to the soil top layer: $$F_{Leached} = \frac{F_{Water,dung}}{F_{Water,dung} + F_{Solid,dung} \cdot K_{D,dung} \cdot \rho_{Dung}}$$ $F_{water,dung}$: water content in dung=0.88 $F_{solid,dung}$=solid content in dung=0.12 ρ_{Soil}: the soil density (kg/m^3)=1500 H_{Mix}=Mixing depth (m)=0.05 D: daily dosage. See Table 6 for data on this $F_{spreading}$: fraction of soil receiving drug or drug residue=0.01.	T: days of treatment F_{Urine}: fraction of antibiotics excreted with urine. See Table 6 for data on this. F_{Dung}: fraction of antibiotics excreted with dung. See Table 6 for data on this $T_{Storage}$: total storage of manure (d)=180 P_N: daily production of manure (kg N/d): 0.0263 (fattening pigs), 0.0299 (beef cattlee) k_{Slurry}: degradation of antibiotic in manure or slurry. See Table 6 for data on this $Time_i$: time from medication, i, to spreading of manure (d)
Determination of $PEC_{Steady\text{-}state}$		$$PEC_{steady\text{-}state} = \frac{PEC_{Initial}}{1 - F_{remaining}}$$
Parameters		$F_{remaining}$: fraction of antibiotics remaining prior to the next "application" $$F_{remaining} = e^{-k \cdot T_i}$$ T_i: the time between each application (d)=180 dk: first order degradation constant in soil. See Table 6 for data on this

Table 5 Data and calculation results for the four veterinary antibiotics. Bold PEC values indicate that the risk quotient is above 1

Parameter	Antibiotic			
	Sulfadiazine	Chlortetracycline	Oxytetracycline	Tylosin
Spectrum	Gram positive and Gram negative Bacteriostatic action	Gram positive and Gram negative Bacteriostatic action	Gram positive and Gram negative Bacteriostatic action	Gram positive Bacteriostatic action
Dose Injection Peroral with water	Pigs and calves: 200 mg per 15 kg bw	Pigs:	Pigs and cattle: 5–10 mg per kg bw 25 mg per kg bw, 3–5 days	Pigs and cattle: 5–10 mg per kg bw 5–10 mg per kg bw,
Feed administrated drug.	30 mg per kg bw, 3–5 days.	40 mg per kg bw, 5–7 days.		4 mg per kg bw, 21 days (pigs)
F_{Urine} [73]	0.9	0.65	0.65	1
F_{Dung} [1]				
$k_{slurry}(day^{-1})$ [73]. Primary degradation	ln(2)/30	ln(2)/100	ln(2)/100	ln(2)/21
$k_{soil}(day^{-1})$. Primary degradation	ln(2)/90 No degradation data for soil found, but the substance is very degradable [67], so the half-life is set to the conservative but low value of 90 days	ln(2)/320. A temperature of 10 °C is assumed. Extrapolated from data given in [53] at 20 °C, assuming that the half-life is doubled for every 10 °C decrease in temperature	ln(2)/320. Assumed equal to the biodegradation rate of chlortetracyline. Measured halflives in anoxic sediment are 9 days and 419 days respectively [53]	ln(2)/160. Estimated from data given in [72]
$LogK_{OW}$	0.12±0.26 [68] −0.08(pH 4.0–8.0, ion-corrected)	−0.04±0.72 [74]	−1.12 [68]	2.50±0.84 [68]

Table 5 (continued)

Parameter	Antibiotic			
	Sulfadiazine	Chlortetracycline	Oxytetracycline	Tylosin
K_D(soil) (L/kg)	0.3 (estimated from $K_D=f_{oc}\times K_{OC}$, $f_{OC}=0.025$; $\log(K_{OC})=0.51\times\log K_{OW}+1.12$)	700 (assumed equal to the soil partition coefficient for oxytetracycline)	Values between 417 and 1026 measured for four Danish soils [73]. Average value=700 used	Values between 8.3 and 62.3 [73]. Average value=52 used.
K_D(manure) (L/kg)	5 (estimated from $K_D=f_{oc}\times K_{OC}$, $f_{OC}=0.42$; $\log(K_{OC})=0.51\cdot\log K_{OW}+1.12$)	5 (estimated from $K_D=f_{oc}\times K_{OC}$, $f_{OC}=0.42$; $\log(K_{OC})=0.51\times\log K_{OW}+1.12$)	81 [74]	240 [74]
$PEC_{Initial}$ (µg/kg)				
Grazing animal	240 (pigs) 528 (cattle)		98 (pigs) 286 (cattle)	115 (pigs) 338 (cattle)
Manure; dosage as injection	0.4-27.4 (pigs) 1.2–79.5 (cattle)		4–23.7 (pigs) 11.6–69 (cattle)	0.06–21.6 (pigs) 0.2–62.8 (cattle)
Manure; dosage as feed administrated	4.7–308 (pigs) 13.5–895 (cattle)	155–921 (pigs)		0.5-182 (pigs)
$PEC_{Steady\text{-}state}$ (µg/kg)				
Manure; dosage as injection	0.5-36.5 (pigs) 1.6–106 (cattle)		12.4–73.4 (pigs) 35.9–214 (cattle)	0.1–39.9 (pigs) 0.4–116 (cattle)
Manure; dosage as feed administrated	6.3–411 (pigs) 18.0–1193 (cattle)	480–2853 (pigs)		0.9–336(pigs)
PNEC (µg/kg)	1 (based on a lowest EC50=0.135 mg/l (algae))	319 (based on a lowest EC50=0.028 mg/l (sludge bacteria))	1179 (based on a lowest EC50=0.14 mg/l (sludge bacteria))	30 (based on a lowest EC50=0.034 mg/l (algae))
GUS	1.4 (non-leacher)	−0.5 (non-leacher)	−0.5 (non-leacher)	0.5 (non-leacher)

4.4.1.2 Ecotoxicological Effects

Existing data from different studies on the effects on different bacteria, soil and water dwelling invertebrates and micro-algae were collected and used to derive a PNEC in accordance with the principles in the technical guidance document [1]. Ecotoxicity data for aqueous solutions was extrapolated to soil ecotoxicity data by assuming that only the dissolved part of the antibiotics contributes to the observed effects.

4.4.1.3 Leaching to Groundwater

In this preliminary assessment, the leachability of the antibiotics is evaluated based on measured soil partition coefficients and calculated GUS indices.

4.4.2 Results and Discussions

4.4.2.1 PEC

The highest PEC is obtained for grazing animals. The PEC in both the manure and receiving soil (Table 5) is higher for antibiotics administered through medicated feed compared to injections [60]. Depending on the drug, the PEC in the soil due to medicated feed ranged from 0.5 to 1000 µg/kg soil, whereas, the PEC in the soil due to injected antibiotics ranged from 0.05 to 70 µg/kg soil. Antibiotic levels in manure have been chemically analysed in a few studies [62, 63]. For example, in one study in Denmark, three different farms were studied on which three different dosages of tetracyclines were used during the period when manure was being stockpiled. For the three dosages of 285, 345 and 6229 g, the resulting manure concentrations were 42, 81 and 698 µg/l and the soil concentrations were 0.6, 1.3 and 14.5 µg/kg soil, respectively [62]. Similar results exist for oxytetracyclin [63].

Very little information is available on the degradation rates of antibiotics when mixed into the soil after tilling and the biodegradation rates presented here should be used with care. Ingerslev recently presented an overview of the biodegradation of antibiotics [64]. Sulfonamides were found to be very degradable, whereas the tetracyclines were found to be extremely persistent. In this study, the estimated steady-state concentration of sulfonamide (sulfadiazine) is only 33% higher than the initial PEC, whereas for the other antibiotics the steady-state PEC is 2–3 times higher than the initial PEC. It should be stressed, however, that the soil partition coefficient used for sulfudiazine has been estimated, and that this value is probably too low.

4.4.2.2 Effect Assessment (PNEC)

Antibiotics are developed to kill or reduce the growth of bacteria. When evaluating the effects of antibiotics on a bacterial community, it is important to be aware of the target organisms of the different antibiotics. Antibiotics may have a broad spectrum of activity or they may be designed to be specifically active against either Gram-negative or Gram-positive bacteria. An indigenous community of bacteria is very complex and heterogenic. Together with the microfauna, they carry out important processes in the cycling of nutrients in the environment. Therefore, the overall impact of antibiotics on the total numbers of microorganisms or on soil respiration may tell very little about the potential risk to specific soil functions. Halling-Sørensen et al. [65] assessed the potency of several antibiotics on both the growth rate of sludge bacteria and the ability of the sludge to nitrify. Results showed that the broad spectrum antibiotics were potent with EC_{50} values in the microgram/l range. As expected, nitrification was inhibited for all Gram-negative acting and broad-spectrum antibiotics. No information was available on any indirect effects in the soil ecosystem due to the alteration in the heterogeneity of the soil microorganisms.

The acute effects of a number of antibiotics on soil macro-organisms, such as collembolla and earthworms, were found in the gm/kg soil level [66, 67]. Studies with microalgae and crustaceans show that antibiotics are especially potent to blue-green algae [68, 69]. All effect data measured in aqueous solutions was extrapolated to the soil conditions by assuming that only the dissolved part contributes to the effects. The PNEC was then estimated from the lowest observed EC50 for the soil divided by an assessment factor of 50. It should be stressed that the estimated PNEC is very sensitive to the soil partition coefficient used, which depends on the soil type. The soil partition coefficient for sulfadiazine was estimated, as no experimental soil partition coefficient was available for sulfadiazine. The estimated PNEC for sulfadiazine is considered to be conservative, as the applied soil partition coefficient is probably too low.

4.4.2.3 Leachability

The most mobile antibiotic is sulfadiazine with an estimated GUS index of 1.4. None of the four antibiotics is considered to be leachers. Tylosin and especially oxytetracycline are highly immobile in soil, with K_D values of more than 100 and 1000 respectively [70] and GUS indices below 1. No correlation between sorption of the test antibacterial agents, and their respective physicochemical characteristics were found. This indicates that the soil partition coefficient for an antibiotic cannot be predicted based on the organic carbon partition coefficient. This is consistent with similar findings in other investigations [71, 72].

4.4.2.4 Risk Assessment

Only ecotoxicological effects on soil organisms and sludge bacteria have been included in the assessments. Thus, resistant bacteria and viruses were not included in the risk assessment, and both may also exhibit a risk in connection with recycled organic waste.

The calculated risk coefficients for all four antibiotics is in the range between 0.03 and 400, so it cannot be excluded that these antibiotics may exhibit a risk to the soil microorganisms. However, it cannot be concluded that these antibiotics exhibit a risk, due to the great uncertainties in the estimated risk quotients. However, it has to be taken into account that the estimated PNEC soil values are highly depended of the distribution coefficients K_D between pore water and soil. The applied K_D value in the model is a rough estimate and gives no indication of the variety between different soil types.

The highest risk quotients are obtained for grazing animals, followed by spreading of manure containing feed-administrated antibiotics. To assess,whether the three antibiotics can cause unacceptable effects on the soil ecosystem, more detailed studies on both fate and effects are required. Also monitoring studies, where the soil functions in the fields receiving antibiotics should be compared with the soil functions in fields not receiving antibiotics, could be relevant. Even though a risk assessment of recycled manure shows that the content of antibiotics may effect the soil ecosystem, is should be taken into account that the recycled of nutrients is an important part of self-sustainable agriculture.

4.4.3 Summary of Findings

This case study outlines the environmental impact of veterinary antibiotics and residues contained in organic wastes. Both the direct emission of pharmaceutical chemicals via urine and faeces, and their inclusion in manure that is spread as a fertilizer, was discussed. In the first case, the exposure route is based on the use pattern of the drug, drug excretion rate, fraction and routes, the lipophilicity of the drug, the number of daily animal defections and animal husbandry practices. In the second case, the exposure route is based on the use pattern of the drug (dose and dosage), physiological parameters of the target animals, existing regulations for manure usage, animal husbandry practices, and on the kinetics in the animal, stored manure and soil. In general, higher soil concentrations occur due to excretion from grazing animals, since some degradation occurs in manure stockpiles before spreading. Some antibiotics are water-soluble and will leach to the groundwater and surface waters. However none of the four antibiotics studied were considered a risk to groundwater and surface water when spread on the field. Sorption and degradation studies determining better kinetics under different redox conditions are urgently needed. Existing substances should be examined because realistic scenarios using re-

alistic degradation kinetics indicate that the PEC in the soil for some antibiotics will exceed 10 µg/kg soil, which in some cases is above the concentration, where effects can be excluded.

5
General Conclusion

In order to evaluate whether the recycling of waste products causes undesirable effects, answers should be given to the following questions with respect to the contaminants in the waste products:

- Will contaminants accumulate in the soil to an unacceptable level? (this question is relevant in case of repeated applications of sewage sludge and manure)
- Will contaminants affect soil-dwelling organisms?
- Could contaminants leach to the groundwater?
- Could contaminants be transported to surface water? And, if so, will they have unacceptable effects on organisms living in the water?
- Will contaminants have unacceptable effects on humans?

Surface water, soil ecosystems, humans and groundwater are thus targets of concern in the assessments of recycled hazardous waste.

Different methods for assessing the risk to the above four targets were illustrated in four case studies. The first example described the modelling of pesticide transport to and within streams after pesticide application to agricultural fields in a catchment area. The second example was based on a case from the construction of the Copenhagen Metro, in which underground material (muck) containing chemical residues was to be used as landfill material. The third case was an example of recycled sludge from a pesticide factory (Cheminova phosphate) applied to agricultural soil. The fourth case described the assessment of recycled manure with focus on its contents of pharmaceutical residues.

5.1
Surface Water

The first case study focussed on the hazard to surface water due to transport of chemicals from soil to surface water. A modelling system for estimating the transport of contaminants from soil to surface water was described. The modelling system requires information of the type of chemicals in the waste material and their approximate concentrations.

5.2
Groundwater

The assessment of the potential risk of leaching was illustrated in the case studies 3 and 4. It was suggested to carry out the assessment stepwise. On a

screening level, the GUS-index was calculated for the substances in question (pesticides and antibiotics and their degradation products). Were found to pose little risk to groundwater (all studied antibiotics and some of the pesticides and their degradation products). For the remaining chemicals, the next step was to use a simple method to calculate the concentration in the percolate at a depth of 10 cm in the soil column. It was concluded that if these concentrations exceeded the limit values, the leaching behaviour of these substances should be studied in more detail using more complex models, e.g. the MACRO model or MIKE SHE. The simulations with the MACRO model showed that none of the studied pesticides or their degradation products were expected to occur in concentrations above the limit value for pesticides in groundwater.

5.3 Soil Ecosystems

Methods for assessing the potential risk to soil ecosystems from waste products were described in case studies 2, 3 and 4. The effects of a complex waste product may be studied at two levels: at a substance and at a product level. The advantage of studying waste products at a substance level is that it is possible to assess both the fate and the effects of single substances whereas it is more complicated to assess the fate of complex products. A disadvantage of studying waste products at a substance level is that not all substances present in the waste product may be identified and potentially hazardous substances may be overlooked. Another disadvantage is that the interaction of the substances in the waste product is not taken into account. A combination of the two approaches is therefore recommended.

The risk quotients were calculated in all three case studies, i.e. the ratio of the predicted concentration (PEC) to the predicted no effect concentration (PNEC).

5.3.1 PNEC

For the chemicals involved in the three case studies, existing data from different studies of the effects on different relevant organisms were collected and used to derive a PNEC in accordance with the principles in the EU Technical Guidance Document. Ecotoxicity data on aqueous solutions were extrapolated to soil ecotoxicity data by assuming that only the dissolved part of the substances contributes to the observed effects. Resistant bacteria and viruses were not included in the risk assessment of antibiotics even though they may constitute a risk in connection with recycled organic waste.

The ecotoxicological effect of the Cheminova phosphate in soil was evaluated by both the above approach and by testing the entire product with three soil-dwelling organisms and deriving a PNEC for the whole product.

5.3.2 PEC

Relatively simple models were used to derive the PECs in the three case studies. In principle, the PEC was calculated from the dosage of the substances in question, the mixing depth and by assuming first-order degradation in the soil. Leaching was considered in case studies 2 and 3 but was observed to be of minor importance with respect to the mass balance of the substances. The dosage of the antibiotics was determined based on the use pattern of the drug, treatment frequency, the physiological characteristics of the target animals, existing regulations for the use of manure, farmers' practices, and the kinetics of the antibiotics in the animals (i.e. pharmacokinetics) and in the stored manure. The dosage of the chemicals in the case studies 2 and 3 were determined by chemical analysis of the waste products and the dosage of the waste products. The model used in the case study 2 was partly validated by column experiments whereas the models used in the other case studies were not validated.

Based on the investigations described in case study 2, the contractor was allowed to deposit the muck on a site in Copenhagen, as long as the contents of the substances of concern in the waste product did not exceed specified concentrations. The contractor was obliged to have muck samples analysed for the most problematic substances during the construction period. In this case, the modelling was used to decide how to handle the potential hazard of using of a waste product as a landfill material.

The two different approaches used to evaluate the ecotoxicological effects of the Cheminova phosphate yielded quite different results. When the components were assessed individually using mainly aquatic ecotoxicity data, the Cheminova phosphate appeared to be persistently toxic to soil organisms. However, when soil organisms were exposed to the Cheminova phosphate, there were no significantly different ecotoxicological effects between the Cheminova phosphate and a reference phosphate fertilizer without heavy metals and organic xenobiotics. Thus, the single substance approach may be valuable for ranking specific substances according to their toxicity but it should be supplemented with tests of the entire complex product for a risk assessment using organisms from the target compartment.

It could not be excluded that the studied antibiotics constitute a risk to the soil-dwelling organisms. On the other hand, it could not be concluded that the antibiotics exhibit a risk, due to the great uncertainties in the estimated risk quotients. In order to assess whether the studied antibiotics may cause unacceptable effects on the soil ecosystem, more detailed studies of both fate and effects are required. Also monitoring studies, in which the soil functions in fields receiving antibiotics are compared with the soil functions in fields not receiving antibiotics, might be relevant. Even though a risk assessment of recycled manure shows that the contents of antibiotics may affect the soil ecosystem, it should be taken into account that the recycling of nutrients is an important part of self-sustainable agriculture.

5.4 Humans

Methods for assessing the potential risk to humans were described in the case studies 2 and 3. One of the objectives of these studies was to identify the main exposure routes. As the area with landfill material from the construction of the Copenhagen Metro (case study 2) is not intended to be used for crops, the daily intake was estimated by considering human exposure via inhalation, dermal contact and ingestion. Exposure via crop intake was considered the most important human exposure route when sludge from a pesticide factory is used in the agriculture (case study 3). The crop uptake and the daily intake (DI) were estimated. In both case studies, the DI was compared with the acceptable daily intake (ADI). For all pesticides (case study 3), the DI was several orders of magnitude lower than the ADI. For all considered chemicals used in the construction of the Copenhagen Metro the soil ecosystem was found to be more sensitive than humans, and the potential risk to humans was therefore not a critical factor.

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Environmental Impacts of Leachate from Portland Cement Concrete (PCC) with and Without Plasticizer in Highway Construction

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Abstract Portland cement concrete (PCC) is widely used in transportation networks. In addition to its use in pavements, PCC is the primary construction material in bridges, tunnels, over passes, under passes, and similar vital structures in our highway systems. Other related applications include grouting, pipe bedding, and soil stabilization. Use of PCC is also associated with the use of a large number of admixtures. The leaching of chemical constituents from PCC and the effect of removal, reduction, and retardation (RRR) processes on these con-

stituents were assessed by a series of laboratory tests and analyses. PCC leachate was subjected to chemical and toxicity testing to identify specific constituents that are responsible for the observed aquatic impacts. PCC leachate without the plasticizer admixture exhibited a low aquatic toxicity for the test organisms *Selenastrum capricornutum* and *Daphnia magna*. PCC-with-plasticizer leachate indicated high growth inhibition (toxicity) for *S. capricornutum*. It is likely that the small amount of plasticizing admixture and significant levels of aluminum in the leachate contributed to the toxicity observed in the PCC leachate. Complete detoxification of PCC leachates by three representative test soils, Woodburn soil (*Mollisol*), Olyic soil (*Ultisol*), and Sagehill soil (*Aridisol*), was observed during soil sorption tests. No significant changes in the algal EC_{50} values by photolysis, but a three fold decrease in toxicity due to biodegradation, were observed for *S. capricornutum* when compared with the control leachate. Results suggest that the observed toxicity in PCC with-plasticizing-admixture leachates is readily reduced or removed only by the environmental processes of soil sorption and biodegradation.

Keywords Portland cement concrete · Highway materials · Leaching · Toxicity · Plasticizer

List of Abbreviations and Symbols

PCC Portland cement concrete
C&R Construction and repair
RRR Removal, reduction, and retardation
EC_{50} Median effective concentration
LC_{50} Median lethal concentration
NTE No toxic effect

1 Introduction

Prediction and management of the impacts of constituents leached from highway construction and repair materials (C&R) on surface and ground waters across the nation poses many challenges. Leachates from such materials can migrate from roadways under operating conditions to the surrounding environments and present a potential source of pollution. The extensive use of highway materials and continued increase in introducing new, non-conventional construction materials require the development of a quantitative basis for planning, design, and selection of construction and repair materials and a means of assessing the environmental impact of their use. The viability and integrity of our system of highways depend 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, wood preservatives, and additives. 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 used in grouting, shotcreting, pipe bedding, and soil stabilization. Portland cement is also associated with transportation infrastructure construction. During the wet seasons, there is a potential for leaching of the chemical constituents in these ma-

terials and the possibility of transport to adjacent surface and subsurface water bodies. Toxic chemicals from these materials could result in adverse environmental 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 potential environmental risks posed by leaching of PCC into surface and ground waters is investigated by conducting a battery of chemical and toxicological tests. Chemical and toxicity evaluations performed on Portland cement and Portland cement concrete leachates in both Portland type I/II cement and Portland type I/II cement concrete, with and without a plasticizer admixture, are presented here. Laboratory tests to evaluate leachate source strength and the effect of removal, reduction, and retardation (RRR) processes included batch and long-term leaching, flat plate leaching, photolysis, biodegradation, and soil sorption. The basic approach was to measure the mass transfer of chemicals under controlled conditions to determine rates that can be applied to specific mathematical models. A comprehensive description of this approach and technical discussion are provided in the literature [1–3]. An algal chronic toxicity test was performed to assess the integrated effects of a variety of chemicals present in the PCC leachates. The measurement of toxicity allows a laboratory to measure quantitatively the direct effects of a leachate on aquatic organisms. Significant research has indicated that laboratory toxicity testing is a useful tool for prediction of the effects in the field if carried out in an appropriate manner. Specific support for the use of toxicity testing and the overall rationale for applying laboratory results to field conditions are reported in the literature [4–11].

2 Portland Cement Concrete as a Hazardous Waste from Highway Construction

Portland cement concrete (PCC) is used as a surfacing in only 6% of all paved public roads. Yet even at this relatively low level of use, more than 800 square miles are covered by PCC. Portland cement is made from a mixture of lime and clay bearing materials that are calcined to form a clinker consisting essentially of hydraulic calcium silicate. Portland cements are composed chiefly of three oxides: silica (SiO_2), lime (CaO), and alumina (Al_2O_3), with small quantities of MgO, SO_3, and Fe_2O_3 also present. Use of Portland cement is also associated with the use of a large number of admixtures. These admixtures improve the concrete properties with respect to workability, durability and strength. A list of common additives include air entraining admixtures to introduce a system of small air bubbles into the fresh concrete during mixing, usually anionic surface-active agents (e.g., organic salts, organic acids, fatty acids and detergents), plasticizers to reduce the water requirement of concrete (e.g., lignosulfates, lignosulfonic acids, sulfonated naphthalene, sulfonated melamine, zinc salts),

and other common admixtures such as strength accelerating agents, coloring agents, fillers (fly ash, bottom ash and furnace slags) and pumping acids [12]. ASTM C150 [13] deals with Portland cement and treats such things as physical and chemical composition, handling, and test methods. ASTM C150 gives specification covering five types of Portland cements, which are intended to cover the principal areas where special properties are needed. Type I is the ordinary Portland cement for use where special properties are not required. Type II is a moderate variation of Type I and is used where somewhat lower heat of hydration is needed. Type III cement is designed for use where high strength is needed because of a particular construction situation. Type IV cement is for use where the heat of hydration must be kept to an absolute minimum. Finally, Type V cement is specified for use where there is extensive exposure to sulfate. Of the five types available, Type I and Type II are the most widely used and are best for the normal situation.

Whether the road surface is unpaved or paved with asphalt or Portland cement concrete, aggregates make up the majority of the paving material. Coarse and fine aggregates constitute roughly two-thirds of a typical PCC mix, 95% of an asphalt mix and nominally 100% of most unpaved roads. In addition to virgin materials, transportation agencies have been actively recycling highway materials such as asphalt and Portland cement concrete for many years. Recently, legislated mandates, increasing disposal fees and conservation efforts have led many agencies to expand their use of solid wastes and by-products. A recent National Cooperative Highway Research Program (NCHRP) synthesis [14] showed that more than two dozen waste materials or by-products have been used in at least three dozen different highway applications (Table 1). The waste materials identified by Collins and Ciesielski [14] can be used in one of three ways. They are used to replace or partially replace aggregates. Reclaimed asphalt and Portland cement concrete pavement are examples of this use. If the

Table 1 State highway usage of waste materials as indicated from questionnaire responses and a review of available literature (after Collins and Ciesielski [14])

Waste material	Number of states using
Reclaimed asphalt pavement	49
Coal fly ash	42
Scrap tires	42
Mining waste	33
Blast-furnace slag	25
Reclaimed concrete pavement	21
Plastic waste	15
Coal bottom ash	15
Steel slag	14
Wood waste	13

resulting waste-modified product can be shown to be equal or superior to the unmodified product at the same or lower cost, then this use may consume a large portion of the waste and by-products produced in the US A second use places smaller quantities of the waste in a product to improve the material properties. For example, the addition of one percent (by mass of mix) finely ground tire rubber to an asphalt binder has been shown to reduce low temperature thermal cracking in asphalt pavements. The addition of a waste material may provide an economic alternative to disposal while reducing the toxicity of the resulting product.

3
Laboratory Methods

3.1
Experimental Approach

Important processes that affect the chemical composition, toxicity, and fate of leachates from C&R materials in highway applications have been evaluated in a series of laboratory tests. The leaching tests provide information on the mobility of constituents in C&R materials under a range of conditions thought to provide reasonable estimates of expected leachate chemical concentrations [15, 16]. The laboratory methods for the RRR experiments are designed to simulate the possible removal/reduction/retardation processes to which a C&R leachate may be exposed in the environment. The soil sorption experiment provides a retardation coefficient, while the photolysis, volatilization, and biodegradation experiments provide decay coefficients of C&R materials in highway environments. Leachate from the short-term (24-h) procedure was evaluated for removal of toxicity and chemical constituents by RRR process tests, including photolysis, volatilization, biodegradation, and soil sorption, where appropriate. No volatilization in PCC-with-plasticizer was expected due to conservation of polymerized plasticizer organic compounds in the leachate. Therefore, we did not perform volatilization tests for both PCC with-and-without-plasticizer leachate.

3.2
Materials

3.2.1
PCC Preparation

PCC was prepared from Tilbury cement with and without plasticizer admixture. A standard 28-day water cure was used prior to testing. Concrete specimens were prepared into standard cylinders in accordance with ASTM C31 [17]. Mixture proportions are shown in Table 2. A high-range water reducer (plasticizer)

Table 2 Concrete mix proportions

Material	Quantity (kg/m^3)
Cement (ASTM Type I/II)[a]	275
Coarse aggregate (washed)[b,c]	1025
Fine aggregate (washed)[b,c]	865
Water	155
Plasticizer (when added)	1000 ml per 100 kg of cement

[a] Cement Manufacturer – Tilbury.
[b] Uncrushe driver gravel from local source, maximum size is 25 mm.
[c] Combined gradation meets ODOT concrete aggregate specification.

was added to some of the prepared specimens. For Portland cement (type I/II) concrete with plasticizer, approximately 2–3% plasticizing admixture was added to a batch of Portland cement concrete. For leaching purposes, the specimens were crushed to ≤1/4 inch nominal maximum size using a jaw crusher after the 28-day water cure. The crusher was thoroughly cleaned to avoid possible cross contamination between specimens. For flat plates, test specimens were prepared by cutting the standard concrete specimens into 4-inch diameter×4-inch cylinders.

3.2.2 Soils

Three soils were selected to determine the effect of soil adsorptive capacity on the reduction of toxicity in leachates prepared from construction and repair materials. The selected soils were:

1. *Mollisol* – the order Mollisol is distributed throughout the Ohio and Upper Mississippi Valley. The Mollisol for this study is of the Woodburn Series and was collected from Benton County, Oregon. The soil is typically described as montmorillonitic that contains moderate quantities of organic matter. It may be slightly acidic to moderately alkaline.
2. *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.
3. *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.

3.3 Testing Methods

3.3.1 Batch Leaching

The batch leaching test is preformed on solids crushed and sieved to ≤1/4 inch, extracted by distilled water (1:4 solid:liquid mass ratio) in a sealed 2-l polycarbonate bottle, tumbled at room temperature, and filtered to remove solids. The short-term batch leaching test lasts for 24 h, while the long-term batch leaching test continues until the solution concentrations (as measured chemically) reached a plateau (up to several days). Samples may be taken during the batch leaching test in order to quantify leaching kinetics. Chemical and toxicological analyses of the leachate during the batch leaching process provide the chemical composition and toxicity data needed for initial evaluation of the test material (detailed procedures for these tests are described in [18].

3.3.2 Flat Plate Leaching

The flat plate tests determine the leaching rates from a defined surface where mass transfer across solid/liquid boundary controls the leaching or flux rate (expressed in mg/cm^2 h). The flat plate test 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 placed in the bottom of a glass container containing distilled water. The material is leached into the water phase, which is mixing 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 a material surface, such as a highway surface.

The PCC flat plates and controls are produced in duplicate, at a minimum. In these tests, the PCC plates (78.5 cm^2 of flat surface, 6.25 cm deep) was placed in the bottom of a beaker and the beaker. The test cylinder, sealed such that the top flat surface is exposed, is immersed in a 2-l glass beaker containing 1 l distilled water and mixed above the flat plate with a paddle stirrer. The flux of contaminants (mg/cm^2 h) then was determined by the increase of concentration in the overlying water as a function of time. The test continues for ten days with samples taken at one, three, five, seven, and ten days to determine leaching kinetics and flux rates for compounds of interest. The flux of contaminants (mg/cm^2 h) is determined by the increase of concentration in the overlying water as a function of time. The toxicological and chemical analyses to be performed on the flat plate samples should be decided upon before the start of the experiment so that adequate sample volumes are produced. The analyses chosen should be based on the results of the screening experiments.

3.3.3 Soil Sorption

The solution used in the isotherms is prepared by a 24-h batch leaching experiment with the solid test material and distilled water; this leachate, before it is used in the soil sorption experiment, is the material control. The PCC-with- and without-plasticizer were leached for 24 h, filtered through a 0.45-μm filter, and added to Olyic, Woodburn, and Sagehill soils. Chemical analysis of the material control solution will reveal the initial concentrations of the constituents in the leachate, C_0. A soil control is also prepared for each of the test soils by conducting a 24-h batch leaching experiment with the soils and distilled water. The soil control samples are used to determine the concentrations of the constituents eluted from the soil alone. The ratio of soil to leachate concentration is selected to evaluate the capability of environmental soils to adsorb available contaminants at equilibrium. The soil particles must be fully dispersed within the aqueous phase to achieve complete adsorption. Typical soil/leachate mass/volume ratios are 50 g l^{-1}, 100 g l^{-1}, 150 g l^{-1}, 200 g l^{-1}, and 250 g l^{-1} [19].

3.3.4 Photolysis

Photolysis is induced by exposing a test material leachate to "solar radiation" from a Xenon-arc lamp. Through photolysis, light can affect the chemical composition and toxicity of organic compounds. This study exposes the leachate to a Xenon arc lamp to mimic solar radiation at about 30 Watts/m^2 in a 20 °C constant temperature room. This light intensity is about one tenth the intensity of ambient sunlight. For the photolysis test, leachate aliquots from the 24 h batch leaching test were placed in 2-l Pyrex brand borosilicate glass bottles with stoppers and exposed to the Xenon arc lamp light. An initial sub-sample of the leachate is removed (time=0) followed by additional sub-sampling with time to determine the photolysis degradation rate.

3.3.5 Biodegradation

For the biodegradation test, leachate aliquots from the 24-h batch leaching test were placed in 2-l Pyrex beakers, inoculated with fresh primary settled sewage and a nutrient feed solution, and incubated under aeration in the dark. Samples were taken daily over the ten-day test for chemical and toxicity analyses.

3.3.6 Toxicity

Toxicity testing involves the use of standard test organisms in laboratory exposures to samples or solutions leached from PCC materials. Then 96-h *Selenas-*

trum capricornutum algal chronic toxicity tests [20] and 48-h *Daphnia magna* (water flea) acute mortality tests [21] were performed on solutions generated from leaching tests (leachates) and on leachates subjected to RRR tests. A definitive test is conducted to determine the concentration (percent of full-strength leachate) 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* relative to a control. Lower EC_{50} and LC_{50} values indicate greater toxicity, because the material is toxic even at low concentrations (high dilutions).

4
Results and Discussion

4.1
Batch Leaching

Chemical characterization of 24-h batch leachates from PCC both with and without plasticizer indicated metals concentrations of about 2–5 mg l^{-1} of aluminum, 700 mg l^{-1} of calcium (Figs. 1 and 2) and TOC concentrations of about 10 mg $l^{-1}$and 18 mg l^{-1} for the PCC-with-and without-plasticizer, respectively (Figs. 3 and 4). Leachates were generated following the standard highway materials leaching procedures of this study documented in [18] and briefly described above. PCC leachate was generated for source strength evaluation by the short-term batch, long-term batch, and flat-plate procedures.

Long-term batch leaching tests based on total organic carbon (TOC) concentration indicated that the PCC-with-and without-plasticizer leaching rates was highest initially and decreased exponentially over time (Figs. 3 and 4, re-

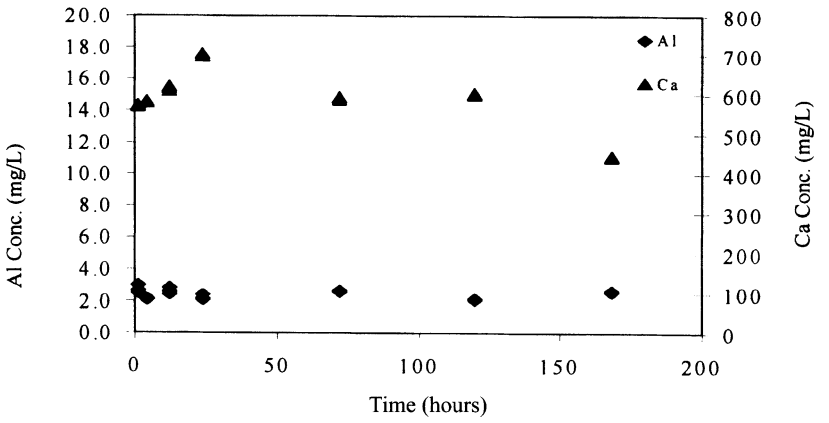


Fig. 1 PCC-without-plasticizer long-term batch leaching experiment (calcium and aluminum concentrations as a function of time)

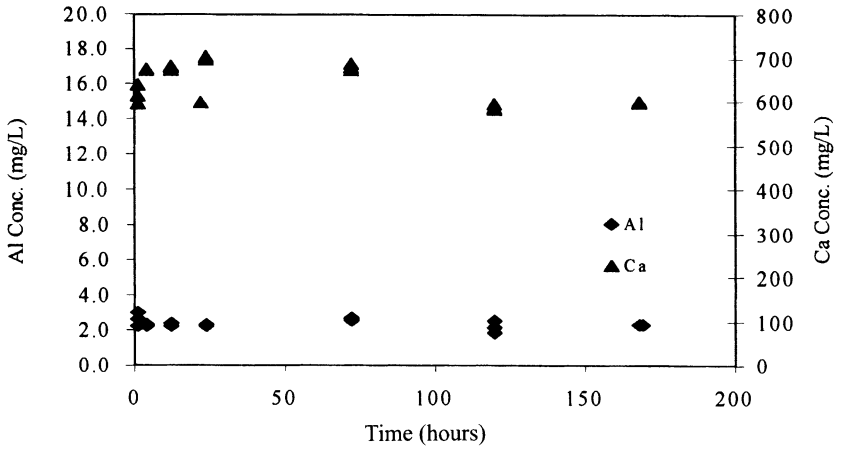


Fig. 2 PCC-with-plasticizer long-term batch leaching experiment (calcium and aluminum concentrations as a function of time)

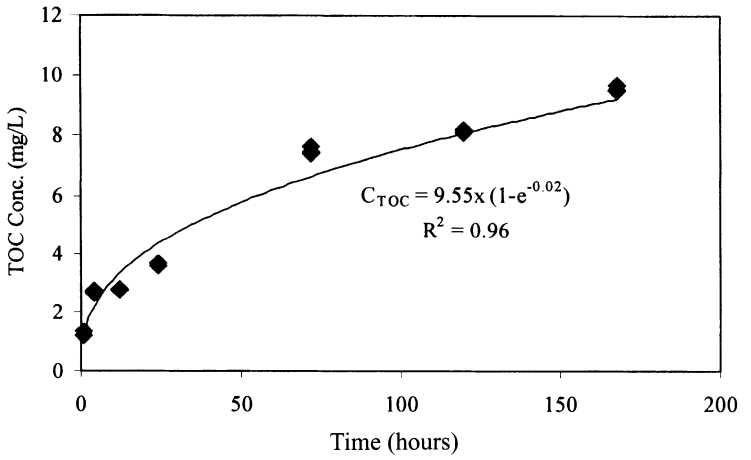


Fig. 3 PCC-without-plasticizer batch leaching experiment (TOC concentration as a function of time)

spectively). Conversely, TOC concentrations for both PCC-with-and without-plasticizer continually increased but at a decreasing rate with time. The TOC in batch leaching experiments for PCC without and with plasticizer were modeled as:

PCC-without-plasticizer	$C_{TOC}=9.55\times(1-e^{-0.02t})$	$R^2=0.96$
PCC-with-plasticizer	$C_{TOC}=6.70\times(1-e^{-0.05t})$	$R^2=0.96$

where C is concentration in mg l^{-1}, t is time in hours. Comparisons of PCC leachates show that for metals (Ca and Al) the results are the same for PCC leachates

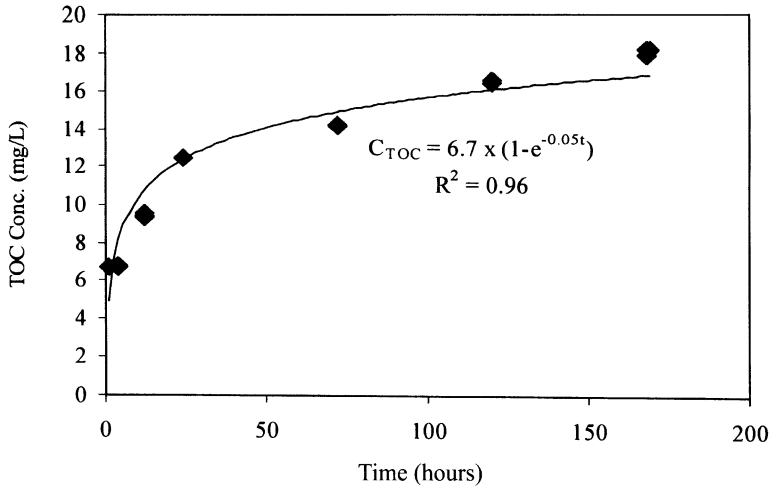


Fig. 4 PCC-with-plasticizer batch leaching experiment, TOC concentration as a function of time (triplicate experiments)

without and with plasticizer (Figs. 1 and 2, respectively), while TOC results show higher values for PCC with-plasticizer leachates than those without plasticizer (Figs. 3 and 4, respectively). The calcium concentration initially was about 600 mg l^{-1} and decreased with time to about 400 mg l^{-1} (Figs. 1 and 2), most likely due to precipitation at the high leachate pH values near 12.0. Aluminum concentration was about 2 mg l^{-1} after seven days of leaching time (Figs. 1 and 2). Leaching rates during the 24-h short-term test probably represent well the case of first-flush chemical releases from new construction materials; typical leaching rates of weathered materials probably are best described by the slower loss rates observed after several days of leaching.

Algal EC_{50} values were observed to be ~14% and ~44% for PCC with and without plasticizer, respectively (Fig. 5). Conventional approaches to identify toxicants using analytical methods often limit their search to "priority pollutants" that are only a fraction of all the existing chemicals. Even if all the chemicals are identified, trying to pinpoint the cause for toxicity in such complex mixtures is likely to fail because this approach does not include matrix effects, and toxicant bioavailability. PCC leachates with only aluminum and calcium at significant levels pose a similar question regarding the cause for observed growth inhibitory effects in algae. To find an answer to this question, it is important to understand the various mechanisms by which aluminum and calcium can cause growth inhibitory effects in algae. Other investigators [22, 23] have reported the removal of phosphorus by aluminum in water. Cooke et al. [24] have shown the use of dissolved aluminum (as alum) to precipitate phosphate and particles in treatment of lakes, further indicating the phosphorus removal capacity of aluminum in water. According to Kong and Chen [25], aluminum can also affect the enzyme (acid phosphatase) production in *S. capricornutum*

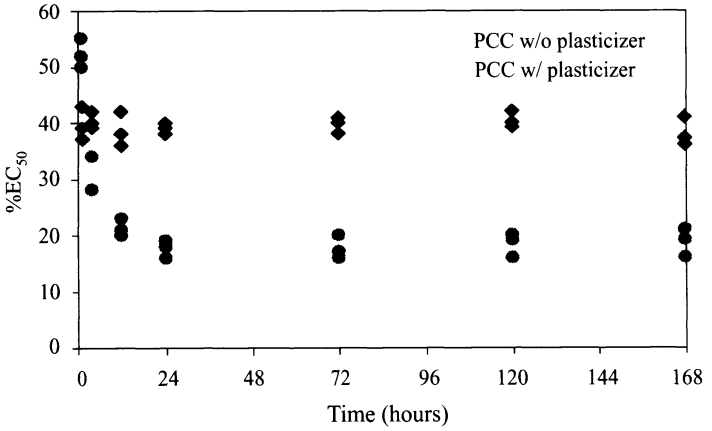


Fig. 5 Algal $\%EC_{50}$ values for PCC leachates with and without plasticizer as a function of batch leaching time (triplicate experiments)

algae. Acid phosphatase is an important enzyme that significantly contributes to phosphate availability in algal cells. Additional tests (not reported here) determined an aluminum EC_{50} value of about 0.6 mg l^{-1} for *S. capricornutum* [26]. Based on the studies cited above, the primary mechanism that causes growth inhibition in algae from PCC leachates appears to be limitation of phosphorus, an essential nutrient for the growth of algal cells.

4.2 Flat Plate Leaching

Flat plate leaching tests were used to determine the rate of leaching of contaminants from a material surface. Results for calcium and TOC in leachate from the PCC without and with plasticizer in the flat plate experiments are shown in Figs. 6 and 7, respectively. The equations for power function increase of calcium and aluminum concentrations (determined by linear regression) are given as:

Calcium: PCC-without-plasticizer	$C_{Ca} = 4.2t^{0.32}$	($R^2 = 0.94$)
Aluminum: PCC-without-plasticizer	$C_{Al} = 4.27t^{-0.55}$	($R^2 = 0.41$)
Calcium: PCC-with-plasticizer	$C_{Ca} = 5.83t^{0.26}$	($R^2 = 0.93$)
Aluminum: PCC-with-plasticizer	$C_{Al} = 10.95t^{-0.19}$	($R^2 = 0.19$)

For example, at a time of 1 h, for a volume of 1 l and surface area of 78.5 cm^2, the release rate, dC/dt, is 1.34 mg l^{-1} h^{-1}, and the resulting flux is $F=1.91\times10^{-1}$ mg cm^{-2} h^{-1} for calcium. Aluminum concentration in the flat plate leachate was about 2 mg l^{-1} after 24 h, subsequently decreasing with time as pH decreased over the ten-day test period (Fig. 7).

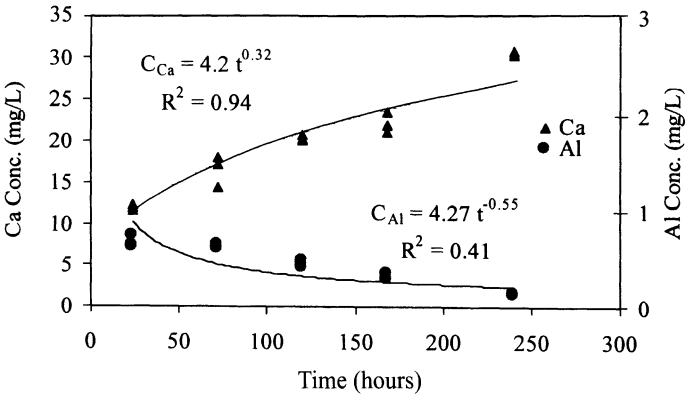


Fig. 6 Flat plate leaching results for PCC-without-plasticizer (calcium and aluminum concentrations as a function of time)

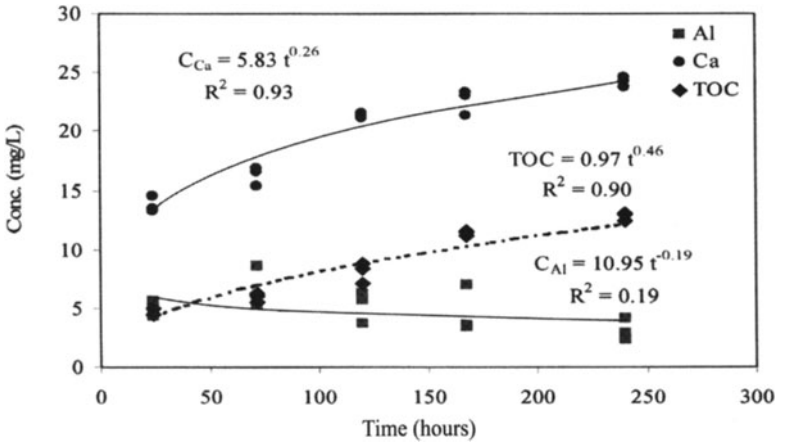


Fig. 7 Flat plate leaching results for PCC-with-plasticizer (calcium, aluminum, and TOC concentrations as a function of time)

Results for PCC-without-plasticizer indicated no detectable toxicity for *S. capricornutum* in the flat plate leachates collected from day 1 through day 10. The flat plate leachates from PCC-with-plasticizer exhibited moderate algal toxicity after one day (EC_{50} value of 31%) that increased slightly up to day 10 (EC_{50} value of 27%; Fig. 8). In the flat plate leachates aluminum concentrations were the same for both PCC-with- and without-plasticizer, but the TOC concentration was slightly high for the PCC-with-plasticizer. It is likely that small amounts of plasticizing contributed to the moderate algal toxicity of the PCC-with-plasticizer in the flat plate leachates.

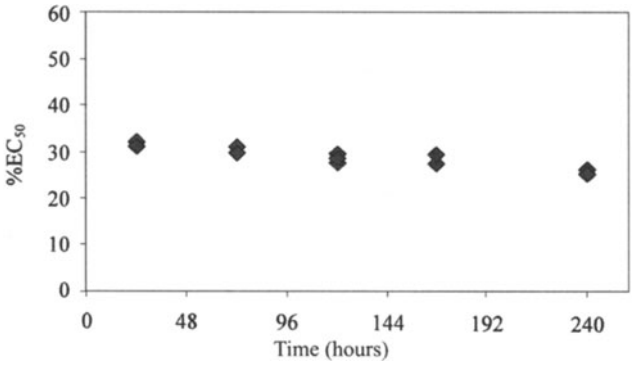


Fig. 8 Algal toxicity of PCC-with-plasticizer leachates as a function of leaching time in flat plate experiment

4.3 PCC Soil Sorption

Soil sorption of leachate from PCC with and without plasticizer was studied by preparing 250 g l^{-1} of soil:leachate mixture. For Portland Cement (Tilbury, Type I/II), 96-h *S. capricornutum* chronic toxicity test and 48-h *D. magna* acute toxicity test results are illustrated in Table 3. Standard 24-h PCC-without-plasticizer leachate (control) exhibited a low toxicity for *S. capricornutum* (43% growth inhibition in 80% leachate) and *D. magna* (37% mortality in 100% leachate). Detoxification of PCC leachates due to soil sorption was evaluated using 250 g l^{-1} Woodburn, Olyic, and Sagehill soils (Table 3). Toxic constituents were not present after soil sorption in concentrations that would give EC_{50} or LC_{50} values in the definitive toxicity tests. PCC-with-plasticizer leachates

Table 3 Toxicity results for PCC leachate without plasticizer for soil sorption test

Sample	*S. capricornutum* $\%EC_{50}$	*D. magna* $\%LC_{50}$
24-h leachate	43% growth inhibition in 80% leachate	37% mortality in 100% leachate
Olyic Soil 250 g l^{-1}	NTE[a]	NTE
Woodburn soil 250 g l^{-1}	NTE	NTE
Sagehill soil 250 g l^{-1}	NTE	NTE

[a] NTE – Nontoxic effect.

Table 4 Toxicity results for PCC leachate with plasticizer for soil sorption tests

Sample	*S. capricornutum* $\%EC_{50}$	*D. magna* $\%LC_{50}$
24-h leachate	10	42
Olyic soil 250 g l^{-1}	NTE[a]	NTE
Woodburn soil 250 g l^{-1}	NTE	NTE
Sagehill Soil 250 g l^{-1}	NTE	NTE

[a] NTE – Nontoxic effect.

exhibited high toxicity for *S. capricornutum* (EC_{50} value of 10%) and moderate toxicity for *D. magna* (LC_{50} value of 42%). It is likely that small amounts of plasticizing admixture and aluminum contributed to the high toxicity of the PCC leachates, possibly by additive effect. Complete detoxification of PCC-with-plasticizer leachates by all three soils was observed as leachates exhibited no toxic effect for both test organisms after leachate sorption in 250 g l^{-1} soil solutions (Table 4). All three soil types demonstrated the ability to adsorb metal ions and organic compounds and reduce toxicity in algal and daphnia tests.

4.4 PCC Degradation

4.4.1 Biodegradation

Biodegradation testing of PCC-with and without-plasticizer leachate was conducted in the laboratory using 24-h batch leaching solutions and following the method as described in the experimental approach section. PCC-without-plasticizer inhibited algal population growth by only 43% in a solution. For PCC-with-plasticizer the EC_{50} value for the control leachate (24-h batch leachate, 0-h degradation) was 13% while the EC_{50} value after the biodegradation test was 41% for *S. capricornutum*. For PCC-with-plasticizer a threefold decrease in toxicity for *S. capricornutum* due to biodegradation was observed when compared with the control leachate. Results suggested that the toxic organics in the leachates due to plasticizing admixture could easily be reduced and removed biodegradation.

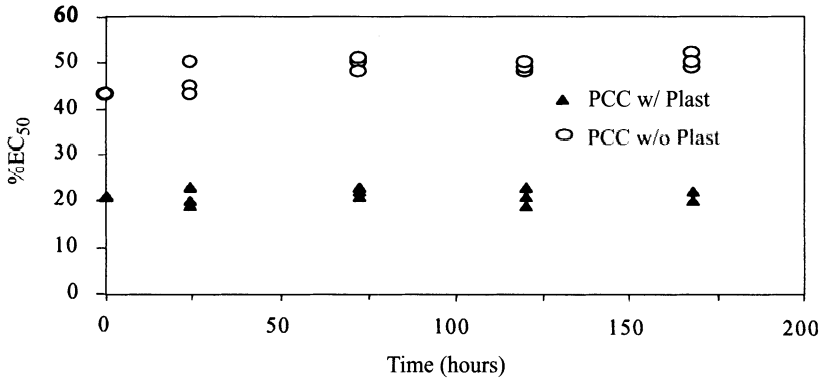


Fig. 9 Algal toxicity of PCC-with-plasticizer leachates as a function of leaching time in photolysis experiment

4.4.2 Photolysis

Photolysis experiments were performed to investigate the reduction in toxicity of PCC leachates. The EC_{50} values for the control leachates (24-h batch leachate, 0-h photolysis) for PCC-with-plasticizer and PCC-without-plasticizer leachates were 21% and 43%, respectively. After photolysis, day 1 and day 10 PCC-with-plasticizer leachates exhibited EC_{50} values of 20% and 21% respectively. Similarly, day 1 and day 10 PCC-without-plasticizer leachates exhibited EC_{50} values of 46% and 50% after photolysis (Fig. 9). It is evident that there was no significant change in the algal EC_{50} values by photolysis for both PCC with- and without plasticizer leachates. Correspondingly, chemical analyses also indicated no detectable change in the metal and TOC concentrations of the leachates during the photolysis of both the leachates.

5 Summary and Conclusions

Both PCC-with and without-plasticizer leachates showed high levels of calcium (~700 mg l^{-1}) and significant levels of aluminum (2–5 mg l^{-1}). PCC-with-plasticizer had slightly higher level of TOC compared with PCC-without-plasticizer. Algal growth inhibitory effects by PCC leachates were attributed to phosphorus limitation and co-precipitation due to high levels of calcium and aluminum at alkaline pH. The higher inhibitory effect exhibited by PCC-with-plasticizer leachate compared with PCC-without-plasticizer could be due to the additive effect of plasticizer along with calcium and aluminum nutrient inhibition. Complete detoxification of PCC with and without plasticizer leachates by Woodburn, Olic, and Sagehill soils was observed, as leachates exhibited no toxic

effect for both tested organisms. Biodegradation reduced toxicity of the leachate due to removal of toxic organic plasticizer. Photolysis was not effective in reducing the toxicity of PCC with- and without plasticizer leachates for *Selenastrum capricornutum* and *Daphnia magna*, as the EC_{50} and LC_{50} value were almost the same as the control leachates. In conclusion, although leachates from both PCC materials contain Al and Ca at levels likely to cause algal growth inhibition, once leached into the soil significantly reduce the bioavailability and subsequent toxicity of these contaminants. These results indicate that the use of PCC and PCC with plasticizers should not be of concern regarding aquatic toxicity.

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Environmental Impact Assessment of Lignite Fly Ash and Its Utilization Products as Recycled Hazardous Wastes on Surface and Ground Water Quality

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Abstract Combustion residues, such as alkaline lignite fly ashes, are produced worldwide in ever-increasing quantities. Combustion residues, however, may pollute the environment because they are enriched in potentially toxic elements relative to soils and sediments. For a proper assessment of the environmental impact of the utilisation and disposal of the ash it is necessary to understand the effect of the mobilisation of potentially hazardous elements from ash residues. Trace metals, though present as a relatively small fraction in fly ash, are of special interest, due to their cumulative build up, long life, and high toxicity to man, plants, and animals. Since trace elements existing in fly ash can leach out and contaminate soil as well as surface and groundwater resources, their study has recently been regarded as important in connection with the protection of the environment.

The management of fly ash produced by coal fired power plants remains a major problem in many parts of the world. Although significant quantities are being used in a range of applications and particularly as a substitute for cement in concrete, large amounts are not used which requires disposal. Those quantities are disposed sometimes on unlined landfills. The original ash contains certain amounts of toxic elements and heavy metals. Such material, if inadequately deposited, can produce surface and ground water leachate pollution.

Uses of fly ash have included the manufacture of lightweight aggregate, road base construction, landfill liners, sewage sludge treatment, as a filler in plastic composite materials, as well as the manufacture of Portland cement, etc. The use of fly ash in the ceramics industry and particularly as a component in the manufacture of bricks and tiles has also been investigated. This industry uses large volumes of silicate-based raw materials and therefore has the potential to utilize significant amounts of fly ash. Research is therefore needed to develop new alternative applications that can further exploit fly ash, which needs to be increasingly regarded as a raw material with a potential for processing into new products rather than a waste.

Samples of lignite fly ash from the thermal power plant "Nikola Tesla" (Serbia) were investigated in the Case Study. Sintering, as a method of fly ash recycling, reduces leaching concentrations of elements. Special attention was paid to the determination of leaching properties by the Generalized Acid Neutralizing Capacity Procedure (GANC). Results of the analysis emphasise that the fly ash samples sintered at different temperatures have much lower leaching concentrations than the raw fly ash samples.

Keywords Water quality · Ash · Impact assessment

List of Abbreviations

AAS	Atomic absorption spectroscopy
ASTM	American Society for Testing and Materials
EDTA	Ethylene diamine tetraacetic acid
EPA	Environmental Protection Agency
GANC	Generalized acid neutralizing capacity procedure
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
JUS	Yugoslav standard
PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
XRD	X-ray diffraction

1 Introduction

The management of lignite fly ash, including deposition, utilization and, eventually, remediation of directly or indirectly polluted segments of the environment is a major problem for many countries. Although significant efforts are made to utilize fly ash, e.g. as a substitute for cement in concrete, large amounts, unfortunately, still require disposal. The disposal sites are often exposed to weathering and, since fly ash contains certain amounts of toxic trace elements, these elements may enter surface and ground waters and cause serious, and often, long-lasting, pollution. The study of ash-originating trace elements (though they are present in small amounts in fly ash), due to their long life, high toxicity to man, plants, and animals, is becoming more and more important from the environmental point of view, not only because of the increasing amounts of lignite burned, but, especially, because of increasing need for potable water, the resources of which are more and more threatened by pollution. This pollution does not occur only directly, by intrusion of water that had leached fly ash on dumps or its utilization products, but also by airborne ash particles, settling down over various segments of the environment, and also, by remobilisation (due to changes of physico-chemical conditions in the polluted aquifer, soil, sediment etc.) of trace elements that have already polluted the environment in some of the ways named above.

Although, as already said, utilization products (cement, bricks, tiles) may also release trace elements, this is by far less a danger for the environment, hence, research is needed to develop more applications of fly ash, since this material must not be regarded as waste anymore, but as an important raw material.

2
Raw Lignite Fly Ash as a Hazardous Waste

2.1
Generation

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. It is removed by dust collection system as a fine particulate residue from the combustion gases before they are discharged into the atmosphere. By definition, fly ash is a fine powder of mainly spherical, glassy particles having pozzolanic properties and consisting essentially of SiO_2 and Al_2O_3.

2.2
Characterization

According to ASTM C 618, fly ash can be divided into two classes:

- Class F, normally produced from bituminous coals
- Class C, normally produced from lignite or subbituminous coals.

The Class C ashes differ from the Class F materials principally in often having a capacity for self-hardening in the absence of cement. The most notable chemical difference between these two classes of ash is that the Class C ashes contain high levels of calcium that has led to the use of an alternative and in some ways preferable terminology: high-calcium and low-calcium ash for Classes C and F, respectively.

2.2.1
Grain Size Distribution

Fly ash particles are typically spherical, ranging in diameter from 10 to 200 μm, the majority being between 20 and 60 μm. The range of particle sizes in any given fly ash is largely determined by the type of dust collection equipment used.

2.2.2
Chemical Composition

The chemical composition of fly ash is determined by the types and relative amounts of incombustible matter in the coal used. More than 85% of most fly ashes comprise chemical compounds and glasses formed from the elements silicon, aluminium, iron, calcium and magnesium. Generally, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal. Unburned coal collects with the fly ash as carbon

particles, the amount being determined by such factors as the rate of combustion, air/fuel ratio, and degree of pulverization of the coal. In general, fly ash from subbituminous coals contains very little unburned carbon. Plants that operate only intermittently (peak load stations), burning bituminous coals, produce the largest percentage of unburned carbon [1, 2].

Chemical composition of fly ash depends, amongst other factors, on the coal type from which it is produced. Chemical composition of Class F fly ash is listed in Table 1 [3].

Class F fly ash contains large quantity of silica (SiO_2), alumina (Al_2O_3), and ferric oxide (Fe_2O_3), and small quantities of various other oxides and alkalis. Carbon content is dependent upon efficiency of a particular boiler unit and the fineness to which coal is pulverized.

Table 1 Chemical composition of fly ash, %

	Range	Average
SiO_2	31.1–60.8	51.3
Al_2O_3	11.9–35.6	27.7
Fe_2O_3	3.8–37.5	8.2
CaO	0.8–9.6	3.0
MgO	0.1–1.9	1.0
Na_2O	0.1–0.6	0.3
K_2O	0.3–2.7	1.1
SO_3	0.1–1.8	0.4
Loss on ignition	1.1–26.5	6.5

Table 2 Bulk chemical composition data for typical fly ashes from various origins

Fly ash sample origin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Free CaO	LOI[a]
UK	50.09	28.10	11.70	1.62	1.54	0.28	0.62			1.27
USA	52.24	19.01	15.71	4.48	0.89	0.82	2.05	1.34		0.92
Netherlands	50.46	25.74	6.53	4.32	2.24	2.04	4.43			3.95
Japan	57.50	26.10	4.00	5.10	1.30	1.50	1.35	0.40		1.60
Taiwan	48.75	23.21	4.15	3.93	1.00	0.24	1.10			10.39
Poland	50.80	23.90	8.60	3.60	2.80	0.80	2.90	0.80		2.90
Saudi Arabia	52.30	25.20	4.60	10.00	2.20			0.60		0.40
Spain	49.80	17.30	8.70	24.90	1.90	0.30	1.70	4.30	11.40	2.30
Greece	26.00	10.60	6.59	42.10	1.48	0.17	0.80	5.57	10.00	4.55
Turkey	27.40	12.80	5.50	47.00	2.50	0.20	0.20	6.20	18.60	2.40

[a] Loss on ignition. Values are in percentages.

Typical chemical composition of class C fly ash is around: 40% SiO_2, 15% Al_2O_3, 5% Fe_2O_3, 25% CaO, 5% MgO, 3–20% SO_3. Due to higher contents of CaO and SO_3, class C fly ash is rich in calcium trialuminate, and calcium sulfoaluminate. In addition, class C is higher in fineness and richer in sphere content. Therefore class C fly ash is not only higher in pozzolanicity but also demonstrates cementitious properties.

Fly ash is rich in sulphur, calcium, strontium, boron, molybdenum and selenium, generally. Fly ash leachate is alkaline, and contains high quantities of soluble salts. Table 2 presents data obtained for other fly ash samples from various countries.

2.2.3 Physico-Chemical Properties and SEM Micrographs

Important physico-chemical properties for various purposes of utilization and landfilling are specific gravity (important for the problems of homogenous mixing with other substances), bulk density (landfilling or silo-design), sieve residue (larger particles are undesirable because of unburnt carbon content; pozzolanic activity; grain size distribution important for utilization in cement or concrete), specific surface area (important for compacting or utilization in cement or concrete) and the water demand for standard consistency (important for utilization in cement or concrete). Physico-chemical properties of Class F fly ash are listed in Table 3, while SEM micrograph of the fly ash are shown in Fig. 1.

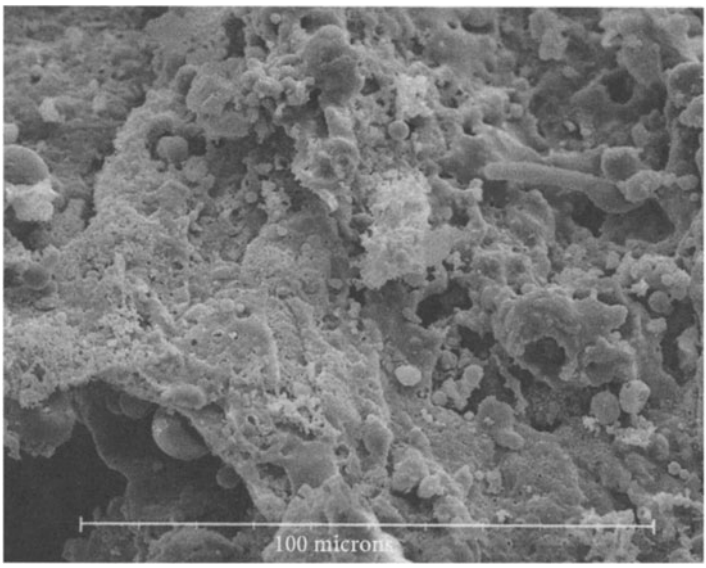


Fig. 1 SEM micrograph of the fly ash

Table 3 Physico-chemical properties of fly ash

	Range	Average
Specific gravity	1.92–2.85	2.13
Bulk density, kg m^{-3}	531–1261	780
Sieve residue, 45 μm, %	13.4–97.3	59.8
Sieve residue, 90 μm, %	0.6–77.8	22.2
Specific surface area, $m^2 kg^{-1}$	118–651	330
Water demand for standard consistency, %	27.3–66.7	48

2.2.4 Pozzolanic Activity

Main parameters which are of interest for using fly ash as a pozzolanic material are: loss on ignition, sulphates, fineness, water demand, pozzolanic activity and moisture content on delivery.

Fly ash exhibits pozzolanic activity. A pozzolana is defined as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. Fly ashes contain meta-stable alumino-silicates that will react with calcium ions, in the presence of moisture, to form calcium silicate hydrates.

2.2.5 Mineralogical Composition (XRD)

Chemical and mineralogical content of fly ash depends on the coal types, its genesis, burning regime and the type of tail. Typical glass contents of fly ash ranges from 50% to 80%. The usual primary crystal structures are around following values: quartz 10%, mullite 2%, magnetite 3% and hematite 1%. Felspar could also be present, so as the sodium hydroaluminosilicates.

The glassy phase is very important because it is the portion of ash which makes it pozzolanic. Quartz crystals makes fly ash a very abrasive material, which is very important for the transport to the landfill. X-ray data of typical fly ash are presented in Fig. 2 [4].

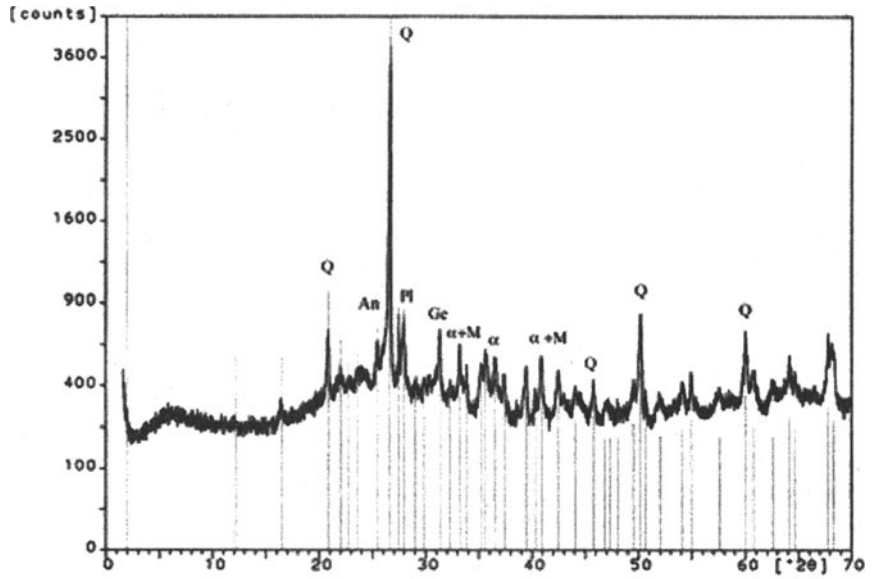


Fig. 2 X-ray data of typical fly ash

2.3 Disposal

2.3.1 Landfill

Large thermal power plants, especially those using lignite, produce huge amounts of fly ash (300–500 g kW^{-1} h^{-1}), which is often disposed of by landfilling. Ever-increasing demand for power increases the production of fly ash and related problems. Fly ash occupies precious land space and cause permanent environmental pollution, with pollution levels depending on the maintenance of the landfill. Whenever fly ash is deposited on the land, some of its toxic substances and heavy metals are subject to leaching as water passing through the landfill carries these materials into aquifers or surface streams. These leaching contaminants may pollute surface as well as ground waters and endanger public health [5].

To avoid landfilling, fly ash is being used in cement, lightweight aggregate and concrete production. Numerous researchers explore the role of fly ash in pastes, mortars and concrete, in order to improve fly ash characteristics and enhance its use. A potential use of fly ash as liner for waste contaminant is being explored as well. However, in some developing countries only a tiny portion of the excessive yearly production of fly ash is being re-used and the majority has to be disposed of and stored, usually in landfills. Various engineering and environmental problems have to be solved during the operation of fly ash landfill, e.g. use of geo-

textiles as filters in decanting wells, the long-term filtration behaviour of geotextiles with fly ash, and the leaching behaviour from fly ash landfills.

2.3.2
Environmental Impact Assessment

Atmospheric emission and land disposal of fly ash subject the material to leaching by atmospheric moisture and by water used to transport the ash or to irrigate fly ash amended soils and vegetation establishments on fly ash deposits. The composition of aqueous fly ash systems is helpful in determining the potential contamination of ground and surface waters with fly ash leachate. Low solubility of a number of trace elements is expected on the basis of the high alkalinity of the ash extracts. An increase in extractability is noticed for all elements as the acidity of the extract is increased. Literature [6, 7] indicated that elements capable of forming anionic species, such as boron, chromium and vanadium, remain relatively soluble in an alkaline environment while the more metallic cations would be precipitated.

Ground and surface water quality monitoring around landfill site boundaries must be undertaken on at least a quarterly basis for a range of potential contaminants arising from unplanned leachate. The range of parameters to be monitored and the required frequency of monitoring may be site-specific, as related to the sensitivity of the potential water as receptor, and as related to the former uses and possible contamination in the area, and finally to the state of the landfilled waste over time. Leachate contaminant concentrations will vary over time as reflecting the age and degree of waste reactivity, microbial behaviour and pH of the landfill environment. Although it is important that analyses are formulated, as required under landfill guidance. Where any elevated (10% variation) contaminant concentrations are observed between up-flow and down-gradient samples then additional actions will be required to assess both the cause and the potential adverse impacts. Additional borehole sampling points may be necessary as a first step in evaluation of the extent of external environmental impacts.

3
Mechanisms of Leaching Processes from Fly Ash and Their Products

3.1
Release Mechanisms from Recycled Wastes

3.1.1
Leaching Studies – an Overview

It is generally accepted that ash obtained by coal combustion is jeopardizing surrounding surface and ground waters due to the release of different, potentially, toxic trace and major elements during and after its transport to the dump.

Further on, leached elements are entering soils and sediments and through biosphere can enter food-chain [8]. In order to estimate possible detrimental influence on the environment, to find out the facts about the constitution of the ash, different leaching studies are being performed [9]. These studies have also been driven by need to find a more economic alternative to the storage or disposal of the fly ash in landfill systems, and to estimate potential pollution by different ash products. With this intention, regulatory agencies and technical institutions have developed standard laboratory extraction procedures to simulate natural leaching conditions [10] in the absence of field data on leachate.

There are lot of different approaches to the problem of leaching experiments of coal ash. Some authors are applying modified sequential extraction procedure that is used for evaluation and speciation of elements to the different portions of sediment and soil samples [11–14]. It should be pointed out that coal ash is structurally different from soil and sediment samples, because it doesn't contain (in most cases) carbonates and sulfides that are present in the soils and sediment samples, but it does contain elements adsorbed to the material that are present in minor amounts in sediments and soils. That is the reason why extraction that is merely coping standard soil and sediment extraction procedure [15, 16], without previous investigation of ash composition, is giving result with limited value. However, modified procedures of sequential extraction that are changed in order to answer to the needs of investigation of ash, are very often used with significant conclusions drawn [17]. These experiments are not only yielding concentrations of certain elements in certain phases, but can also tell us a lot about different associations of trace and major elements [18]. Also, leaching experiments between carefully chosen sets of samples of ash can estimate the amount of trace and major elements that are washed during ash transport (if extraction results of filter ash, and filter ash previously extracted with river water used for transport are compared) [19], or estimate long-term pollution potential and retention capacity of ash dumps [20].

The other approach is to create some sort of leaching test, bulk or column, that is imitating natural conditions, or yielding the results that can either be related to behaviour of ash in the environment, or that can give the results about the composition of the ash. Waste characterization techniques must be scientifically valid, comprehensive, and thorough. There are a lot of experimental characteristics that can influence the final outcome.

Like in the leaching experiments performed with other materials, liquid to solid ratio plays a great role in the leaching of elements, usually making the concentrations of elements extracted larger in the extractants in experiments with smaller liquid-to-solid ratio [21]. Although the concentrations present in those extractants are higher, the total amounts of leached elements are bigger in solutions with large solid-to-liquid ratio. Time of extraction is important, and as a rule of a thumb it can be said that with the increase of extraction time there is an increase of extracted concentration [10] approaching to the asymptotic value.

3.1.2 Causes of Toxic Element Release

As previously said, coal ash in the environment (on the dump; airborne particles deposited on the soil surface, etc.) is exposed to various influences, and solubilization processes take place, sometimes transforming almost insoluble metals to soluble species, and leading to pollution of water and soil. There are several mechanisms of metal mobilisation:

1. Mobilisation due to change in pH. This mobilisation can be caused by neutralisation processes between the alkaline ash and the slightly acidic atmospheric water (pH 5–6), or acid rain (pH 4 or lower). Large fluctuations of pH of atmospheric and surface waters are possible in the vicinity of the power plant, originating from SO_2 emissions (causing acid rain), dissolution of alkaline fly ash components, etc. It is experimentally proven that with the decrease of pH the amount of elements extracted is increasing. However, Cox et al. [22] are saying that in experiments they performed "the total quantity of boron leached does not depend significantly upon pH". Over the pH range 6–8, the percent of boron leached is 50±5, at pH 10, 38% is leached. However, they found out that pH has an important role on rate of leaching. With increased acidity, the initial rate of dissolution is increasing. Other authors are confirming that increase in acidity is yielding increase in concentrations of different elements, with the possibility that in the area of basic pH values there is also a small increase of amount of leached ion, like in the case of fluorides [23]. The increase in the leachability of elements at lower pH levels is usually attributed to an increase in intensity of attack on the ash mineral phases that contain these elements [24]. Bioleaching, that cannot be considered as a major process is also influenced by pH [25].
2. Mobilisation due to change in redox-potential. The deposition of coal ash on dumps in the presence of organic substance (originating from the surrounding soil or from surface waters), can cause microbial oxygen consumption processes and redox-potential decrease with burial depth. Consequently, Fe and Mn oxides, as well as associated microelements, may become dissolved, leading to ground water pollution. Most of the sequential extraction procedures involve dissolution of the matrix (e.g. with oxalate that is dissolving iron and manganese oxides), thus misleading the investigator in establishing the amount of elements bound to this fraction.
3. Mobilisation due to change of ionic strength. Ionic strength variations in the aquatic environment will necessarily cause ionic exchange reactions on the ash particles. Moreover, the ash itself is a significant source of abundant cations, e.g. of calcium. Hence, one can expect calcium-rich waters, leaving the dump, to cause mobilisation of microelements present in the surrounding soils and sediments. Popovic et al. [26] proved that concentrations of all of the elements extracted increase with increasing ionic strength over the whole range of ionic strengths applied in the experiment. However, concentrations

of calcium, chromium, manganese and lead depend logarithmically on the ionic strength of the applied extractant. In the range of "low" ionic strengths (common for river water), calcium, chromium, manganese reveal a close to linear dependence on the applied ionic strength. Changes in river water ionic strength are expected to have a significant influence on pollution by these elements. Concentrations of zinc, nickel and copper are close to constant for low ionic strength, while in general, they reveal logarithmic (zinc, nickel), or linear dependence (copper). Hence, usual variabilities of river water ionic strength should not influence pollution by these elements. Concentrations of magnesium, arsenic and iron do not show regularities at low ionic strength, while in general, there is an increase of element extractability. In the case of these elements, it is difficult to predict effects of ionic strength on pollution processes in the vicinity of the dump. Adding of zeolites to ash can decrease the amount of elements leached, which is and indirect prove of the importance of ionic strength in leaching processes [27]. Also, ionic strength plays its role in binding of heavy metals on organic substance that can enhance leaching due to its complexing ability [28].

4. Mobilisation due to presence of complexing agents. Some of the elements can be transformed to soluble complexes in presence of complexing agents that are either natural (dissolved natural matter, like humic substances) [29] or anthropogenic (gluconic acid, [30]) in origin. In the laboratory tests some of the chemicals that are widely used in extraction experiments, like ammonium acetate, also have complexing ability, while some complexing agents are used in order to complex metals on purpose, in both sediment and ash samples [31].

3.1.3 Chemical Transformation of Toxic Trace Elements During Release

During release the trace and major elements are present in soluble forms, either as ions, or different complexes with inorganic or organic ligands. Although this problem is poorly understood, it is hard to expect any sort of increase in oxidation state, due to the fact that coal ash underwent drastic oxidising conditions already. Some reductions may be present, especially in cases of interaction of ground waters that are penetrating through the dump and entering the areas deep in the dump where the organic substance has spent all the oxygen that was present. In cases of reducing environment, not only the redox state but also the ionic form of the element can be changed [32].

As well as when considered chemical transformations of elements during release, it should be said, that there are little relevant field or laboratory investigations about chemical transformations occurring immediately after entering surface and ground waters. That relative lack of evidence is disturbing because it is well-known that the physical and chemical form of the pollutant is most important for forecasting its influence. For example, elemental beryllium is nontoxic to man compared with its salts.

Mercury is known to cycle between the geosphere and biosphere. Once it is in the hydrosphere, it can be converted by sediment flora into highly toxic methylmercury whereupon it is incorporated into aquatic life and ultimately accumulates in human food chains [33]. Limited bacterial conversion of inorganic into organic mercury has been shown to occur in humus and animal tissue as well. It was predicted that arsenic, selenium and tellurium will be methylated in the environment, too. It was also found that the trivalent arsenic form would be oxidized to pentavalent in the presence of oxygen in waters.

Trace components that enter aquatic ecosystems are usually taken up initially and most rapidly through adsorption by components having the highest surface-to-volume ratio, primarily the small suspended solids and sediments. The largest reservoir of trace contaminants over the time is the sediment where the complex association of inorganic and organic components form a system which governs, to a large extent, the availability of the trace components to the rest of the ecosystem. If ions of opposite charge are present in waters, it is possible that, depending on solubility of the possible combination, some of the products of leaching can precipitate in surface and/or ground waters.

3.2
Transportation Mechanisms of Toxic Trace Elements Through Aquatic Systems

3.2.1
Environmental Fate

Trace elements, especially toxic ones, have already been mentioned as highly important and environmentally mostly relevant products of coal ash leaching processes. Here, we shall give a short overview of some characteristic ways of their geochemical behaviour in the environment, especially aquatic systems, i.e. surface and ground waters, sediments and soils, with special emphasis on interactions they are involved in, including their most relevant substrates, as well as transport and accumulation processes.

The term "heavy metals" is very often used if environmental pollution is concerned, be it with toxic elements, or with metals in general. Besides "real" toxic elements, like, e.g. lead, mercury, cadmium, arsenic, selenium, barium, hexavalent chromium, silver, literature sources often include also iron, manganese, beryllium, copper, zinc, cobalt, and, in general, metals that are being found in increased concentrations in some ecosystems, regardless if they are "real" heavy metals (specific mass>5), or if they are even toxic. Furthermore, we shall consider as "heavy metals" all those harmful trace elements (metals or not), which have an average lithosphere concentration below 1000 ppm. Hence, we shall, of course, exclude iron and manganese, but not their highly important role (in the form of hydroxides) in accumulating heavy metals.

From hydrogen (1) to uranium (92), practically all elements are constituents of magmatic rocks and the lithosphere in total, and for all environments, there

Table 4 Trace element concentrations in some environments (in ppm)

Element	Magnatic rocks (average)	Shales (average)	Soils	Lake sediments
Cr	117	90	5–1000	25–180
Co	18	19	1–40	3–40
Ni	100	68	5–500	30–250
Cu	70	45	2–100	20–80
Zn	80	95	10–300	45–220
Hg	0.06	0.4	0.03–0.3	0.15–1.20
Pb	16	20	2–200	8–75

is an average concentration, a natural level of the observed element [34, 35] (Table 4).

Depending on their biogeochemical behaviour, elements will be more or less present in a specific environment. Their chemical stability, the solubility of their minerals, co-precipitation effects, ion exchange, the energy of adsorption processes on various substrates, involvement in coordination processes – these are all factors which affect the mobility of an element, hence, its distribution in the environment. Some of the most important accumulation and mobilization processes (occlusion within hydrous oxides and carbonates, humic substance complexation, adsorption, ion exchange, etc.), are well-known. Hence, heavy metals (if we have accepted these term instead of "trace elements"), are present in the natural environment (in low concentrations), and many of them (Co, Cu, Zn, Mo) are even essential for biota, mostly as constituents of enzymes and other biologically active molecules, and being sorbed by plants and microbes from soil and water. Of course, after their decay, the trace element cycle starts over.

Anthropogenic contamination with heavy metals is one of the most acute problems of modern society and is permanently and increasingly being investigated. The real extent, significance and consequences of these processes are still not completely evaluated, and the public opinion is, unfortunately, disturbed only when health and human lives are severely endangered, as in the case of the "Minamata" disease in the fifties, caused by bioaccumulation of mercury in fish and shells [36] – this was only the beginning of a series of severe accidents in the following decades.

Even if we regard only the danger of food poisoning, there is an enormous number of ways how heavy metals may enter the food web. The entire environment is endangered by heavy metals – airborne trace elements, originating from Central Europe, reach even Norway, severely contaminating the soil [37].

Anthropogenic heavy metals most severely jeopardize aquifers, due to spills, e.g. from industrial plants, or to infiltration of contaminated river water into bank sediments and Raney-wells. Therefore, besides serious control of raw

water, much attention is paid to investigation of sedimentary contamination processes, bearing in mind the well-known accumulation and re-mobilization processes of pollutants from sedimentary phases.

The wide application of heavy metals, their alloys and compounds, in metal and chemical industry, in agriculture and other branches, necessarily leads to environmental pollution. As by-products or dump material, they are also present in mining, construction, and huge amounts (often bigger than released by "natural weathering" – erosion of rocks, ore deposits etc.), are being released with coal ash.

The characteristic of heavy metal pollution is its permanent character – namely, contrary to organic pollutants, which are, to a greater or lesser extent, degradable in natural conditions in a reasonable time span, and their degradation products are, in the final instance, completely harmless, heavy metals are indestructible in normal environmental conditions.

3.2.2 Interactions with Mineral and Organic Components – Effects on Solubility and Toxicity Changes in the Aquatic Environment

As far as metal toxicity is concerned, humic substances can significantly decrease it, by binding toxic ions of, i.e., cadmium [38], decreasing hereby its availability for aquatic and other organisms. On the other hand, there are indications that metal-humic substance binding may increase their toxicity [39], and it was shown that low-molecular metal humates can penetrate cell membranes [40].

Heavy metals may be very firmly attached to mineral phases – in that case, they do not represent an "acute" threat to the environment. This is most illustratively represented in the case of mercury, which is being transformed into the practically insoluble sulfide – if these (reducing) conditions persist, the environment is practically safe. There are more examples like this one, but they should more be regarded as an exception, than as a rule.

Fine colloid dispersions of organic substance and hydrous oxides are highly important control factors of the mobility and fate of adsorbed trace elements – as their transporters, but, in case of coagulation, also as their immobilization factors [41]. Nolting et al. [42], for example, have shown that manganese oxides are the dominant substrates, and, hence, "immobilisers" of lead and zinc.

Zinc, which tends to form relatively stable $ZnCO_3$ [35], precipitates mostly because of this "mixing" with the calcite substrate [43]. Furthermore, the formation of the mixed calcium/cadmium-carbonate phase can significantly contribute to the removal of cadmium from polluted water [44]; hence, carbonates are not often identified as dominant zinc and cadmium substrates in sedimentation environments [45].

Microorganisms can transform metals into "environmentally more acceptable" forms, be it toxicity decrease ($Cr^{6+} \rightarrow Cr^{3+}$), mobility increase (sulfide→ sulfate), of course, with subsequent leaching, or mobility decrease ($U^{6+} \rightarrow U^{3+}$), with subsequent deposition mechanisms, etc. Microorganisms can also methy-

late trace elements (mercury, arsenic), and methylated forms, as exceptionally mobile, are more easily removable (though they are definitely more toxic, which might be a hardly soluble problem [46, 47]).

3.3 Dominant Substrates in Soils, Sediments and Aquifers – Mechanisms of Potential Sorption of Toxic Trace Elements

3.3.1 Substrates

3.3.1.1 Aluminosilicates

Ion-exchange capacities of clays are known for a long time, with hydrous aluminosilicates mostly contributing to this property – the so-called clay minerals. Besides their significance in pedological investigations, ion "sorption" (including adsorption and ion-exchange, often hardly distinguishable) on clays is of utmost importance for water quality [48], bearing in mind the fact that clay formations are not only constituents, but also, often, impermeable fundaments of aquifers. There is a highly significant positive correlation between the clay content and the content of practically all trace elements [49] – rubidium, for example, is similar to potassium, even stronger accumulating onto clays [50], caesium shows high affinity towards montmorillonite [51], similar to copper [52], whereas vanadium easily replaces aluminium in the crystal lattice of clays [49]. On phyllosilicates containing Fe^{2+}, Cr^{6+} can be reduced to the less toxic Cr^{3+}, which, being less mobile, becomes sorbed that way [53]. Some metals are becoming sorbed in the form of anions, e.g. chromate on kaolinite [54]. Organic matter significantly affects sorption processes, building "bridges" between functional groups of clay and humic substances, e.g. by means of hydrogen bonds between water from hydration layers of the metal ion on the one hand, and the carboxyl group of the fulvic acid, on the other [55], etc.

Sorptive characteristics of hydrated aluminosilicates are weaker than in the case of some other substrates, which are, for example, organic matter and hydrous oxides [56, 57]. However, this fact does not diminish the importance of clay minerals, for several reasons – first, with their abundance they significantly "compensate" their weaker sorptive characteristics [58]; second, clay minerals bind "stronger" substrates on their own surface (organic matter, hydrous oxides), indirectly contributing to sorption processes [56]; and third, during diagenesis, the connection between trace elements and the silicate phase constantly increases – namely, biogenic heavy metals, like Cu and Zn, due to biological decay, "lose" their primary substrate and, if they stay within the sediment, they become attached to the most abundant inorganic substrates, which are, again, silicates [59].

3.3.1.2 Hydroxides

Hydrous oxides significantly contribute to the accumulation of heavy metals in soil. This refers to Cr^{3+} in particular, because of the chemical similarity with the iron ion [60] – investigators regard that in controlling the Cr^{3+} concentration in soil, a significant role must be attributed to the mixed amorphous hydroxides, $(Fe,Cr)(OH)_3$ [61]. This is similar for mercury [62], caesium, technetium and uranium [63], as well as for molybdenum, which can be bound to iron oxides even in the form of the molybdate anion [64]. In some soils, hydrous oxides represent dominant substrates of copper [65] and cadmium [66]. The highly toxic, hexavalent chromium is by far more mobile than the trivalent, which makes its reduction in the environment especially important [67], although it also sorbs onto hydrous oxides [68].

In oxidative sedimentation environments, hydrous oxides of iron and manganese almost exclusively determine the fate of trace elements like P, As, Cu, Zn, Co and others [69–71], whereby the role of the "carrier" mostly belongs to silicates [70]. Copper adsorption is mostly pronounced on manganese compounds, less on alumina, and at least on iron hydroxides [72]. Besides adsorptive characteristics, oxides also tend to occlude metals, whereby the association strength may vary extremely – on the example of goethite it was observed that Cd and Zn are bound very strongly, and Pb by far weaker [73]. In the fluvial environment, iron compounds seem to be the most important [74], often in association with oxides of aluminium and manganese [45,75], and because of the fine dispersion they form [76], they are easily being incorporated into river bank sediments [77]. Iron and manganese oxides have also been shown to significantly participate in Cr, Co, Ni, Cu, Zn and As accumulation on coal ash dumps [78].

Some authors quote that hydrous oxides take part in metal accumulation mostly indirectly, via the organic matter adsorbed on themselves [79]. In any case, organic compounds enhance sorption onto oxides, as it was shown on the role of glutaminic acid in copper adsorption, on the influence of ethylenediamine on Ag and Cu sorption onto hydrous silica [79, 80], as well as on the influence of organic ligands on metal sorption on alumina [81]. A special role, again, belongs to the humic substances, which drastically increase the negative charge of hydrous oxides, hence, increasing their affinity towards cations [82].

Besides iron, manganese and aluminium, the role of hydrous silica can also not be neglected (e.g. α-quartz), though this substrate's significance in the mentioned processes is by far less environmentally significant [70, 83].

3.3.1.3 Carbonates

In soil and freshwater systems, carbonate minerals are, as heavy metal substrates, less important than silicates and hydrous oxides; neither are they as

abundant as silicates, nor do they have such a high sorptive capacity as hydrous oxides. Therefore, most authors, investigating freshwater sediments, regard these substrates as almost marginal [70, 84], and it is similar with soils, as Xian and Shokohifard [85] have shown on the examples of Cd, Zn and Pb. Adsorption on carbonates is weak, mostly because of the relatively small free surface [86] – the adsorption of zinc on calcite is possible on 10% of the potentially available surface, and the process is based on the exchange of surface Ca^{2+} with Zn^{2+} and $ZnOH^{+}$ [87]. A similar mechanism was observed for cobalt, and the affinity towards calcite decreases in the order Cd>Mn>Zn>Co. However, in carbonaceous aquifers, especially if they do not contain too much silicates and hydroxides, adsorption on carbonates can be a really important metal distribution factor, as was shown for zinc and cadmium especially [88].

Co-precipitation on carbonates was observed to represent an environmentally highly relevant process, based, in fact, on the formation of mixed carbonate phases. Besides zinc and cadmium, as already mentioned, carbonates are also a significant substrate of strontium [89], with accumulation factors up to 40× [35]. Moreover, for sorption processes it is not absolutely necessary for the carbonate to be solid – colloids of $CaCO_3$ also take part in sorption processes [90]. Carbonates, besides being important substrates of lead in aquatic systems [57, 91], have the same role in soils, too [92]. Elements shown to be easily precipitated as carbonates in soil are also Ca, Sr, Ba, Fe(II), Zn, Cd and Pb [93]. Siderite, $FeCO_3$, can represent an important trace element substrate in marine sediments, as well as in interactions which occur in ground waters [94, 95].

Since it becomes obvious that the differences between the various accumulation types are sometimes based on their strength, persistence and durability only, the reader should not wonder if the phrase "sorption" more and more often replaces all accumulation mechanisms, and so it will stay furthermore, especially, as shown below, where accumulation types will be studied in more detail, and, if regarded all together, sometimes replaced with one word – "sorption".

3.3.1.4 Sulfides

Among various sulfides, only the most abundant ones, the iron sulfides – pyrite, FeS_2, and mackinavite, FeS – can be regarded as real potential trace element substrates. Besides co-precipitation processes with pyrite and mackinavite [96], the second environmentally relevant mechanism is occlusion within, and adsorption onto hydrous oxides – namely, trace elements will mostly remain associated with iron even if the (hydr)oxide, under reducing conditions, in later phases of sediment transformation, becomes transformed into sulfide [97]. Surface adsorption on sulphide minerals has also been investigated – it was found that these surfaces show a relatively high affinity toward ions of mercury, lead, zinc and cadmium [98].

3.3.1.5 Organic Matter

As far as metal substrates are concerned, besides silicates and oxides, organic matter is the substrate mostly investigated and quoted in literature. Often, "triple interactions" (when all three "major" substrates simultaneously act as substrates) are mentioned, too. Talking about organic matter in sediments and soil is often a synonym for humic substances – humic and fulvic acids, for their abundance, but also because of their absolutely dominant role in these accumulation processes. Though, let us also mention some sorption processes on "non-humic" matter: coordinative binding onto porphyrins and phthalocyanines [99], the role of N-terminal structures of aquatic protein material in copper sorption [100], Ni-bounding onto di- and tricarbonic acids [101], etc. Heavy metals are also being sorbed on "living" organic matter, e.g. on algae cell walls, i.e. on their pectine functional groups [102].

As already mentioned, it is always questionable whether complex formation decreases or increases metal mobility, toxicity, etc. Copper, for example, forms water-soluble chelate complexes [103], but can also cause aggregation of two fulvic acid molecules [104], reducing hereby the solubility of itself and the fulvic acid, too. As far as toxicity is concerned, humic acids influence its decrease, as well as its increase, which has also been mentioned above [38, 39].

Humic substance is the dominant copper substrate in the fluvial environment [105], carrying up to 99% of Cu [106], and these associations remain preserved in the sediment, too; hence, practically the entire copper can be found to be associated to humic substances [107]. The accumulation factor (compared to the rest of the sediment), can be up to 40× [108]. In soil, organic matter also plays the major role in copper accumulation [109] – in interstitial water up to 99,5% [110]. Zinc is also being accumulated onto organic matter of recent sediments [111], but shows affinity towards other substrates, too (sulphides, carbonates), hence, the association zinc-organic matter vanishes relatively quickly [107], and the affinity to humic substances is also lower than in the case of copper [108]. Still, the affinity to organic matter is high enough to cause significant zinc enrichment of surface soil layers (where the organic matter content is the highest) [112] – besides, plants accumulate zinc in their root system, contributing to zinc accumulation at the surface, too [113]. Also, nickel and lead concentrate in the surface soil layer [112], and Pb is being transported through soil mainly in the form of soluble chelates [114]. Trivalent chromium builds very strong associations with organic matter: they inhibit its oxidation into the toxic form, Cr^{6+} [115] – the problems of chromium transformations have been quoted several times. Cadmium mostly forms relatively weak bonds with organic matter – adsorptive and ion-exchangeable [116]. However, cadmium, in the first place sorbed onto hydroxides, may "change" its substrate later – and this will mostly be organic matter [117]. Quantitatively almost insignificant, but, at the same time, one of the most

dangerous metals, mercury, becomes preferentially bound to organic matter, as shown in investigations of soil [93], river sediments [57], and estuarine sediments [71].

As we shall see later, accumulation processes are reversible – under certain conditions, the accumulated metals may be released again, by desorption or due to destruction of their substrates. They will re-enter (and, of course, endanger) the aquatic environment. However, let us resume all "sorption" mechanisms first.

3.3.1.6 Sorption Mechanisms

We have already started using the term "sorption" as a synonym for all accumulation mechanisms. Now we gather all mechanisms together under the heading "Sorption mechanisms". In a narrower sense, "sorption" can be used as a summary term for "adsorption" + "ion- exchange". In fact, for the purposes of environmental investigations, these two processes, although different in nature, can often be regarded as one continuum, from the weakest van der Waals adsorption to the strongest ion-exchange process, with no harsh border dividing them. Especially if the (re-)mobilization capacity of trace elements is concerned, it is most important whether, and under which conditions they are going to be released or not. Of course, we shall try to distinguish adsorption and ion-exchange as much as possible, but mentioning "sorption" below will mean both of them together, mostly in cases when it is hardly possible to distinguish them or to distinguish them strictly, since they often occur at the same time. Mentioning it below will mean that we encompass all mechanisms of trace element binding.

3.3.1.7 Adsorption

In certain environments, aluminosilicates represent dominant trace element substrates – an investigation of estuarine sediment formations in the USA has shown that almost all investigated trace elements (Cr, Co, Ni, Cu, Zn, etc.), and even the abundant elements like iron and manganese, show preferential affinity towards this substrate, whereas organic matter dominantly accumulates only cadmium and mercury [58]. However, as already stated, organic matter can significantly influence sorption processes on clay minerals, by forming "bridges" [118]. Sorption of trace elements on clay minerals most certainly represents an environmentally extremely important process. Although characterized by weaker bonds than in the case of organic matter and hydrous oxides, clay mineral sorption processes, due to their abundance and wide distribution, due to adsorption of "stronger" substrates, and due to a higher geochemical stability, determine the environmental fate of trace elements enormously [56, 59]. Since arsenic and chromium, contrary to cadmium and lead [18–20, 78], were shown

to be easily extracted from coal ash dumps, for example, they should be regarded as dominantly adsorptively, unselectively bound. Lead can also be very mobile in sedimentary phases and soil, as shown in samples polluted after major burning of leaded gasoline [119, 120].

We have already shown that hydrous oxides of iron, manganese, aluminium and silicon are major "controllers" of the trace elements' fate, and this refers also to adsorption processes [70, 72, 121, 122], regardless of being "autonomous" substrates, or "carried" by clays [79], or organic matter [81, 82]. A special influence on these sorptive processes exerts humic matter, by increasing the negative charge on oxide particles, affecting hereby their affinity towards cationic species [123].

Because of the relatively small free surface and surface energy – characteristics on which "unselective binding" (a term often used as a synonym for adsorption) depends – this process is practically insignificant on carbonates [87] and sulfides [98], of course, compared to the "strong" substrates, like the already mentioned silicates, hydrous oxides, and, of course, organic matter, on which sorption also occurs, but complexation dominates.

3.3.1.8 Ion Exchange

On ion exchange characteristics of clay minerals several details have been presented earlier. The ion exchange mechanism is relatively simple – if in the crystal lattice of, e.g. montmorillonite (a highly abundant clay mineral) isomorphic exchange of aluminium with a lower-charged element (e.g. magnesium) occurs, a "surplus" of negative electric charge will appear, with the tendency to be neutralized. Neutralization will occur by incorporation of cations within the layers. Ion exchange also occurs on the surface of the aluminosilicate crystal, mostly as a result of some "error" within its structure, or if, caused by some mechanical "defect", chemical bonds break up [124]. The existence of "vacancies" in the silicate structure is not the only determining factor – ion exchange also depends on the exchanging ion itself – its hydration degree, electrical density and diameter.

Competing with heavy metals in their ion exchange processes, potassium is quoted most often, with its diameter and geometry ideally "fitting" into the aluminosilicate matrix. This is the reason why clay minerals have a much greater affinity for potassium, for example, than for calcium and magnesium, regardless of their higher electric charge [125, 126]. Potassium is regarded as the characteristic clay formation constituent, often serving as a measure for the clay mineral content in sediments [127]. Potassium appears as most firmly bound to montmorillonite [128]. It is interesting that sedimentary formations even with a clay mineral content less than 0.1% "extract" potassium from waters very efficiently [129].

As we have already stated, the relatively small surface of carbonates results in small ion-exchange capacity [130].

3.3.1.9 Coordination Mechanisms

A very important way of metal accumulation is complexation, mostly to humic substances. From the ecochemical point of view, several questions arise: has the mobility become decreased or increased, does it affect toxicity, what about the strength of these bonds, is re-mobilization possible, how high is the binding capacity, etc. Besides coordination mechanisms, sorption onto humic substances encompass weaker bonds, too – the exchange capacity comes from weakly dissociated acidic, sulfhydryl, phenolic and carboxyl functional groups. On the other hand, carboxyl groups form also "real" ionic bonds, whereby salts are being formed – humates and fulvates [131]. From the environmental aspect, again, the exact nature is maybe less important (we can hardly expect to identify "pure" ionic, semipolar or adsorptive bonds here – it is by far more important to know the strength of each interaction, since this is the most relevant parameter in determining the environmental fate of organically bound metal ions. The bond strength will depend on binding locations, i.e. on the distribution of functional groups (ligands). The location maybe a monodeprotonated salicylate ring, and the carboxyl groups may originate from relatively distant ring structures within the macromolecule [132]. When the ion, e.g. Fe^{3+}, is bound within the interior of the macromolecular structure, these bonds are regarded as "strong", and the ion is protected by a tetrahedron/octahedron complex. "Weak" Fe^{3+}-bonds are formed on the surface of the humic macromolecule, and here, they are exposed to the influences of exterior reducing and complexing agents [133]. It is assumed that thiol groups – to a significant extent, diagenetically formed in anoxic sedimentation environments (via the reaction humic substance – hydrogen sulfide [134]) – are highly important loci for transient metal bonding [135]. The bond strength between the humic macromolecule and the metal ion is best represented by the stability constant (KML or ML). In case of trivalent ions, log KML can show values up to 9 (e.g. in the case of Fe^{3+}); for divalent ions it is mostly in the range between 4 and 6, except in the case of earth-alkaline metals, where log KML is the lowest (approximately 2–3) [136]. Since the distribution of the vast variety of functional groups on the humic macromolecule is highly complex, we cannot talk about ONE stability constant for a specific metal – various functional groups form different bonds (of different strength), and stability constants, cited in literature, represent, in fact, "average stability constants" for a specific system humic macromolecule-metal [137]. "Average stability constants", defined like this, are thermodynamically not exactly defined [132] – namely, they are not real constants, since for each multiligand system these values depend on the concentrations of all components – ligands and metals [138, 139] – hence, for the description of sorptive characteristics another term was introduced – "the affinity spectrum". The affinity spectrum depicts the entire KML value area as a continuum, as a variety of a great number of non-equivalent functional groups, characteristic for each humic substance-metal system in particular [140].

3.3.1.10 Occlusion

About the specific chemical nature of hydrous oxides, particularly of iron and manganese, as well as about the significance of transformations of the various forms of these elements in the environment – from the aspect of trace element binding in particular – a lot has been told already. Abundant literature data on this item, especially in the last decades, indicate that hydrous oxides in many sedimentary environments represent the main, or one of the main trace element substrates. Here we shall quote the sequence of affinity of some characteristic heavy metals towards goethite in soil: Cu>Zn>Co>Ni>Mn [93]. Goethite, α-FeOOH, is regarded as one of the main trace element substrates in the environment, and laboratory investigations have contributed a lot to the understanding of iron substitution with trace elements, like germanium [141], chromium [142], and others in goethite. Based on these investigations, Gerth [143] concludes that similar processes can be expected in natural conditions, especially in the case of cobalt, nickel, copper, zinc and cadmium. Hem et al. [144] have precipitated manganese oxide in the presence of copper, identifying, besides MnO_2, or β-MnOOH, also CuO and $Cu_2Mn_3O_8$. The authors assume that similar processes, along with occlusion/co-precipitation, should occur in the environment, too.

Occlusion in carbonates may also be a very significant process, in fact, mixed carbonate phases are often being formed. Due to occlusion, carbonates represent a significant "sink" of strontium [89], with accumulation factors up to 40x [35], as already mentioned. It should be mentioned that manganese carbonate also forms mixed crystals with calcite, and this association, besides in marine sediments [145, 146], is also abundant in freshwater sediments [97], and its significance for controlling manganese concentration in interstitial waters has already been mentioned [147]. As far as the mechanism of occlusion is concerned, it is assumed that it occurs in several steps – after a quick ion adsorption, a somewhat slower diffusion into the interior of the hydrated surface layers of the substrate occurs, followed by dehydration and carbonate bond formation, with the formation of a solid carbonate solution at the end [95]. The greatest contribution to this model, which, in fact, encompasses adsorption and occlusion processes as a continuum was given by Comans and Middelburg [148], who applied the already established surface precipitation model onto metal oxides [149], on carbonates. Zachara et al. [150], have investigated zinc precipitation on calcite, observing parallel $Zn_5(OH)_6(CO_3)_2$ precipitation, however, the authors did not have the intention to apply these results on environmental conditions. It should be mentioned that zinc, as the most frequent object of investigation in connection with carbonate sorption processes, besides co-precipitation in the form of, e.g. smithsonite (most often), is also mentioned in processes of precipitation in the form of amorphous, as well as crystal (various forms) zinc-hydroxide, of course, in aquatic systems of appropriate pH. Soil carbonate is extremely heterogeneous, with incorporated salts like $BaSO_4$,

$ZrSiO_4$, etc. [49]. Carbonate minerals in geochemical investigations, besides accumulation factors, also play the role of "dilution factors" for elements like chromium, iron, copper and many more [43]. Namely, most trace elements in freshwater environments are being accumulated within clay minerals, hence, onto aluminosilicates and onto, tightly associated, hydrous oxides and organic matter, and the accumulation capacity of these substrates is much higher than in the case of carbonates.

The tendency of certain trace elements to form sulfides in reducing conditions, i.e. in soils and sediments (including occlusion processes), and the significance of these processes, has already been mentioned, and here we shall just mention some additional authors that have been involved in these investigations [93, 151, 152].

3.4 Consequences of Aquifer Contamination with Toxic Trace Elements

3.4.1 Direct Effects

3.4.1.1 Biota

It is most evident that the sorption of trace elements onto clay minerals is of utmost importance for biota, especially if biologically essential elements in soils are regarded. Moreover, zinc adsorption onto suspended clay particles in the aquatic environment can significantly increase the availability of this metal for aquatic organisms, too [153].

Lead, for example, becomes accumulated on shells of marine organisms, and in the digestive organs of higher organisms. It can be very easily extracted by hydrochloric acid, enter their muscle tissue, and, hence, become a potential threat to human health [154]. Parallel investigations of metal concentrations in river water, sediments and insects have shown that metals are most slowly released from insects [155]. The second way for heavy metals to enter the food web is via plants, which are, in some cases, very potent accumulators of these pollutants [37].

3.4.1.2 Water

Besides the significance in pedological investigations, the process of ion sorption on clay minerals, as we have already seen, is of similar importance for ground water quality [48]. This, especially if we bear in mind the wide distribution of clay formations and the fact that they represent the most important hydrogeological isolators, i.e. the basis for aquifers, particularly for alluvial formations. The clay fraction is abundant in sand and gravel fractions of the

alluvial sediment, too, hence, we can state that clay minerals represent one of the most relevant factors of interaction with ground water, and that its composition/quality will, to a great extent, depend on sorptive processes that occur on clay minerals.

If we want to gain insight into sorptive processes of heavy metals/trace elements on clay minerals, we must stress, at the very beginning, that these processes, quantitatively, are almost insignificant compared to the same processes in which major elements take part, mostly, calcium, sodium, magnesium, potassium, aluminium, iron and manganese. "Competing" for the same substrate, major elements will most certainly come out as "winners" because of their, by far higher, concentrations in the aqueous medium, which are immeasurably more relevant than the high affinity that clay minerals show towards some heavy metals. It is well-known that calcium and aluminium, with their competitive binding in the process of ion-exchange, almost completely suppress binding of heavy metals on clays, e.g. of cadmium [156]. Cadmium and lead, contrary to arsenic and chromium, have already been shown to be a minor threat to aquatic systems, at least as coal ash dumps are concerned [18, 21, 78].

In rivers, extremely important for water supply (e.g. from Raney-wells), hydrous oxides of iron, manganese, aluminium and silicon are known for their importance, because of their infiltration into the alluvial sediment. These processes are also very important for artificial lakes, used for drinking water supply [157].

Investigations performed in Japan have shown that the release half-times of some heavy metals from heavily contaminated ecosystems (agricultural areas, aquatic systems etc.) can last for up to centuries [158].

3.4.1.3 Soil/Sediment Quality

Ion-exchange capacity is a crucial parameter used for estimating the quality of agricultural soils, representing the capacity of bionutrients sorption, though its influence on the physical characteristics is not negligible – it determines to which extent agricultural land will be compact, water-permeable etc. Ion capacity of clay minerals is mostly between 10 and 100 mg/100 g [159], and it constitutes of two components – besides the so-called "pH-independent capacity", determined by the already mentioned isomorphic cation substitution, relatively early, it was determined that the capacity depends on pH, too [160]; hence, the term "pH-dependent ion-exchange capacity" was introduced [161]. This capacity depends on structural hydroxyl groups, i.e. on their dissociation degree [162]. In the cases of kaolinite and halloysite, for example, the pH-dependent ion-exchange capacity represents the dominant component of the entire exchange capacity [163].

Although the sorption of abundant elements on clay minerals is quantitatively dominant, from the environmental aspect it is relevant only as a competitive ion-binding process – competitive to trace element binding. Regarded

as an isolated process, for environmental quality it is irrelevant whether the clay in an aquifer will be saturated with potassium or aluminium, for example, but it is most certainly relevant whether we can find even traces of highly toxic metals like cadmium or mercury. The clay fraction of soils really represents a major trace element accumulation factor.

It should be mentioned here that, on the basis of pyrite content in sediments, significant conclusions on redox-reactions can be brought, and these conditions determine the qualitative and quantitative aspects of trace metal sorption on organic, as well as on inorganic substrates.

On the profiles of recent sediments, changes of trace metal levels can often be observed, chronologically directly connected with the intensity of metal contamination, i.e. with the industrialization process in the investigated area [35, 164–166], or, as we have already seen, as a consequence of accidental situations, e.g. excessive burning of leaded gasoline and consecutive pollution with lead [167, 168]. In order to identify a contaminated sediment layer, sometimes the trace element concentrations have to be "normalized", i.e. compared to a very abundant, non-anthropogenic element, for example, aluminium [58] – the contaminated layers are, by using this method, easily being identified on the basis of the high metal/Al ratio.

3.4.2
Indirect Effects

3.4.2.1
Remobilisation Due to Physico-Chemical Changes (pH, Redox-Potential, Ionic Strength, Chemical Composition, etc.)

Very often, aquatic systems are jeopardized by remobilisation effects of trace elements. If, during river bank filtration, trace elements become adsorbed onto clays, each intrusion of high-ionic strength river water might lead to exchange, remobilisation, and, hence, to their potential infiltration into (Raney-)wells. Acid rains very efficiently desorb heavy metals from most substrates in soil and it is reasonable to predict dangerous consequences affecting soil, agricultural products, ground water etc. In investigations of pH effects on various heavy metal substrates [169], an especially interesting phenomenon has been observed in the case of zinc, an element which, in case that oxidation of pyrite occurs in an previously anoxic sediment, becomes remobilised again – the reason is not its desorption from pyrite, but from silicates – because of sulfuric acid release and pH decrease [170].

River water, which, in summer months, due to the disturbance of the carbon-dioxide-carbonate-equilibrium, deposits carbonate, and heavy metals associated with it (e.g. zinc, cadmium, strontium) will soon be re-enriched with them, as soon as conditions allow it (pH decrease). There are opposite examples, too, like, for example, the harsh summer increase of trace element in lakes. Namely, parallel with oxygen level decrease in river water (be it a result of temperature

increase or microbial uptake) hydroxides of iron and manganese, deposited on the lake bottom, become dissolved, which all results in a rapid release of occluded trace elements [117, 171].

It is obvious that in-depth knowledge on trace element release mechanisms is of high importance for an overall environmental protection, since this is the only way for performing an ecologically relevant (qualitatively and quantitatively) estimation of the effects of these processes on aquatic systems, plants and animals, and this is all in the function of water and the entire food web protection leading to Man's health itself. In order to achieve this, it is insufficient to know the values of total metal concentrations in soils and sediments, but the forms of their existence, strength and nature of bonds they are involved in. The bond strength will directly determine its mobility – weak, adsorptive bonds will lead to an easy and prompt solubilization, whereas humic associated metals will remain strongly bound to their substrate. Of course, if this humic molecule is soluble, the associated heavy metal ions will be soluble, too, (even if they are, in their "free" form practically insoluble or show the tendency to form "insoluble" compounds under the given conditions.

Hence, from the very beginning of trace metal ecological investigations, there was a need to perform their "speciation" in geological samples, i.e. to define and quantify, as precisely as possible, the forms in which they appear in soil and sediments, as well as to identify association forms they are involved in, preferentially in order to assess their mobility, as well as the risk of their remobilisation in changed circumstances. In other words, it became necessary to distinguish variously mobile fractions of heavy metals, from the most mobile, easily accessible to plants, over fractions which will become remobilised under various environmental influences (ionic strength change, pH fluctuations, redox-changes, etc.), including those fractions, environmentally practically irrelevant (immobile). The method which enables, by using successive application of extractants of increasing extractability, the distinction of discrete, specifically associated fractions of trace elements/heavy metals from the same sample, is known as sequential extraction, being intensively developed during the last several decades, giving extraordinary results and enabling highly relevant estimates of remobilisation effects. For its development special respect should be paid to Goldberg and Arrhenius [172], Schwertmann [173], Chester and Hughes [174], Gibbs [175], Nissenbaum and Swaine [107], Deurer et al. [43], and, most of all, to A. Tessier [176, 177] and U. Förstner [178–180].

3.4.3 Remobilised Toxic Elements – Effects on Environmental Quality

The aim of selective, sequential and other extractions applied in environmental investigations is determination of heavy metal mobility in geological material, definition of their substrates, as well as prognosis of further accumulation and/or mobilization processes, as we have already seen, can be very effective in tracing

pollution in practically unpolluted river [166]. This knowledge is accessible on the basis of element distribution within the extraction phases, i.e. by identifying heavy metal phases with the corresponding substrates, i.e. substrates affected (ion exchanged, dissolved, reduced etc.) with the corresponding extractants applied.

These types of extractions were shown to be very useful for the purposes of remediation (e.g. of soil heavily contaminated with lead, where significant results were achieved by EDTA extraction [181]). Much was achieved in remediation efforts performed on soils polluted by radionuclides. On the basis of these results, investigators came to the conclusion that in the case of soil contamination with technetium and neptunium, for example, the most efficient remediation process is elution with acidic solutions, whereas in the cases of pollution with uranium and thorium (since these elements form bonds with organic matter), a completely different treatment is necessary, e.g. extraction with organic acids [63]. Sequential extraction has, for example, presented most valuable data about the mobility of artificial radionuclides, deposited on the soil surface after the Chernobyl disaster – it was concluded that radioactive strontium is much more mobile and, hence, more available to plants, compared to radioactive caesium [182]. Besides that, comparing the mobility of the stable and the radioisotope of caesium it was concluded that the radionuclide is slightly more mobile [66]. Various aspects of mobilization of uranium from polluted sediments under hydrological regime changes have also been investigated in detail [183].

Selective and sequential extractions offer useful information in cases of bioremediation, too. Namely, besides controlled bioaccumulation – sorption on cell walls, by intra- and extracellular sedimentation reactions, the ability of microorganisms to oxidize/reduce metals is also used. Microbial demethylation is being applied, too, in order to reduce toxicity [46, 47].

Except in the cases of soils and sediments, selective (using only several, necessary steps) or sequential extraction (encompassing the entire sequence) is used wherever it is necessary to assess the possibility of heavy metals remobilisation and the degree of threat to the environment – for example, in various cases of dump deposition [18, 20, 178] or exposure of ores to atmospheric influences [184].

Intensive ecochemical investigations of various ecosystems within a river confluence area (e.g. the Danube), can lead to significant conclusions about trace element behaviour in downstream artificial accumulations or (in the case of Danube) the Black Sea itself [119, 168].

4
Industrial Use/Recycle of Fly Ash in Construction and Building Materials

Difficulties which are caused by landfills could be lightened and almost eliminated. Common denominator for the solving of all mentioned problems (adhe-

sion in the pipelines, landfill influence on the groundwaters and environment), beside certain technical solutions, is the decreasing of fly ash for transport and landfilling.

In developed countries, fly ash is intensively used in various areas of civil engineering. Everywhere in the world, fly ash has successful history of the utilization in concrete which lasts over 50 years. In the USA, more than 6 million, and in the Europe more than 9 million tonnes of fly ash is utilized in the cement and concrete. It is hard to design concrete constructions today without using fly ash. Some of the most prestigious projects of today were designed on the basis of fly ash. Some of the examples in Europe are: thermo power station building, oil platforms, tunnels, highways, pavements, commercial and residential buildings, bridges etc. [185, 186].

4.1 Lightweight Aggregate Manufacturing

The main intention for use of the aggregate is in the construction of lightweight concrete. The use of fly ash in the production of lightweight aggregate is also well established. The ash is first pelletised on an inclined disc pelletiser with 5–10% water and is then fired at a temperature of about 1000 °C. The resultant material is open textured with small voids that are interconnected and permeable to water. Such lightweight aggregate has a loose bulk density of approximately 825 kg m^{-3}, and is capable of producing concretes with strengths in excess of 40 MPa. It is well established material and has been used in a number of large scale projects [187, 188]

Lightweight concrete consists of cement and/or lime and sand, fly ash or other siliceous material. It is manufactured by preparation of slurry, generation of gas, cutting and then curing with the high pressure steam. In most cases, they are manufactured in autoclaves under a pressure ranging from 1 to 1.5 MPa. As lightweight concrete is light in weight, it reduces the weight of building which plays an important role in the development of construction: reduces the cost of foundation and main structure, makes construction more reasonable and shortens construction period, speeds up the development of precast industry, liable to construct buildings more high-rise. The density generally ranges from 400 kg m^{-3} to 800 kg m^{-3}.

4.2 Road Base Construction

Fly ash has a high potential for utilization, and some of the applications concerned the re-use of coal fly ash stabilized with cement as a road base construction material, as a substitute for sand-cement stabilization.

One of the most important things with the road construction is making quality road stabilization. This problem is very hard to solve because the cement is too strong and the lime is too weak a binder for road stabilization. Mixing of fly

ash with cement, hydraulic binders specially designed to satisfy requirements of road construction could be obtained.

From the experimental results, it was confirmed that coal ashes possessed favourable engineering properties as a material of base course in road and a structural fill material. When fly ash with hydrated lime and cement was properly compacted, it showed a good compaction effect and great strength gain with curing time. Compacted fly ash stabilized with 5% cement (or cement plus gypsum) successfully fulfilled the requirements of the strength and the resistance against the immersion in water as a material in road [189].

Fly ash, lime and crushed stone mixture is also a subbase material with hydraulic and retarding property. After placing and compacting, this mixture will form slab-shaped material with bigger flexural strength and uniform load distribution. Its strength will increase with age. Therefore, subbase at the initial strength is flexible, and at the latter strength is rigid. Subbase is the footing of the road. Its design strength has a certain influence on the thickness of the road. The rebound modulus of subbase design is a comparatively complicated problem. It will be affected by the properties of raw material, hydrologic condition, compactness, homogeneity and height of embankment, etc., which are usually determined through site measurement and statistical analysis [190].

4.3 Landfill Liners

Composite of coal fly ash, lime dust and bentonite represents potential barrier material for a landfill. Hydraulic hardening has been observed when lime is mixed with silica and water. The reaction forms calcium silicate hydrates, which also common in cement hardening. A similar hardening reaction was observed for a mixture of coal fly ash/lime/bentonite and water. This property suggests the potential use of coal fly ash mixture as a landfill barrier material. The other way is mixing of fly ash with bitumen, making the composite in several uniaxial layers, impermeable landfill liner could also be obtained. The composite was found to have a hydraulic conductivity of 4.3×10^{-8} ms^{-1} with water. More importantly, the composite material had chemical barrier properties for metal ions in the leachate liquid. The pH in the coal fly ash barrier is controlled by the hydroxides and carbonates of calcium and magnesium, mainly from lime kiln dust. The retarding mechanism for the heavy metal ions carried by the leachate through the barrier is precipitation. The contaminant metal ions studied (Fe, Zn, Pb) precipitate in the barrier as either hydroxide or carbonate depending upon the solubility constants of the two solid species. Ferrous iron and zinc ions precipitate in the barrier as hydroxides; lead ion precipitates as carbonate. The migrating front of heavy metals in the coal fly ash barrier under landfill conditions was estimated to be less than 0.10 m in 15 years assuming a leachate pH of 6 [191].

4.4 Sewage Sludge Treatment

With some primary treatment, sewage sludge can be mixed with fly ash to yield more than just a fertilizer. Combining the sludge's nitrogen and organic matter with the minerals found in fly ash yields a potent soil replacement substance.

Coal fly ash can be used as a stabilizing agent for anaerobically digested sewage sludge, and the utility of this mixture as a soil conditioner. Mixtures of sewage sludge and coal fly ash improved the fertility of soil. Investigation showed that heavy metal concentrations in leachate are below the regulatory standard through the stabilization period. Nitrate concentrations are decreased during the process of stabilization and are lower than the regulatory limit in groundwater. The pH of soil increased after being applied with sludge-ash mixture, then decreased through stabilization process. In soils with smaller portions of coal fly ash, pH which increased initially, but could not be maintained since decomposition of sludge led to soil acidification. Cation exchange capacity and heavy metal adsorption capacity of soil are enhanced with application of sludge-ash mixture. Optimal mixing ratio of sludge and coal fly ash which could protect soil from heavy metal toxicity and acidification is 1:0.8 on the basis of dry weight.

Fly ash reduces bulk density, increases water holding capacity, buffers pH (soil acidity), and adds both macro- and micro-nutrients. The major elements are potassium, phosphorus, calcium, magnesium, and carbon from unbound coal. Potential trace elements include boron, molybdenum, selenium, nickel, copper, zinc, and many exotic elements whose functions are not fully understood in plant physiology. Most important for plant nutrition is that the trace element concentrations are beneficial, i.e. that they are within the (often very narrow) range between potential malnutrition and toxicity.

In certain badly depleted soils where climatic conditions and long use have eroded soil and leached out nutrients, the fly ash mix seems more effective than standard chemical fertilizers. In poorly operated programs where eucalyptus trees get one application of chemical fertilizer at planting and no subsequent watering, only half of the trees may survive, growing to a spindly and useless few centimetres in diameter after seven years. With more careful planting and tending in good social forestry programs, harvest-ready trees can be produced in the same length of time. The question is whether or not this new technology produces higher yields in the same time span [192].

4.5 Plastic Composite Materials Filler

Mineral fillers are widely used in plastic products to improve performance and reduce resin costs. More than 17% of plastic products contain mineral fillers. Fly ash, since it is essentially a spherical alumino-silicate powder, represents a potentially attractive replacement for these mineral fillers. It may offer cost,

processing, and perhaps even property advantages over traditional fillers. Calcium carbonate, the most common mineral filler, accounts for about 70% of the current plastic filler market. The use of as-received fly ash as collected at coal burning power plants as a filler to replace commercial fillers such as $CaCO_3$, talc, and glass spheres has been evaluated previously. These studies concluded fly ash could replace commercial fillers in PVC, polypropylene, polyethylene, and nylon with no loss of mechanical properties. However, a survey of plastics manufacturers indicates a reluctance to use fly ash as a filler because of its low brightness, improper pH and presence of broken cenospheres. Beneficiation of as-received fly ash is a feasible way to remove residual carbon, cenospheres, and magnetic particles, thereby improving its acceptance by the plastics industry. The physical properties are influenced by both the fly ash concentration and the plastic binder composition. The specific gravity of composite made with 80% fly ash and 20% plastic binder is similar to the specific gravity of expanded clay. Using EPA approved test methods for detection of total and leachable trace metals available, both the fly ash and composite were tested and it is concluded that the plastic binder encapsulates the trace metals elements within the composite particles [193].

4.6 Ceramics, Bricks and the Tile Industry

The addition of fly ash to cold stabilized clay mixtures for the cold stabilized bricks [194] greatly improves the various properties of the final products. The shrinkage and the weight loss are lowered in comparison with the reference. Better mechanical resistances are recorded. The aim of the fly ash use in such material is to improve the performances and the qualities of this product and to contribute to reduce the pollution they might cause in the environment.

The use of fly ash in the ceramics industry and particularly as a component in the manufacture of bricks and tiles has also been investigated. This industry uses large volumes of silicate based raw materials and therefore has the potential to use significant amounts of fly ash [195, 196].

Recent research has also investigated the production of glass-ceramics from fly ash [197]. The production process involves melting fly ash mixed with other materials such as ground glass cullett and dolomite to control the composition and produce a glass that is then heat treated at lower temperatures to cause nucleation and growth of new crystalline phases. It is reported to produce very stable materials that may be used as erosion resistant materials and tiles. However glass-ceramic production is relatively energy intensive and may not always be considered appropriate for processing fly ash.

Coal fly ash has also been incorporated into conventionally sintered ceramics [198]. Sub-bituminous coal ash from a Spanish power station was mixed with significant amounts of clay to form compositions suitable for firing. The ceramics formed contained mullite and feldspar and had potential for use as paving stoneware, tiling and bricks.

Sintered fly ash brick is an ordinary solid brick produced through firing, with fly ash as its main material, its porosity not exceeding 15%. The clay, gangue and shale were used as binder for sintered fly ash bricks. Requirement of chemical composition of raw materials is not strict for sintered bricks, allowing a quite big variable range. A rough requirement can be seen as follow: 50–80% SiO_2, 5–25% Al_2O_3, 2–15% Fe_2O_3, 0–15% CaO, 0–5% MgO, 0–3% SO_3.

5
Leaching of Sintered Lignite Fly Ash – a Case Study

5.1
Introduction

The management of fly ash produced by coal fired power plants remains a major problem in many parts of the world. Although significant quantities are being used in a range of applications and particularly as a substitute for cement in concrete, large amounts are not used and this requires disposal. For example, coal fired power plants in Yugoslavia produce approximately 5000 kilotonnes of ash per year. Of this, only 20 kilotonnes is currently used in the cement industry and for production of paving slabs, building blocks and ready mixed concrete. The remaining ash is disposed of in ash repositories. This is not an ideal situation as there are concerns that this may cause long-term adverse environmental effects.

Although use of fly ash in construction and other civil engineering applications is expected to increase, it is unlikely that this will ever use all the ash being generated. Research is therefore needed to develop new alternative applications that can further exploit fly ash, which needs to be increasingly regarded as a raw material with potential for processing into new products rather than a waste.

In this work, all was done at the laboratories of Imperial College in London, lignite coal fly ash has been sintered to form ceramic materials using conventional powder processing based on milling, powder compaction and firing, without the addition of organic binders or other inorganic additives. The particle size of ceramic powders is a key process variable that controls sintering and the properties and microstructure of the materials formed and wet ball milling is routinely used to reduce the particle size of raw materials in the ceramic industry.

5.2
Experimental

5.2.1
Materials

Fly ash was obtained from the 'Nikola Tesla' power plant, situated near Obrenovac, Serbia. This is the largest power producing complex in Serbia with two plants, A and B, generating a total of 2890 MW from the combustion of

lignite coal obtained from the nearby Kolubara open cast mine. This coal produces about 19.5% ash giving a production rate of approximately 500 g of fly ash per kWh of power generated.

5.2.2 Production of Sintered Fly Ash Samples

As-received ash was milled for 8 h using a water to ash ratio of 2. The particle-size distributions of the as-received ash and the milled slurries were determined in the range 0.4 to 900 μm using laser diffraction. Milled slurries were de-watered. The filter cakes produced were then oven-dried overnight at 105 °C and ground in a mortar and pestle to form fine powders suitable for pressing. Cylindrical 'green' samples were produced by uniaxially pressing the dried milled powders and the as-received fly ash at 32 MPa. Samples were then sintered at temperatures between 1130 and 1190 °C using a ramp rate of 6 °C min^{-1} and a dwell time at the maximum temperature of 1 h, before being allowed to cool to room temperature with the furnace.

5.2.3 Characterization of Sintered Specimens

Dry density, water absorption and shrinkage were determined on sintered samples. Crystalline phases present in the as-received ash, and sintered samples were analysed by X-ray diffraction (XRD, Phillips PW1710) using 50-mA, 40-kV Cu K α-radiation, on samples ground to >150 μm. The microstructures of sintered samples were assessed from secondary electron images of gold-coated fracture surfaces using scanning electron microscopy (SEM-Jeol JSM-35CF).

5.2.4 Leaching Test (Generalized Acid Neutralization Capacity Test) Procedure

Leaching of the fly ash and sintered products was assessed using the generalised acid neutralisation capacity (GANC) test [199]. In this, separate 1-g samples of as-received and sintered fly ash ground to pass ASTM sieve No.40, were placed in a series of 125-ml acid washed bottles and mixed with acetic acid solutions ranging in concentration between 0 to 16 equivalents of acid per kilogram of dry solids. A fixed leachate to solids (L/S) ratio of 20 l kg^{-1} was used and the samples were agitated on a rotary shaker for 48 h. Leachates were then separated from the leached residue by filtering through a 0.45-μm Whatman PP filter membrane.

5.2.5 Leachate Measurements

Leachate analysis was conducted using either atomic absorption spectroscopy (AAS) using graphite furnace or flame techniques or using inductively coupled

plasma atomic emission spectroscopy (ICP-AES), depending on the metal and the concentration range.

5.3 Results and Discussion

5.3.1 Fly Ash Characterization

The average chemical composition of the 'Nikola Tesla' fly ash is presented in Table 5. The majority of the 'Nikola Tesla' ash (85.7%) consists of SiO_2, Al_2O_3 and Fe_2O_3. The CaO (5.96%) and SO_3 (1.02%) levels are relatively high, while the levels of MgO and other alkali metal oxides are typical of other ashes.

Fly ashes are classified by ASTM according to the coal source and the contents of major specified element oxides [200]. Class C fly ashes are derived from lignite or sub-bituminous coals and should contain a minimum of 50% of (SiO_2+Al_2O_3+Fe_2O_3). This category therefore includes the 'Nikola Tesla' ash, which is also reported to satisfy the requirements of the Yugoslav standard for pozzolanas (JUS B.C1.018) [201].

Particle size distribution of the fly ash has shown that the average particle size decreased from 82.0 μm for the as-received ash to 7.3 μm after 8 h milling. Milling has a number of effects on the fly ash. It clearly destroys the original fly ash particle structure and increases the available surface area. Milling also has the effect of washing or leaching the ash, as readily soluble components such as alkali metal salts will be removed in the aqueous effluent produced by wet milling.

5.3.2 Effect of Firing Temperature on the Physical Properties of Sintered Fly Ash

The 8-h milled samples had a maximum density of 2.48 g cm^{-3} that was achieved by firing at 1170 °C for 1 h, and this was a dark brown/black hard ce-

Table 5 Major oxide composition of 'Nikola Tesla' fly ash

	Chemical composition (%)
SiO_2	52.56
Al_2O_3	26.33
Fe_2O_3	6.81
CaO	5.96
MgO	2.21
Na_2O	0.24
K_2O	1.14
MnO	0.08
SO_3	1.02
Loss on ignition	3.46

ramic material. Firing at 1190 °C resulted in a reduction in density to 2.35 g cm^{-3}. The densities obtained for the sintered milled samples are comparable to those of commercially produced engineering ceramics including clay based sintered materials such as siliceous, cristobalite and aluminous porcelains, steatites, cordierite, glasses and glass-ceramics [202]. The maximum density sintered fly ash could be polished to give a highly reflective, mirror-like finish.

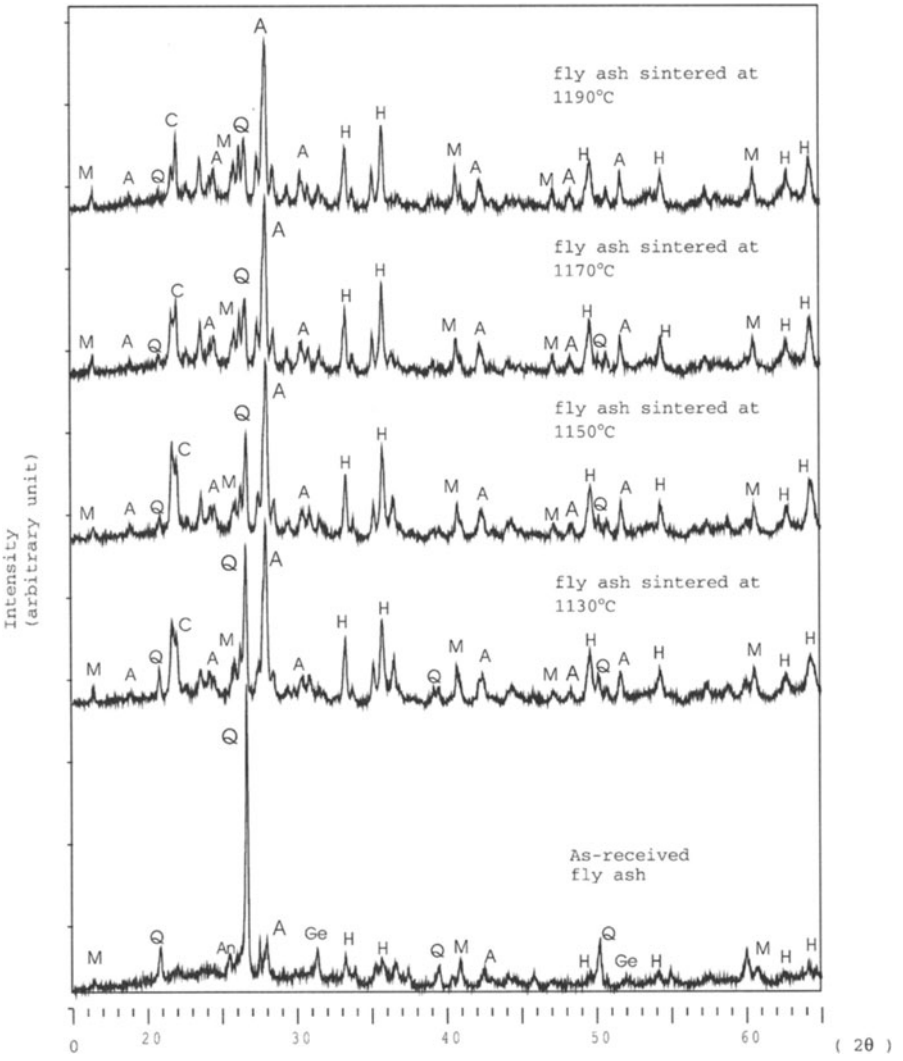


Fig. 3 X-ray diffraction (XRD) data for the as-received ash and 8 h milled ash samples sintered at different temperatures. *A* Anorthite ($CaAl_2Si_2O_8$), *An* Anhydrite ($CaSO_4$), *C* Cristobalite (SiO_2), *Ge* Gehlenite ($Ca_2Al_2SiO_7$), *M* Mullite ($3Al_2O_3{\cdot}2SiO_2$), *Q* Quartz (SiO_2), *H* Hematite (Fe_2O_3)

Shrinkage data is in general agreement with the trends in the density data. The reduced shrinkage observed by firing at 1190 °C indicates that samples are beginning to expand or bloat relative to those fired to maximum density. The water absorption data demonstrates the reduction in open, water accessible porosity that occurs with increased firing temperature. The 8 h milled sample fired at 1170 °C was effectively impermeable with absorption values of less than 0.1%. The bloating at 1190 °C did not introduce significant amounts of open connected porosity to the ceramic material formed.

5.3.3 Microstructural Characterization

X-ray diffraction (XRD) data for the as-received ash and 8 h milled ash samples sintered at different temperatures is shown in Fig. 3. The major crystalline phases identified in the as-received ash were quartz (SiO_2), the plagioclase group mineral anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), hematite (Fe_2O_3) and mullite ($3Al_2O_3{\cdot}SiO_2$). A small amount of anhydrite ($CaSO_4$) was also detected. This is in general agreement with the mineralogy reported for other lignite coal fly ashes [203].

The major crystalline phases identified in sintered fly ash samples were anorthite, quartz, mullite, hematite and cristobalite (SiO_2). Gehlenite and anhydrite, originally present in the fly ash were not detected in sintered samples whereas cristobalite is formed during sintering. This is the high temperature form of quartz and has previously been reported in lignite fly ash heated to 1000–1200 °C. The amount of quartz decreases on sintering, with the intensity of the major peak further decreasing as the sintering temperature increases.

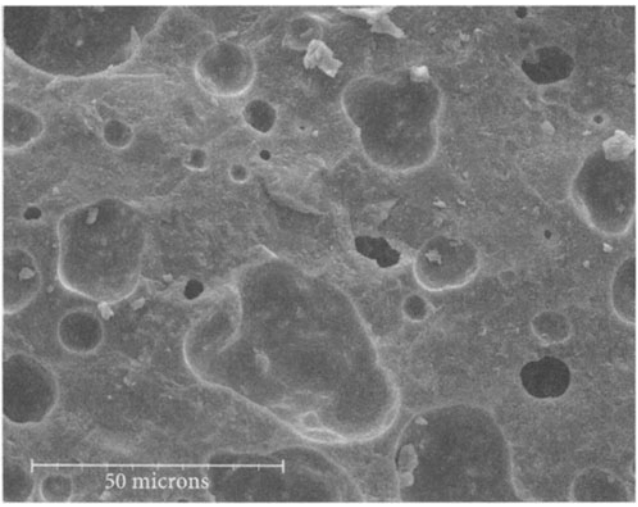


Fig. 4 SEM micrograph of the fracture surfaces of 8 h milled ash samples sintered at different temperatures

SEM micrograph of the fracture surfaces of 8 h milled ash samples sintered at 1170 °C is shown in Fig. 4. The fracture surface of the sample fired at 1130 °C is rough and granular, indicating a relatively poorly sintered material. Increasing the firing temperature to 1170 °C produces a higher density sample that has a much smoother fracture surface. The reduction in density and sample expansion that occurs when firing at 1190 °C is clearly associated with the formation of a significant volume of approximately spherical pores. These are believed to result from softening of the glassy phase present in the ash, together with simultaneous evolution of gas at this temperature.

5.3.4 Leaching Properties

Table 6 shows leaching data for the as-received and sintered fly ash samples fired at 1170 °C leached with distilled water (0 equivalents of acid per kg of dry solids from GANC test data). The final leachate pH of the as-received fly ash is 12.6, but this is reduced to approximately 7.3 by sintering.

Table 6 Leaching in distilled water from 'Nikola Tesla' fly ash as received and sintered at 1170 °C

Elements	Leachate concentration of raw fly ash (mg l^{-1})	Leachate concentration of fly ash sintered at 1170 °C (mg l^{-1})
Calcium (Ca)	169.01	1.99
Sodium (Na)	2.415	0.128
Magnesium (Mg)	0.172	0.362
Potassium (K)	3.905	0.132
Iron (Fe)	0.048	0.046
Aluminium (Al)	2.010	0.253
Boron (B)	0.570	0.022
Barium (Ba)	0.395	0.001
Cadmium (Cd)	<0.001	0.026
Cobalt (Co)	<0.001	0.001
Chromium (Cr)	0.267	0.006
Copper (Cu)	0.003	0.002
Lithium (Li)	0.252	0.011
Manganese (Mn)	0.002	0.016
Nickel (Ni)	<0.001	<0.001
Lead (Pb)	0.012	0.009
Strontium (Sr)	2.068	0.008
Titanium (Ti)	0.011	0.008
Vanadium (V)	0.175	0.003
Yttrium (Y)	0.002	0.0003
Zinc (Zn)	0.109	0.084

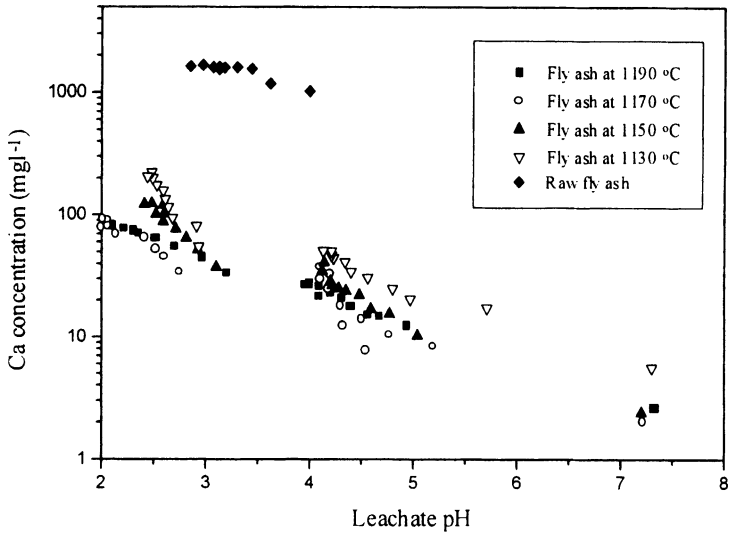


Fig. 5 GANC leach test data for Ca

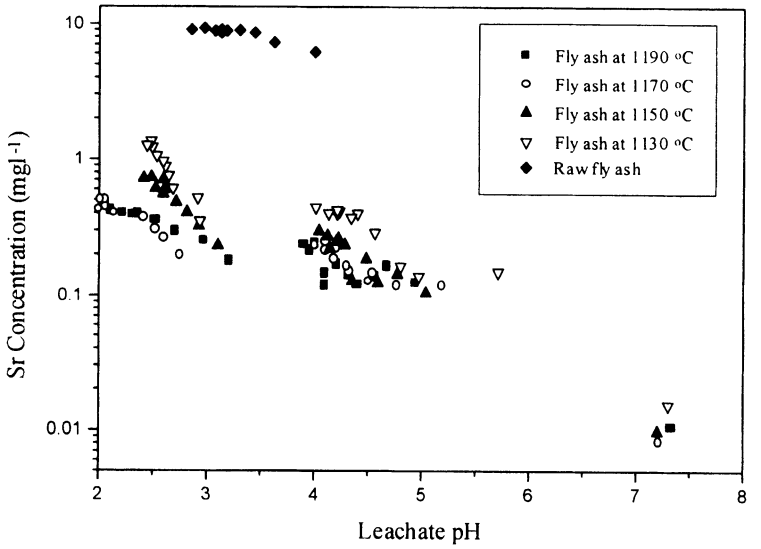


Fig. 6 GANC leach test data for Sr

Figures 5 to 12 show GANC leaching data for Ca, Sr, B, Ti and Cr as a function of leachate pH. Ca was the major metal ion found in leachates from as-received ash (>1000 mg l^{-1}). The other heavy metals for which leaching data is presented were also present at significant concentrations in leachates, with Sr, B and Ti between 5 and 10 mg l^{-1} and Cr>1 mg l^{-1}. Zn, Pb and Cd leached at much lower concentrations and data for these metals are also shown [204].

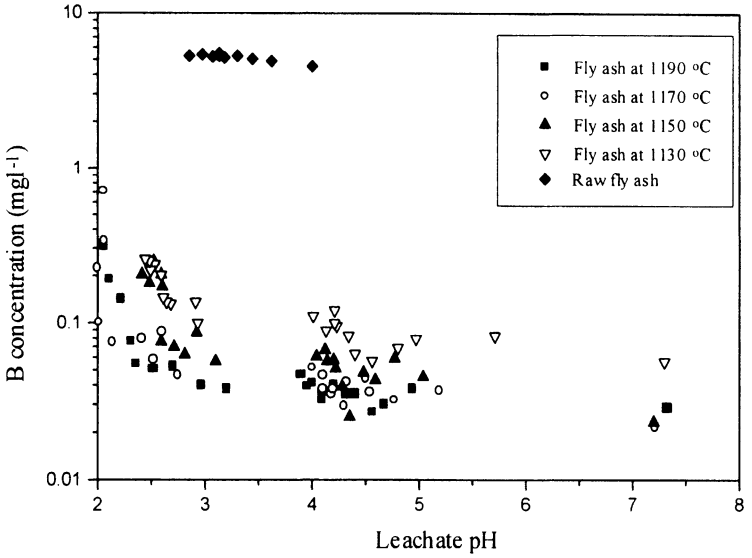


Fig. 7 GANC leach test data for B

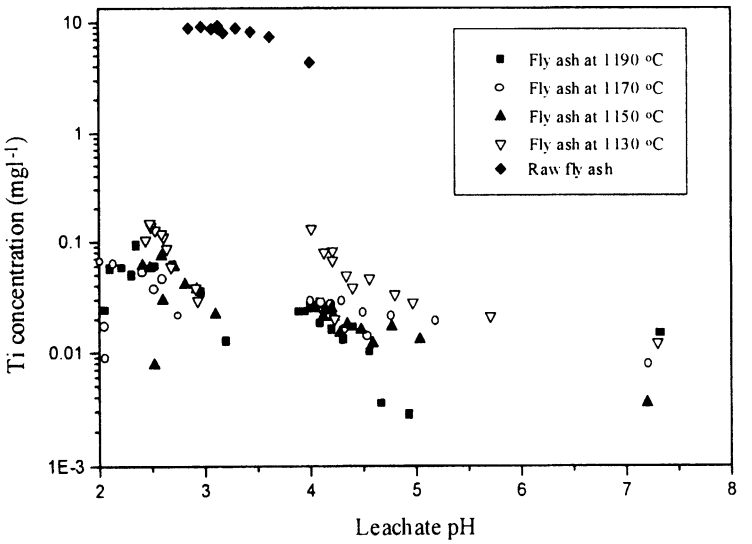


Fig. 8 GANC leach test data for Ti

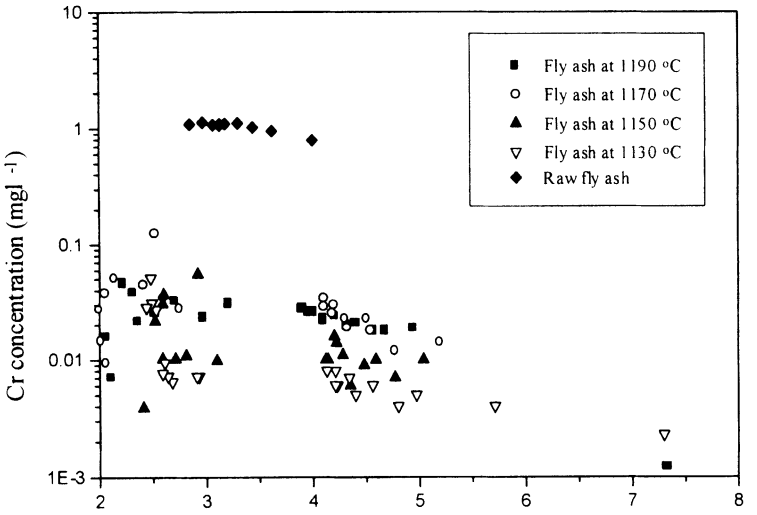


Fig. 9 GANC leach test data for Cr

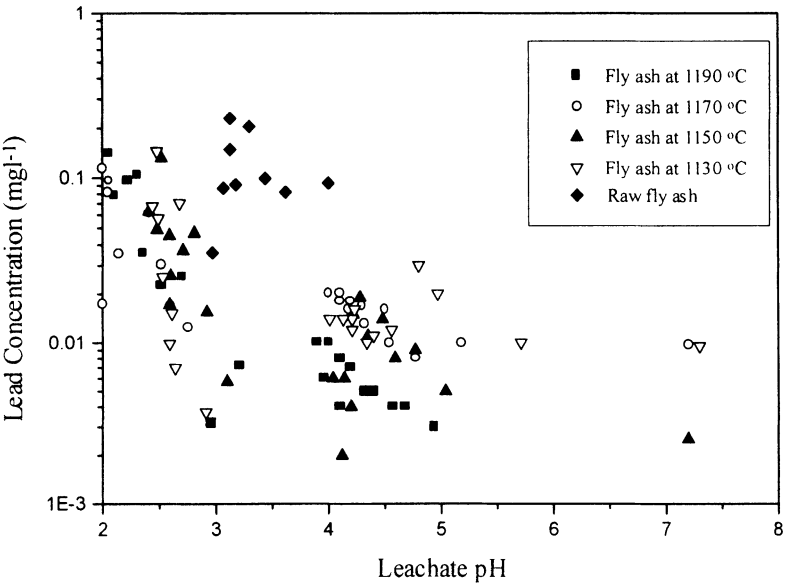


Fig. 10 GANC leach test data for Pb

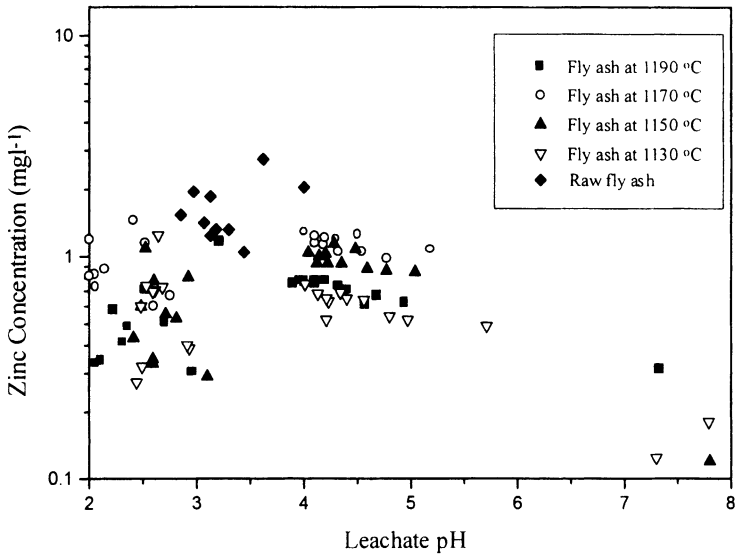


Fig. 11 GANC leach test data for Zn

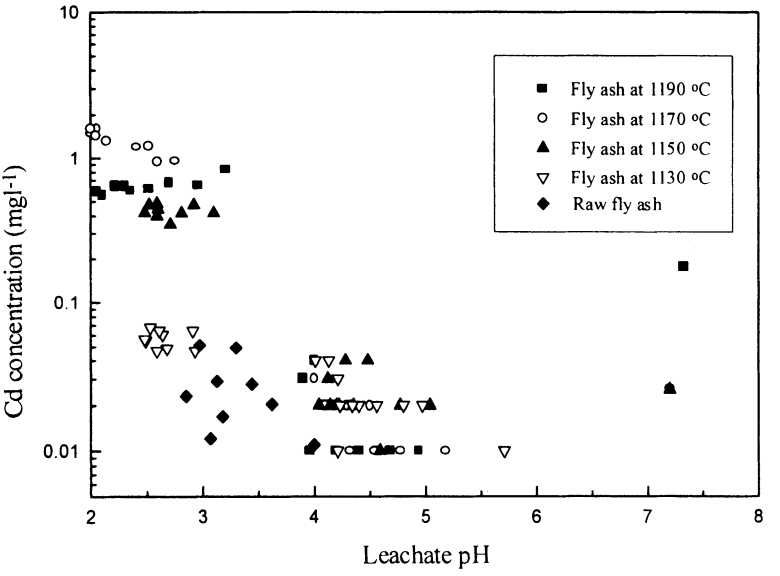


Fig. 12 GANC leach test data for Cd

Similar results are obtained for all the metals examined, with sintered samples leaching significantly lower concentrations of metals. For Ca the reduction is greater than an order of magnitude and this is typical for most other metals. Titanium shows the largest reduction with as-received fly ash leaching a concentration of around 9 mg l^{-1} compared to <0.1 mg l^{-1} for sintered samples. There also appears to be lower concentrations leached from samples sintered at higher temperatures in the range examined although further data is required to quantify this effect [205].

The reduced leaching from sintered fly ash samples is believed to result from the redistribution of elements that occurs during ceramic processing. Fly ash originates from clays incorporated in the original coal seam. During cooling after combustion, inorganic species in the vapour phase condense as thin coatings on the larger particles and also as very fine primary particles, which then grow by coagulation in the combustion zone for several seconds before being quenched. These particles and the surfaces of the larger particles therefore tend to be rich in inorganic components such as alkali sulphates and heavy metals. They are therefore readily available for leaching from the as-received fly ash.

Ceramic processing involving wet milling and high temperature sintering will redistribute heavy metals within the fired microstructure and this acts upon effectively encapsulating them into the material so they are not readily available for leaching. It is likely that the heavy metals are incorporated into the glassy as well as the crystalline phases that are present in the fly ash ceramics [206].

5.4 Summary

Conventional powder processing of lignite coal fly ash involving milling, pressing and firing allows the formation of relatively high-density low porosity ceramic. Optimum materials in terms of density were obtained by firing compacted milled ash in the temperature range between 1150 and 1170 °C for 1 h.

The original ash contains significant amounts of siliceous glass together with the crystalline phases quartz, anorthite, gehlenite, hematite and mullite. Sintering reduces the amounts of the glassy phase, quartz, gehlenite and anhydrite and promotes formation of anorthite, mullite, hematite and cristobalite.

SEM images confirm the formation of a dense ceramic at 1170 °C. Pyroplastic effects cause pore formation and sample bloating at higher firing temperatures.

Processing of lignite coal fly ash by milling, pressing and firing at temperatures between 1150 and 1170 °C allows formation of relatively high-density ceramics. It may be possible to use these materials as a replacement for more conventional ceramics in a range of applications.

Sintered fly ash leaches significantly lower levels of heavy metals compared to the as-received fly ash when tested under acid leachate conditions. This

reduction in leaching is believed to be associated with redistribution and effective encapsulation of heavy metals in the sintered microstructure that results from the ceramic processing methods used.

6
Final Conclusions and Recommendations

For an overall and valid estimate of the environmental impact of fly ash and its utilization products it is necessary to become thoroughly acquainted with the physical, physico-chemical and chemical properties of these materials. This is the case with original fly ash itself, but also with its utilization products, though their production is actually aimed at diminishing deteriorating environmental/pollution effects. Fly ash is well-known for the threat it represents (occupying enormous volumes/surfaces in the form of environmentally mostly inappropriate dumps, as potential airborne particles, and, last but not least, as an enormous potential source of more or less – depending on environmental conditions – harmful leachable substances, mostly toxic trace elements). In this chapter, we have tried to present the dangers that arise not only from (untreated) ash leaching, e.g. from dumps (on the example of trace elements, their leaching and fate in the environment), but also (as a case study) from sintered ash, which has, as expected, shown by far more environmental-friendly properties. To conclude, of course, fly ash has to be utilized as much as possible, but punctilious investigations are very necessary for every method and at each of its steps.

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Application of Whole Effluent Toxicity Test Procedures for Ecotoxicological Assessment of Industrial Wastes Used as Highway Construction Materials

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Abstract Whole effluent toxicity (WET) tests are useful, predictive tools for assessing toxicity impacts on the environment. The general purpose of the WET tests is to identify and characterize the toxic effects of effluents or leachates on aquatic resources. WET tests are applied for ecotoxicological assessment of solid wastes and industrial byproducts for use as highway materials, including coal fly ash and bottom ash, steel-slags, municipal incinerator bottom ash, Portland cement concrete, and phosphogypsum. WET tests integrate interactions among complex mixtures of contaminants and measure total toxic effect, regardless of physical and chemical compositions. They are holistic, simple, cost effective and conducted under controlled conditions. However, there are also limitations in the assessment, such as inherent variability of these tests, differences in species sensitivity, and differences in envi-

ronmental conditions between the laboratory and the receiving environment. In addition, waste and industrial by-products bring in their own set of complexities with respect to the composition of their leachates, which may include pH, alkalinity and hardness values that fall outside the acceptable toxicity test range. Altering these factors to suit the test conditions may effectively alter the speciation and subsequently the bioavailability of chemicals in the waste leachate. For instance, altering the pH of a waste material leachate can cause precipitation of some chemicals effectively altering their bioavailability. Because of these complexities, it is imperative that caution be exercised when interpreting the WET test results and using these values as primary decision guidelines for use of waste and industrial by-products in highway construction.

Keywords WET tests · Highway materials · Ecological risks · Application · Interpretation

List of Abbreviations and Symbols

WET	Whole effluent toxicity
MSWIBA	Municipal solid waste incinerator bottom ash
BOF	Basic oxygen furnace
EAF	Electric arc furnace
C&R	Construction and repair materials
EC_{50}	Mean effective concentration (causing 50% effect)
ERA	Ecological risk assessment
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
U.S. EPA	United States Environmental Protection Agency
TOC	Total organic carbon

1 Introduction

Reuse of waste and industrial byproducts as highway construction and repair materials is of growing interest in U.S and Europe as it has many advantages including overcoming disposal problems and savings in quantity and costs of construction materials [1, 2]. As they are not normal construction materials, there are also concerns about potential release of toxic constituents into surface and groundwaters.

The Clean Water Act states that "it is the national policy that discharge of toxic pollutants in toxic amounts be prohibited" [3]. For control of toxic chemicals in surface waters, the U.S. EPA established a requirement that an integrated approach involving water quality standards for individual chemicals and for toxicity be used [4]. U.S. EPA and several states require that the compliance with toxicity water quality standards, as well as the National Pollutant Discharge

Elimination System effluent permit limitations, be assessed with the WET tests. In 1995, the U.S. EPA amended the "Guidelines Establishing Test Procedures for the Analysis of Pollutants" [5] to add WET testing procedures [6, 7] to directly measure acute and chronic toxicity of effluents and surface waters. These WET testing methods are for use with effluent, surface waters, and other water samples. Application of WET tests as an evaluation tool helps to (a) directly measure the environmentally relevant toxicity of released contaminants, (b) distinguish between contaminant's bioavailable and non-bioavailable forms (speciation), and (c) assess combined effects of complex chemical and environmental variables.

Whole effluent toxicity (WET) tests are useful, predictive tools for assessing toxicity impacts of effluents in the aquatic environment. Their general purpose is to identify and characterize the toxic effects of effluents or leachates on aquatic resources. An evaluation methodology integrating both chemical and biological based approaches was developed by researchers at Oregon State University (OSU) [8–11]. In this study, biological assessment was accomplished using short-term bioassays adapted primarily from U.S. EPA's whole effluent toxicity tests [6, 7].

This chapter describes the application of biological analyses along with chemical analyses for environmental impact assessment of waste and industrial byproducts used in highway construction. Presented are background literature on waste materials evaluation and historical aspects of the toxicity-based approach; an outline of methods and materials preparation; illustration of waste and byproduct material's toxicity information; the environmental relevance of test results; and strengths and limitations of applying WET tests for assessing environmental suitability of waste materials in highway construction.

2
Environmental Aspects

Prediction and management of the impact of highway construction and repair (C&R) materials on surface and ground waters across the nation pose many challenges. Extensive highway construction and continued increase in the use of new, non-conventional construction materials require the development of a quantitative basis for planning, design, and selection of construction and repair materials and a means for assessing the environmental impact of their use. Both new materials and amended waste materials can pose a threat to the environment. New materials often contain extensive suites of potentially toxic organic and metallic compounds. This increased utilization of chemically complex C&R materials and various waste material has resulted in a clear need to integrate and unify approaches toward evaluating their potential environmental impact.

Recent studies have compiled information about environmental leaching tests to evaluate the use of solid wastes in highway construction [12–17]. 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 upon the development of accelerated leaching tests to predict long term leaching behavior [16–20].

Leaching of waste and byproduct materials is a complex phenomenon in which many factors influence the release of specific constituents from them. These factors include major element chemistry, pH, redox (reduction/oxidation) conditions, chemical complexation, liquid to solid ratios, contact time, and biological activity. Leaching tests with variety of eluants has been used for characterization of waste and byproduct materials, for regulatory compliance, and for simulation of on-site effects [21, 22].

The leachates from highway C&R materials are typically chemically complex, often containing a combination of both multiple organic and metallic compounds and ions in solution [23]. Although detailed chemical analysis can be conducted on these leachates, the extensive chemical analysis involved for samples taken from either leachate tests or tests involving modifying environmental factors (e.g., sorption, volatilization, photolysis, biodegradation) can be prohibitively expensive. Often data for making regulatory decisions come from only a small battery of tests. In addition, even when the chemistry of a leachate is completely known, the toxicity of a mixture cannot be predicted.

As a result of the expense and limited usefulness of extensive chemical testing, a combination of toxicity testing and limited chemical analysis appears to optimize information collection to evaluate environmental impacts from leachates. For a given leachate, we believe that impacts can be estimated from chemical concentration of some components (e.g., specific organic compounds or metal ions) or a surrogate (e.g., total organic carbon, or total metal concentration), and the corresponding toxicity data before and after various removal or retardation processes.

3 Toxicity-Based Approach

The measurement of toxicity allows quantitative measurement of the direct effects of a leachate on aquatic organisms. Significant research has indicated that laboratory toxicity testing is a useful tool for prediction of environmental effects. The EPA, "*Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations*" describes the application of short-term bioassay procedures to monitor changes in toxicity of waste/soil mixtures due to soil microbial activity [24]. In studies of the treatability potential for four complex industrial wastes, bioassays were recommended for characterizing transformation and immobilization processes and to complement chemical analyses [25].

A primary advantage of toxicity tests over the exclusive use of chemical analyses of C&R material leachates is the ability to assess the effect of chem-

ically undetected or unidentified constituents. For aqueous leachates from contaminated soils, Peterson et al. [26] used differential chelation/extraction and subsequent algal toxicity exposures to demonstrate that the "apparent" cause of environmental sample toxicity might be misleading. The soils contained concentrations of metals sufficient to produce, by calculation, the observed EC_{50}s at 0.06% of the full-strength soil leachates. However, treatment with methylene chloride extraction to remove organic compounds resulted in significant toxicity removal, showing that additional toxic impacts present were associated with some water-soluble organic components.

Even where the primary toxic factor has been clearly identified, the toxicological properties of a sample may differ considerably from that predicted from bioassays of the pure chemical substance. Miller et al. [27] found that algae and daphnia were much more sensitive to Esteron 99 (a commercial formulation of 2,4-D) than to 94% pure 2,4-D acid. These results suggest that "inert" components of the commercial mixture resulted in significant toxicity, and that toxicity predictions based only on the "active" chemical content would have been misleading.

In a study of off-site surface waters dominated by chromium wastes, Greene et al. [28] reported substantially lower toxicity to algae than would be predicted based on measured chromium concentrations, including consideration of chromium valence. This study found an excellent correlation between predicted and algal-assay measured EC_{50} values for groundwater samples. However, at the point where groundwater surfaced and at subsequent surface water sampling points downstream, unknown environmental factors reduced the accuracy of chemical toxicity predictions.

The advantages of toxicity tests appear to far outweigh the disadvantages when the study objective is to determine the environmental hazard of a group of known or unknown chemicals as are present in leachates from solid wastes. In such cases, the bioavailability of the chemicals is the critical question of concern, rather than the chemical concentration. Bioassays are capable of integrating the effects of speciation, chelation, sorption, and precipitation to provide an accurate indication of toxicity for a particular environmental setting.

The aquatic impact of highway materials can be estimated using two approaches: (a) a toxicity-based approach, or (b) a chemical-specific approach. In the toxicity-based approach, toxicity tests are used to expose living organisms to materials of concern, and toxicity is measured directly. Toxicity test results are generic measurements of complex chemical mixtures that do not permit identification of cause-and-effect relationships. In the chemical-specific approach, chemical analyses and water quality criteria are used to estimate toxicity. If concentrations of specific chemicals in test materials exceed criteria values, then the concentrations are considered to be toxic. For complex chemical mixtures of unknown composition, the toxicity-based approach is generally considered to be the best procedure for estimating potential toxicity [29].

4 Experimental Approach

The waste and by-product material evaluation scheme developed in this study is shown in Fig. 1. First, screening for potential aquatic impact of raw waste and by-product materials is performed using single concentration (pass/fail) WET testing methods. Leachates for toxicity screening were prepared according to Porcella [30] by vigorously shaking waste materials with distilled water at the weight ratio of 1-solid to 4-liquid (distilled water) for 24 h. Samples prepared in this manner represent an extreme, full-strength concentration (100% leachate for *Daphnia* and 80% for algae) for the purpose of aquatic toxicity screening. If a material does not show toxicity under this worst-case scenario, the material can safely be considered nontoxic. Also, no further testing is warranted for that material. Detailed testing, however, is necessitated for raw-waste materials that exhibit a potential for aquatic impact. First, definitive toxicity tests are performed (using at least five leachate dilutions) to determine the $\%EC_{50}$ and $\%LC_{50}$ values for selected test materials. Then the materials are amended with

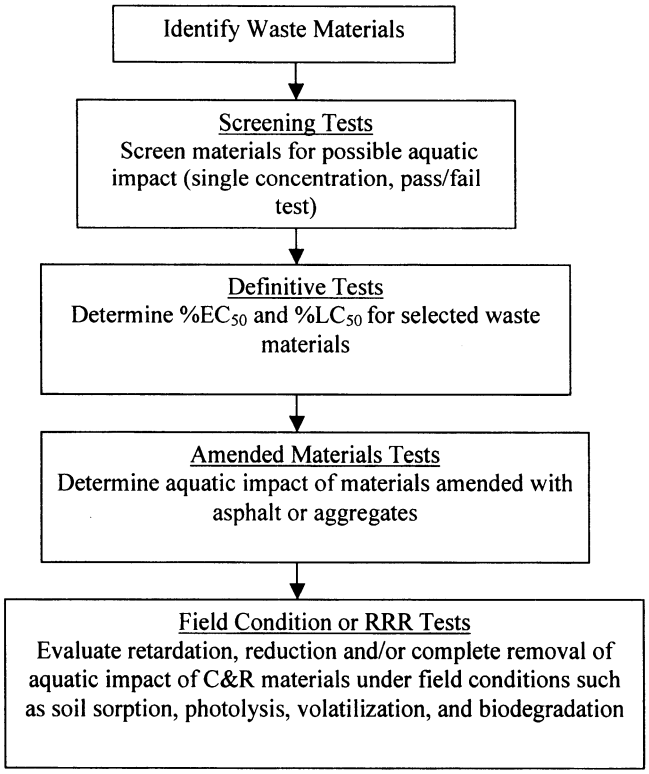


Fig. 1 A simplified experimental scheme for evaluating aquatic impacts of waste materials used in highway construction

either asphalt or aggregate depending on their proposed use (in pavement or fill). A series of laboratory tests is then performed that includes various leaching (batch and flat plate for pavement application or batch and column for fill application) and environmental (soil sorption, volatilization, photolysis and biodegradation) tests. Both chemical and biological analyses are performed for samples generated from these tests.

4.1 Materials

Approximately 30 waste and by-product materials were selected for evaluation, including asphalt concrete, aluminum oven bricks, blast furnace slags, bottom ash, fly ash, foundry sand, cement concrete, and steel slags (Table 1). Material selection and material preparation (adding waste additives to asphalt or aggregate assemblage) procedures for various leaching tests (batch and flat plate or column) are discussed in detail in Nelson et al. [10].

4.2 Methods

Test methods for leaching and environmental tests (identified in experimental scheme, Fig. 1) were conducted according to Nelson et al. [10]. The final leachate is measured for pH, dissolved oxygen, and salinity. If the pH value exceeds the acceptability criteria for survival of the test organisms, the leachate is adjusted using HCl or NaOH. Leachates are stored at 4 °C, in the dark, until toxicity tests and chemical analyses are completed. However, because of the potential that chemical changes will occur during storage, the leachate toxicity tests should begin within 48 h of preparation. This stringent requirement may result in the preparation of several small quantities of leachate rather than one large volume.

Metal analyses were performed with an inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian Liberty 150). Extraction of organic chemicals from the leachate was performed according to EPA methods 1624 and 1625 (Gas Chromatography-Mass Spectrometry Methods for Analysis of the Volatile and Semi-volatile Organic Priority Pollutants). 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.*

Two standard aquatic test organisms were selected for toxicity testing: (a) a freshwater green algae, *Selenastrum capricornutum*; and (b) a freshwater macroinvertebrate, *Daphnia magna*. Toxicity testing protocols developed for material evaluation generally followed those outlined in the standard U.S. EPA WET test methods [6, 7]. Some modifications to the testing procedures were made to investigate special cases (nutrient, hardness, etc.) encountered during this evaluation study. It was considered of critical importance that both a plant and an

Table 1 Screened materials and their aquatic toxicity test results

Material type	Material	Algal % inhibition	Daphnia % mortality
Asphaltic material	Asphalt cement AC 20	100	100
	Asphalt rubber binder	97	100
	Asphalt emulsion CSS-1	96	100
	Dense-graded asphalt mix	19	100
	Premix cold patch	56	100
Cementitious material	ASTM Type I/II Portland cement	99	100
	RSC1	100	100
	RSC2	95	100
	HBA polymer-modified cement	100	100
Portland cement admixtures	Latex modifier	100	100
	Air entraining:		
	AEA1	46	100
	AEA2	100	Low DO
	Water Reducer:		
	WRA1	100	100
	WRA2	99	Low DO
	WRA3	100	Low DO
	WRA4	100	100
	WRA5	98	100
Industrial/ manufacturing	Petroleum refinery residuals	40	100
By-products	Coal combustion fly ash	100	100
	Mine tailings	48	100
	Boiler/bottom ash	88	100
Aggregate	Pennsylvania source	96	0
Dust palliative	DP1	100	Low DO
	DP2	65	Low DO
Wood preservative	Creosote	98	100
	Creosote treated wood	100	100
	CCA treated wood	100	100
Miscellaneous	Asphalt-impregnated fiber expansion-board	100	95
	Reflective glass spheres	82	10
	Ground tire rubber	91	100

animal species be selected for testing of the highway materials. Plants and animals have biological differences that would cause them to react differently (or not at all) to different chemicals. Laboratory quality assurance and quality control procedures as described in Nelson et al. [10] were employed throughout the duration of this study.

5 Results and Discussion

For single concentration screening tests, the effects are determined in the form of % growth inhibition for algae and % mortality for daphnia. The effects (toxicities) are given in the form of percent pure leachate, that is, the percent of full-strength sample at which the effect is noted. For definitive tests and detailed evaluation tests toxicity effects are determined as $\%EC_{50}$ or $\%LC_{50}$ values. An EC_{50} value is the percentage of full-strength leachate at which there is a 50% inhibition of population growth of algae. Similarly, an LC_{50} value is the percentage of full-strength leachate at which there is 50% mortality of *Daphnia magna* relative to the surviving population in a control culture. Thus, a lower percentage indicates a greater impact because the substance inhibits algal growth or kills *Daphnia* even at low concentrations (high dilution).

Toxicity screening test results for 30 waste products are shown in Table 1. These products represent 13 classes of materials commonly used in building highways. The material classes included asphalt concrete, Portland cement concrete (PCC), Portland cement additives, industrial by-products, slags, scrap tires, timber preservatives, dust palliatives, and other miscellaneous products.

All materials tested showed high toxicity to one or both organisms with the exception of reflective glass spheres and ODOT-approved aggregates (Table 1). Performance of the *D. magna* test on the five products marked "low DO" was not possible because the chemical oxygen demand of the products stripped the test solution of dissolved oxygen (DO) which was required for survival. These products inhibited algal population growth by varying degrees: four by 100% and one by 65%.

The test results also demonstrated that simultaneous performance of plant and animal toxicity tests was clearly advantageous to the performance of either test alone. In five tests (i.e., asphalt cement cold patch premix, dense cold mix asphalt concrete, micro air entraining admixture, refinery residual, and mine tailing), the leachates were 100% toxic to *D. magna,* while population inhibition to *S. capricornutum* was only 56%, 19%, 46%, 40%, and 48%, respectively. If these materials were evaluated only by algae toxicity tests, their potential toxicity would have been overlooked.

The test results given in Table 1 are summarized further in Table 2. The numbers shown in parentheses are a count of the materials showing toxicity to the type of organism used. The counts are also shown as percentages of the total number of materials tested (30 materials). The results show that toxicity screen-

Table 2 Summary of screening test results from Table 1

%Toxic effect in leachate conc.	*Daphnia*	Algae	*Daphnia* and Algae
80%≤100%	76.7% (23)	80.0% (24)	96.6% (29)
50%<80%	0.0% (0)	6.7% (2)	3.4% (1)
10%<50%	3.3% (1)	13.3% (4)	0.0% (0)
No effect	3.3% (1)	0.0% (0)	0.0% (0)
No test=Low D.O.	16.7% (5)	0.0% (0)	0.0% (0)

Numbers in parentheses indicate the number of materials that showed toxic effect to the tested organism. They are also shown as the percentage of total number of materials tested.

ing tests using both organisms (algae and *Daphnia*) are superior to using only one organism. For example, examination of the first row of the table shows that using *Daphnia* toxicity tests would have identified the toxicity only in 23 materials from the 30 tested. Similarly, using algae toxicity tests would have identified the toxicity only in 24 materials from the 30 tested. Using both organisms resulted in identifying the toxicity in 29 materials.

Results for the definitive toxicity tests performed for waste and industrial byproduct materials are shown in Table 3. The algal $\%EC_{50}$ values indicate that over 60% of these materials (excluding asphalt and aggregate controls) show potential aquatic impact. Results of screening and definitive toxicity tests support the intuitive expectation that leachates of many waste and by-product materials in their raw form may adversely affect surface and ground waters. However, it should be noted that the toxicity screening and definitive tests were performed to examine extreme conditions. For example, only high concentrations of material leachates (from batch tests) were tested, and the tests did not allow interaction between products or between products and the surrounding environment as they are used in reality (i.e., in the form of the asphalt or aggregate assemblage tests described subsequently). Such interaction, in most cases, reduces the measured toxicity.

Table 4 shows toxicity results from tests of amended materials (waste additives added to asphalt or aggregates). Based on the algal assay test, toxicity impact of the materials was in the following order: ACZA>MMA>MSWIBA/AC>crumb rubber/AC>phosphogypsum/aggregate>foundry sand/AC>shingles/AC. Leachate from the ACZA material was found to have the most toxic impact due to high arsenic, copper and zinc concentrations, as expected for a compound developed to inhibit biological growth in wood. For most of the materials, more than one potential toxicant was identified. Aluminum was often suspected as the predominant toxic metal in most of the materials' leachates; high aluminum concentrations are also of concern in the toxicity testing because of aluminum's potential for inhibiting growth by nutrient inactivation. Other toxic metals found were zinc, copper, lead, and mercury. Although only

Table 3 Algal $\%EC_{50}$ values of raw waste and by-product materials

Material description	Algal $\%EC_{50}$
Asphalt control (no waste additive)	NTE[a]
Base aggregates control (no waste additive)	NTE
Aluminum oven bricks	NTE
Ammoniacal copper zinc arsenate (ACZA)	0.3
Blast furnace slags	NTE
Bottom ash, coal combustion	29
Crumb rubber	4
Crushed concrete	NTE
Fly ash, coal combustion	1.6
Foundry sand	2
Methacrylate sealer	0.64
Mine tailings	NTE
Mine wastes	NTE
Municipal solid waste incinerator bottom ash (MSWIBA)	1
Phosphogypsum	9
Recycled asphalt pavement	NTE
Shingles	5
Steel slag, basic oxygen furnace (BOF)	9
Steel slag, electric arc furnace (EAF)	12

[a] NTE – No toxic effect.

present at low concentrations, these metals could contribute to additive or synergistic effects in the mixture. Materials such as steel slag (EAF)/AC, steel slag (BOF), fly ash/aggregate, bottom ash/AC were found to be non-toxic to both algae and daphnia. Some 48-hour *Daphnia magna* acute mortality tests indicated significant toxicity only in crumb rubber/AC leachates. This was probably due to the presence of mercury at a concentration that could cause a toxic effect to *D. magna* (LC_{50}=0.0013 mg/l [31]).

Many additional tests were performed to determine the effects of environmental reduction, removal and retardation processes. Table 5 shows a comparison of algal toxicities of leachates generated from raw materials, leachates generated from amended materials, and amended materials leachates after soil sorption tests. Aquatic toxicities of leachate from "raw" materials were in all cases greater than for materials in their amended form (e.g., in pavement or fill). In addition, soil sorption removed or greatly decreased toxicity for every material except methyl methacrylate (MMA). Sorption appears to be a major sink for reducing or removing aquatic toxicity of the material leachates. Generally, most negative impacts are mitigated when leachates pass through soil as evidenced in Table 5. Furthermore, all soil sorption tests were conducted at ratios of solid:water no greater than 1:20 by weight. Actual soil or highway base layers will have a solid:water weight ratio more like 5:2, meaning that actual

Table 4 Summary of 24-h batch leaching results for waste additives. Chemical concentrations are given, where measured, even in the absence of toxicity tests

Material	Organism impact		Potential toxicant or surrogate	Conc. (mg/l)
	Algal EC_{50}	*D. magna* LC_{50}		
TCP/Sand	42%	ND[a]	2,4,6-TCP	1.6
ACZA	0.9%	ND	As	23
			Cu	50
			Zn	27
MMA	2.5%	ND	*N*-4-Dimethyl-benzenamine	ND
			Zn	8.6
			Co	4.0
PCC control	44%	NTE[b]	ND	
PCC with plasticizer	14%	NTE	Al	2.6
			Ca	700
Control for crumb rubber/AC	NTE	NTE	Al	1.0
Crumb rubber/AC	17%	44%	Benzothiazole	0.45
			Al	1.5
			Hg	0.02
Control for shingles/AC	NTE	NTE	TOC	5
			Al	0.17
			V	0.015
Shingles/AC	64%	NTE	TOC	6.0
			Al	0.25
			V	0.07
AC control	NTE	NTE		
Base aggregate	NTE	NTE		
Bottom ash/AC	NTE	NTE	TOC	2.0
			Al	0.05
Phosphogypsum/ aggregate	18%	NTE	Al	10.5
			Ca	1350
Steel slag/AC EAF	NTE	NTE	Al	0.8
Steel slag/AC BOF	NTE	NTE	Al	0.5
Fly ash/aggregate	NTE	NTE	Al	0.24
			Zn	0.04
MSWIBA/AC	3%	NTE	Al	25

[a] ND – Not determined
[b] NTE – No toxic effect
EAF – Electric arc furnace, BOF – Basic oxygen furnace, AC – Asphalt concrete, PCC – Portland cement concrete, MSWIBA – Municipal solid waste in cinerator bottom ash, MMA – Methyl methacrylate deck sealer.

Table 5 Comparison of "raw" material algal toxicities with toxicities for their amended or assemblage form and soil sorption leachates. All leaching data are from 24-h batch tests. Flat plate or column tests would yield lower toxicities (higher EC_{50} values)

Material	Raw material EC_{50}	Amended material	Amended material $\%EC_{50}$	Olyic soil sorption $\%EC_{50}$	Sagehill soil sorption $\%EC_{50}$	Woodburn soil sorption $\%EC_{50}$
Fly ash	1.6	Aggregate	NTE	ND[a]	ND	ND
Bottom ash	29	AC	NTE	ND	ND	ND
Steel slag (EAF)	12	AC	NTE	ND	ND	ND
Steel slag (BOF)	9	AC	NTE	ND	ND	ND
Phosphogypsum	9	Aggregate	16	40	NTE	NTE
Foundry sand	2	AC	46	NTE	NTE	NTE
Crumb rubber	4	AC	58	NTE	NTE	NTE
Shingles	5	AC	64	NTE	NTE	NTE
MSWIBA	1	AC	3	75	36	NTE
Plasticizer	54[b]	PCC	14	ND	NTE	NTE
PCC w/o plasticizer (control)	44	N/A	N/A	ND	NTE	NTE
MMA	0.3	N/A	N/A	ND	ND	0.4

[a] ND – Not determined.

[b] Diluted sample: 0.25 ml plasticizer in 1 l deionized water.

NTE – No toxic effect, EAF – Electric arc furnace, BOF – Basic oxygen furnace, AC – Asphalt concrete, PCC – Portland cement concrete, MSWIBA – Municipal solid waste incinerator bottom ash, MMA=Methyl methacrylate deck sealer, N/A – Not applicable,

All soil sorption tests are for 50 g soil per liter (1:20, soil to leachate, by weight) except for PCC w/ and w/o plasticizer where values for 250 g soil per liter (1:4, soil to leachate, by weight) is given.

sorption in the field will be much greater than experienced in the laboratory. Thus, even the positive results shown in Table 5 are conservative.

6
Issues in Toxicity Testing

The usefulness of aquatic toxicity testing methods to assess the effects of whole effluents/complex mixtures on receiving surface water biota has been defined and redefined in the last two decades. The Pellston workshops convened in 1982 and 1995 by the Society of Environmental Toxicology and Chemistry (SETAC), a professional organization with equal representation from government, academia, and business, concluded that (a) toxicologic assessment methods for single chemicals could be effectively adapted to assess whole effluents, and (b) these procedures provided realistic tools to evaluate potential environmental impacts [32]. However, since the receiving systems are more complex and diverse there are several factors that influence the aquatic toxicity and the environmental concentrations of the chemicals. These factors are summarized below. For more thorough review of this topic, see Rand et al. [33].

6.1
Factors Influencing Aquatic Toxicity Tests

Adequate understanding of factors that influence aquatic toxicity tests is critical to their conduct, and to the interpretation and application of toxicity data, whether from laboratory tests or field observations. Factors that are related to: (a) exposure, (b) organism, (c) toxicant, and (d) environmental conditions are known to significantly influence aquatic toxicity. A brief discussion of factors that influence the possible aquatic toxicity of waste material leachates is presented below.

6.1.1
Exposure

For a leachate to have a toxic effect on aquatic organisms, the chemical must come into contact and react at an appropriate target site(s) on or in each concerned organism at a high enough concentration and for a sufficient length of time. The concentration and time required to produce an adverse effect vary with the chemicals, species of organisms, and severity of the effect. This contact-reaction between the organism and the chemical is called exposure.

6.1.2
Organism

Species differ in susceptibility to chemicals. This is due to the differences in the accessibility with certain species, which effectively excludes the toxic medium

for short periods of time. In addition, rates and patterns of metabolism and excretion, dietary factors, and age substantially affect susceptibility of chemicals present in the leachates.

6.1.3
Toxicant

The composition of the toxicant significantly influences its toxicity. Other factors that are directly related to the chemical are its physical and chemical properties such as pH, solubility, and vapor pressure. These factors affect the persistence, transformation, bioavailability, and ultimate fate of the chemical in water.

6.1.4
Environmental Factors

External environmental factors often influence the toxicity of leachates by altering the nature of its chemical components or the nature of exposure. Factors associated with the bioavailability of chemicals in aqueous medium include dissolved pH, solubility, speciation, temperature, and dissolved oxygen.

6.2
Factors Affecting the Environmental Concentration of Toxicants

In the aquatic environment the concentration, transport, transformation, and fate of a chemical are primarily controlled by (a) the physical and chemical properties of the compound, (b) the physical, chemical, and biological properties of the receiving environment (ecosystem), and (c) the sources and rate of input of the chemical into the environment.

6.3
Toxicity Test Interpretation

Aquatic toxicity tests are useful, predictive tools for risk assessment. However, their primary role is that of screening only. They are not perfect tools because they are commonly applied to conditions that do not reflect the test exposures. Thus, toxicity tests should not be used alone without considering site-specific conditions such as the geochemical and biological community of receiving waters. Results should be related to actual leachate concentrations in the receiving environment at the time of testing and not to worst-case conditions. For instance, Table 4 shows that toxicity observed in foundry sand (raw) was significantly reduced by amendment with asphalt and then completely removed by soil sorption. Batch-leaching tests are normally a worst-case scenario and do not take into consideration the various factors that affect the environmental concentration of the toxicants. Thus, it is imperative that caution should be

exercised when interpreting and using these values as primary decision guidelines.

Aluminum appears to be a key element in the algal toxicity assessments of many waste and byproduct materials (Table 4). Algal toxicity associated with aluminum may result directly from soluble aluminum ions and complexes, or may be caused by pseudo toxicity from nutrient inactivation. An investigation of the toxicity exhibited by MSWIBA/AC leachate showed that it was in fact due to the removal of phosphorus (P), an essential growth nutrient, by aluminum (Al). Several studies have indicated that the interaction of P with Al may reduce dissolved P supplies to the point that algal population growth rates could become limited [34–36]. Also, the amphoteric nature of aluminum makes it a critical element in the environmental behavior of the waste material leachates. Laboratory-generated batch leachates of PCC or AC-amended waste materials often fall between pH 9 to 12, a range in which aluminum solubility greatly increases. However, under field conditions where the pH of the leachate is altered towards neutrality (say after mixing with soil or in natural waters) its solubility decreases. Solubility is an important factor that affects the bioavailable form of aluminum and therefore its toxicity [8].

6.4 Environmental Relevance

Toxicity tests can be used as tools to assess toxic effects and, in some cases, to predict effects in the field. The EPA Environmental Research Laboratory at Duluth, Minnesota, has demonstrated that chronic toxicity endpoints can be positively correlated with community structure effects [37–44]. Positive correlations were found between whole-effluent toxicity tests using *Ceriodaphnia* and fathead minnows and field assessments of benthic and fish community structure. Other researchers have demonstrated similar successful laboratory to field test result correlations for terrestrial plants using lettuce seedling emergence (a chronic endpoint) in contaminated soil with field assessments of plant cover at the same site [45].

Recently, several studies have attempted to evaluate the effectiveness of existing aquatic toxicity test methods in assessing: receiving system impacts [46], their usefulness as a regulatory bioassay [47], their usefulness as a risk assessment tool [48, 49], and their environmental relevance [50]. Sarakinos et al. [51], in their study to examine broad-scale correlation between presence of priority substances and whole effluent toxicity of complex industrial effluents, have shown that uncharacterized toxic components in effluents and interactions between chemicals, both synergistic and antagonistic, may have significant effect on toxicity of complex effluents.

7
Summary and Conclusions

The general purpose of the aquatic toxicity tests is to identify and characterize the toxic effects of effluents or leachates on aquatic resources. The aquatic toxicity tests used in this evaluation methodology are standard U.S. EPA WET tests for fresh water organisms, namely *Selenastrum capricornutum* [7] and *Daphnia magna* [6]. These toxicity test end points (EC_{50} or LC_{50}) are calculated from a series of dilutions of leachate samples from leaching and removal, reduction and retardation (RRR) tests. Leaching tests were designed to describe and quantify source term strength. The RRR processes, including photolysis, volatilization, soil sorption, and biodegradation, influence the exposure and corresponding effects on aquatic organisms due to contaminants released from highway materials. To place toxicity results in perspective, one must consider all factors that influence the aquatic toxicity and its environmental relevance. Following conclusions are drawn from the WET test results:

1. The algal toxicity test is more sensitive than the daphnia test for assessing aquatic impacts of metals and many organic compounds in highway materials leachates.
2. Waste and byproduct materials that exhibit significant aquatic toxicity in their unamended form include methyl methacrylate (MMA) deck sealer, ammoniacal copper zinc arsenate (ACZA) treated wood, phosphogypsum aggregate, PCC with plasticizer, and asphalt concrete assemblages that include crumb rubber, shingles, foundry sand, and municipal solid waste incinerator bottom ash (MSWIBA). Aquatic toxicity is eliminated or greatly reduced for materials in their amended forms, e.g., after incorporation into paving or fill assemblages.
3. In the RRR tests, soil sorption appears to be an effective mechanism for reducing or removing aquatic toxicity of the material leachates. Results indicated that soil sorption removed or greatly decreased toxicity for every material except methyl methacrylate (MMA).
4. Identification of specific chemicals in a complex mixture and their associated toxicity has been demonstrated; chemical quantification is feasible if a pure form of the chemical of interest is available.
5. High levels of metals in waste materials leachates, such as calcium and aluminum in PCC leachate, can cause interference in algal toxicity testing due to possible nutrient inactivation in the test media by precipitation of phosphate solid phases.

Overall, the WET tests based evaluation method presented in this study established its ability to ascertain potential environmental impact of waste and byproduct materials used in highway construction.

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Toxicity Evaluation and Human Health Risk Assessment of Surface and Ground Water Contaminated by Recycled Hazardous Waste Materials

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Abstract Prior to the 1970s, principles involving the fate and transport of hazardous chemicals from either hazardous waste spills or landfills into ground water and/or surface water were not fully understood. In addition, national guidance on proper waste disposal techniques was not well developed. As a result, there were many instances where hazardous waste was not disposed of properly, such as the Love Canal environmental pollution incident. This incident led to the passage of the Resource Conservation and Recovery Act (RCRA) of 1976. This act gave the United States Environmental Protection Agency regulatory control of all stages of the hazardous waste management cycle. Presently, numerous federal agencies provide guidance on methods and approaches used to evaluate potential health effects and assess risks from contaminated source media, i.e., soil, air, and water. These agencies also establish standards of exposure or health benchmark values in the different media, which are not expected to produce environmental or human health impacts. The risk assessment methodology is used by various regulatory agencies using the following steps: i) hazard identification; ii) dose-response (quantitative) assessment; iii) exposure assessment; iv) risk characterization. The overall objectives of risk assessment are to balance risks and benefits; to set target levels; to set priorities for program activities at regulatory agencies, industrial or commercial facilities, or environmental and consumer organizations; and to estimate residual risks and extent of risk reduction.

The chapter will provide information on the concepts used in estimating risk and hazard due to exposure to ground and surface waters contaminated from the recycling of hazardous waste and/or hazardous waste materials for each of the steps in the risk assessment process. Moreover, this chapter will provide examples of contaminated water exposure pathway calculations as well as provide information on current guidelines, databases, and resources such as current drinking water standards, health advisories, and ambient water quality criteria.

Finally, specific examples of contaminants released from recycled hazardous waste materials and case studies evaluating the human health effects due to contamination of ground and surface waters from recycled hazardous waste materials will be provided and discussed.

Keywords Human risk assessment · Recycled hazardous waste · Surface water and groundwater contamination · Federal guidelines on water quality · Drinking water standards

List of Abbreviations

ABS	Chromosome aberration assays
ACGIH	American Conference of Governmental Industrial Hygienists
ADI	Acceptable daily intake
ATSDR	Agency for Toxic Substances and Disease Registry
AWQC	Ambient water quality criteria
AWQS	Ambient water quality standards
BAF	Bioaccumulation factors
BBDR	Biologically based dose-response
BMD	Benchmark dose
BMR	Benchmark response
BW	Body weight
CCC	Criterion Continuous Concentration
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CMC	Criteria Maximum Concentration
COPC	Compound/chemical of potential concern
CRT	Cathode ray tube
CSFs	Cancer slope factors
CT	Curbside tailings
CWA	Clean Water Act
DWEL	Drinking Water Equivalent Level
HA	Health Advisories
HEAST	Health Effects Assessment Summary Tables
HEEE	High-end exposure estimate
HI	Hazard index
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
LCD	Liquid crystal display
LOAEL	Lowest observed adverse effect level
LOEL	Lowest observed effect level
MCLG	Maximum contaminant level goals
MF	Modifying factors
MOE	Margin of exposure
MOLY	Mouse lymphoma L5178Y assay
MRLs	Minimum Risk Levels
MTD	Maximum tolerated dose
NCEA	National Cancer Environmental Assessment
NHANES	National Health and Nutrition Examination Survey
NIEHS	National Institute Environmental Health Sciences
NIOSH	National Institute of Occupational Safety and Health
NOAEL	No observed adverse effect level
NOEL	No observed effect level
NTP	National Toxicology Program

PHS	Public Health Service
RALs	Recommended allowable levels
RCRA	Resource Conservation and Recovery Act
RfCs	Reference concentrations
RfDs	Reference doses
RL	Risk level
RME	Reasonable maximum exposure
RSC	Relative source contribution
SAL	Salmonella/microsome mutagenesis assay
SAR	Structure activity relationship
SCE	Sister chromatid exchange
SDWA	Safe Drinking Water Act
OST	Office of Science and Technology
SF	Safety factor
SMCL	Secondary maximum contaminant levels
STT	Short-term tests
TLVs	Threshold limit values
TUBE	Theoretical upper-bound estimate
UF	Uncertainty factor
URFs	Unit risk factors
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
WATERS	Watershed Assessment, Tracking and Environmental Results
WHO	World Health Organization
WOE	Weight-of-evidence
WQS	Water Quality Standards
WQSDB	Water Quality Standards Database

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1 Introduction

After World War II, industries began to produce a whole new generation of industrial and consumer goods made of synthetic organic chemicals such as plastics, solvents, detergents, and pesticides. Industries profited enormously from the production and marketing of these products and consumers became accustomed to the convenience of synthetic products as well as cheap, convenient, throwaway packaging materials. As the industrial production of these products increased, so did the production, accumulation, and disposal of hazardous waste. Prior to 1976, facilities that handled and/or disposed of hazardous waste were not provided with detailed regulations and/or guidance on proper waste handling/disposal techniques and, as a result, there were many instances where hazardous waste was improperly disposed. When chemicals are improperly disposed in the environment, abandoned hazardous waste sites are created that

potentially affect human health and cost our society billions of dollars due to the high cost of not only evaluating human health and environmental impacts but also to performing site clean-ups. An example of one of the most well known incidents of improper disposal of hazardous waste was the Love Canal environmental pollution incident [1]. This incident led to the passage of the Resource Conservation and Recovery Act (RCRA) of 1976. This act gave the United States Environmental Protection Agency (USEPA) regulatory control of all stages of the hazardous waste management cycle from the "cradle-to-grave." Beginning in the 1970s, Congress passed several other acts designed to protect human health and the environment (Table 1).

Based on the legislative directives in these acts, the USEPA has issued numerous rules, regulations, and guidance documents that ensure that the use, disposal, processing, and handling of hazardous waste do not result in impacts to human health or the environment. State governments are authorized to implement these rules/regulations promulgated by the USEPA, to permit facilities that handle hazardous waste in their states, and to create additional state rules and state regulations that apply to the operations of facilities in their specific state. The emphasis in recent years is to prevent pollution by recycling hazardous waste followed by proper disposal practices.

RCRA defines recyclable materials as "hazardous waste that are reclaimed to recover a usable product." Recycling is a broad term that applies to those who use, reuse, or reclaim waste to use as an ingredient to make a product and to use as an effective substitute for a commercial product. A material is reclaimed if it is processed to recover a useful by-product or forms the starting material for

Table 1 Seven major environmental laws implemented by the United States Environmental Protection Agency

Environmental law	Abbreviation	Year enacted
Federal Water Pollution Control Act	Clean Water Act or CWA	1972
Federal Insecticide, Fungicide, and Rodenticide Act	FIFRA	1972
Safe Drinking Water Act	SDWA	1974
Resource Conservation and Recovery Act	RCRA	1976
Clean Air Act	CAA	1976
Toxic Substances Control Act	TSCA	1976, 1988
Comprehensive Environmental Response, Compensation, and Liability Act, as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA)	CERCLA or Superfund	1980, 1986

another process [2]. Facilities that recycle hazardous waste are subject to all the federal requirements for generators, transporters, and storage facilities [3].

Several federal agencies provide guidance on methods and approaches used to evaluate potential health effects and assess risks from hazardous chemicals and contaminated source media, i.e., soil, air, and water. In many cases, these agencies also establish standards of exposure or health benchmark values in the different media, which are not expected to produce environmental or human health impacts. A few of the organizations that determine "acceptable" human risks and standards include the following: i) American Conference of Governmental Industrial Hygienists (ACGIH) – determine health protective threshold limit values (TLVs) in ambient air for industrial workers; ii) Agency for Toxic Substances and Disease Registry (ATSDR) – prepare toxicological profiles and derive acute, subchronic and chronic Minimum Risk Levels (MRLs); iii) National Institute of Occupational Safety and Health (NIOSH) – determines criteria documents for occupational exposure; iv) World Health Organization (WHO) – determines the criteria documents for human exposure; v) The Office of Water – establishes National Primary Drinking Water Standards, Health Advisories (HA), and Ambient Water Quality Criteria. The Office of Water has four individual offices that provide Agency-wide policy, guidance, and direction for USEPA's water-related programs. The major water-related programs relate to water quality, drinking water, wetlands, marine and estuarine protection, and other water-related programs. Each of these agencies uses a variation of a methodology generally referred to as risk assessment.

2
Environmental Risk Assessment Methodology

The systematic scientific approach of evaluating potential adverse health effects resulting from human exposure to hazardous agents or situations occur by the following steps: i) hazard identification; ii) dose-response (quantitative) assessment; iii) exposure assessment; iv) risk characterization [4]. The overall objectives of risk assessment are to balance risks and benefits, to set target levels, to set priorities for program activities at regulatory agencies, industrial or commercial facilities, or environmental and consumer organizations, and to estimate residual risks and extent of risk reduction [5]. Diversity of risk assessment methodology helps ensure that all possible risk models and outcomes have been considered and minimize the potential for error [4]. This section will provide information on the concepts used in estimating risk and hazard due to exposure to ground water and surface water contaminated from the recycling of hazardous waste and/or hazardous waste materials for each of the aforementioned steps.

2.1 Hazard Identification

The first step in the risk assessment process is an evaluation of all human and animal data to determine what health effects occur after exposure to a chemical. Well-conducted human studies are preferred, but occupational or accidental exposures to chemicals also provide useful information. However, in most cases, the results from animal studies are used as models to predict effects in humans since animal studies allow for controlled dose-response investigations and detailed, thorough toxicological analysis.

Some toxicants produce health effects immediately following exposure such as air pollutants that can produce eye irritation in individuals after a few minutes of exposure. Other effects, such as organ damage due to metals and solvents, may not become manifested for months or years after first exposure. The time from the first exposure to the observation of a health effect is called the latent period. The length of this period is dependent on various factors such as the type of pathology induced by the compound/chemical of potential concern (COPC), dose, dose rate as well as host characteristics such as age at first exposure, gender, race, species, and strain. Other host factors that influence susceptibility to environmental exposures include genetic traits; preexisting diseases; behavioral traits such as smoking; coexisting exposures; and medication and vitamin supplementation [5]. Genetic studies include investigations of the effects of chemicals on the genes and chromosomes (genetic toxicology) and ecogenetics, a relatively new field, describes a host's genetic variation in predisposition and resistance to COPC exposure [5]. Ecogenetics involves studies of specific exposures ranging from pharmaceuticals known as pharmacogenetics, pesticides, inhaled pollutants, foods, food additives, to allergic and sensitizing agents [6].

Moreover, induction of a health effect at the molecular level may occur after a single exposure, after repeated exposures, or after long-term continuous exposure. The length of the induction period may be a function of the same variables as the latent period. Effective exposure time refers to the exposure time that occurred up to the point of induction [4]. Ineffective exposure is readily observed in dose-response curves as a saturation of response in the high dose range. An experimental study must follow the subjects beyond the length of the minimum latent period to observe all effects and cases associated with exposure. Under ideal circumstances, a study will follow subjects for their lifetime. Lifetime follow-up is common for animal studies but uncommon for epidemiology studies [4].

Qualitative assessment of hazard information should include a consideration of the consistency and concordance of the findings. Such assessments should include a determination of the consistency of the toxicological findings across species and target organs, an evaluation of consistency across duplicate experimental conditions, and the adequacy of the experiments to detect the adverse endpoints of interest [5].

For consideration of whether a COPC is a carcinogen, qualitative assessment of animal or human evidence is done by many agencies, including the USEPA and the International Agency for Research on Cancer (IARC). Similar evidence classifications are used for both animal and human evidence categories by both agencies. These evidence classifications are used for overall weight-of-evidence (WOE) carcinogenicity classification schemes where the alphanumeric classification levels recommended by USEPA [7] are shown in Table 2. USEPA's WOE carcinogenicity classification schemes were first recommended in the *Guidelines for Carcinogen Risk Assessment* (USEPA, 1986, hereafter "1986 cancer

Table 2 USEPA's carcinogenicity classification scheme [7]

Alphanumeric code	Description
Group A	Human carcinogen; sufficient evidence from epidemiological studies
Group B	Probable human carcinogen; sufficient evidence in animals or limited evidence in humans
Group C	Possible human carcinogen; limited evidence of carcinogenicity in animals in the absence of adequate human data
Group D	Not classifiable; inadequate data or no data
Group E	Evidence of noncarcinogenicity for humans; no evidence of carcinogenicity in adequate studies in at least two species or in both epidemiological and animal studies

Table 3 Weight-of-evidence classification scheme for qualitative assessment of chemical mixtures from Mumtaz and Durkin [9]

Mechanistic understanding: I, II, and III
- I. Direct and unambiguous mechanistic data
- II. Mechanistic data on related compounds
- III. Inadequate or ambiguous mechanistic data

Toxicologic significance: A, B, and C
- A. Direct evidence of toxicologic significance of interaction
- B. Probable evidence of a toxicologic significance based on related compounds
- C. Unclear evidence of a toxicologic significance

Exposure modifiers: 1 and 2
- 1. Anticipated exposure duration and sequence
- 2. Different exposure duration or sequence
- 2.a. *In vivo* data
- 2.b. *In vitro* data
- 2.b.i. Anticipated route of exposure
- 2.b.ii. Different route of exposure

Mixture is additive (=), greater than additive (>), or less than additive (<).

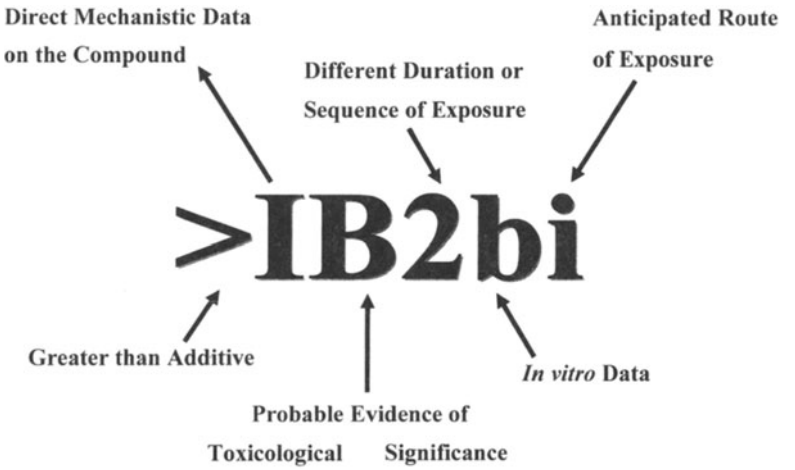


Fig. 1 Example of a qualitative weight-of-evidence (WOE) determination [10]. Adapted from Mumtaz et al. [10]

guidelines") [7]. However, the *Guidelines for Carcinogen Risk Assessment, Review Draft* (USEPA, 1999, hereafter "1999 draft cancer guidelines") [8] recommend a WOE narrative describing a summary of the key evidence for carcinogenicity. The 1999 draft cancer guidelines will serve as interim guidance until USEPA issues final cancer guidelines [43].

For evaluating chemical mixtures of noncarcinogens, Mumtaz and Durkin [9] suggest the interaction data (i.e., independent joint action, similar joint action and synergistic action) and the qualitative and quantitative interaction matrix be taken into consideration when determining the hazard index. A qualitative WOE scheme for evaluating chemical mixtures is shown in Table 3. The WOE takes into consideration the COPC, data, reference doses/concentrations, and hazard index based on additivity [10]. Figure 1 illustrates each of the chemical mixture's WOE determination by a symbol indicating the direction of the interaction followed by the alphanumeric expression in Table 3. The first two components are the major factors for ranking the quality of the mechanistic data to support the risk assessment.

2.2 Dose-Response Assessment

2.2.1 Toxicity Studies

Because toxicity studies must be evaluated to determine the quantitative dose-response relationship between the magnitude of exposure and the extent and severity of the adverse effect, a brief description of various toxicity tests

will be provided. Different methodologies are used to characterize dose-response relationships, depending on whether or not the chemical has been identified as a carcinogen or noncarcinogen. Carcinogens are assumed to pose some risk at any exposure level [4]. Four classes of toxicant-induced health effects include: i) cancer: genotoxic and nongenotoxic mechanisms; ii) hereditary effects: genotoxic mechanisms; iii) developmental effects: genotoxic or nongenotoxic mechanisms; iv) organ/tissue effects: nongenotoxic mechanisms [4].

2.2.1.1 Acute, Subchronic, and Chronic Noncarcinogenic Toxicity Testing

The evaluation of chemicals for acute toxicity is necessary for the protection of public health and the environment. Acute toxicity is generally performed by the probable route of exposure in order to provide information on health hazards likely to arise from short-term exposure by that route (Table 4) [11]. As shown in Table 4, there are four categories ranging from I to IV based on increasing doses. Generally, acute studies evaluate oral, dermal, inhalation, and eye and skin irritation as well as dermal sensitization. The acute inhalation studies are performed from one to seven days while the intermediate studies are performed from seven days to several months [12]. An evaluation of acute toxicity data includes the relationship of the exposure to the COPC and the incidence and severity of all abnormalities, gross lesions, body weight changes, effects on mortality, and any other toxic effects.

An acute exposure is considered to be a one-time or short-term exposure with a duration of less than or equal to 24 h. Acute toxicity testing is conducted

Table 4 Acute lethality studies and categories as defined by United States Environmental Protection Agency [11]*

Acute study	Most severe	Category		Least severe
	I	II	III	IV
Oral	≤50 mg/kg	>50–500 mg/kg	>500–5000 mg/kg	>5000 mg/kg
Dermal	≤200 mg/kg	>200–2000 mg/kg	>2000–5000 mg/kg	>5000 mg/kg
Inhalation	≤0.05 mg/L	>0.05–0.5 mg/L	>0.5–2 mg/L	>2 mg/L
Irritation	*Corrosive*	*Severe*	*Moderate*	*Mild*
Eye	Irritation >21 days	8–21 days	≤7 days	≤1 day
Skin	Destroyed dermis and/or scarring	≥72 h (erythema or edema)	≤72 h (erythema)	No irritation or slight erythema

* Dose or concentration producing death in 50% of experimental animals (LD_{50} or LC_{50}).

up to 7 days of exposure and subacute testing for 7–30 days. Testing periods for the evaluation of developmental effects is less than 15 days since developmental toxicity can occur after short periods of exposure. Subchronic testing is typically conducted for 90 days to 1 year since subchronic exposures are considered to be multiple or continuous exposures occurring for approximately 10% of an experimental species lifetime. Chronic exposures are assumed to be multiple exposures occurring over an extended period of time, or a significant fraction of the animal's or the individual's lifetime.

To minimize the number of animals used and to take full account of their welfare, USEPA recommends the use of data from structurally related substances or mixtures [11]. Review of existing toxicity information on chemical substances that are structurally related to the COPC may provide enough information to make preliminary hazard evaluations that may reduce the need for testing. For example, if a chemical can be predicted to have corrosive potential based on structure-activity relationships (SARs), dermal or eye irritation testing does not need to be performed in order to classify it as a corrosive agent.

2.2.1.2 Chronic Carcinogenic Toxicity Testing

All the human carcinogens that have been identified have produced positive results in at least one animal model. In the absence of adequate human data, it is plausible to regard agents and/or mixtures for which sufficient evidence of carcinogenicity in animals exists to be a possible carcinogenic risk to humans [5]. Therefore, chemicals that cause tumors in animals are presumed to cause tumors in humans. In general, the most appropriate rodent bioassays are those that test the exposure pathways most relevant to human exposure pathways, i.e., inhalation, oral, dermal, etc. Because it is feasible to combine bioassays together, it is desirable to tie these bioassays with mechanistic studies, biomarker studies, and genetic studies to understand the mechanism(s) of toxicity and/or carcinogenicity [13].

A typical experimental design includes two different species, both genders, at least 50 subjects per experimental group using near lifetime exposures. For dose-response purposes, a minimum of three dose levels should be used. The highest dose, typically the maximum tolerated dose, MTD, is based on the findings from a 90-day study to ensure that the test dose is adequate for the assessment of chronic toxicity and carcinogenic potential. The lowest dose level should produce no evidence of toxicity. In the oral studies, the animals are dosed with the COPC on a 7-day per week basis for a period of at least 18 months for mice and hamsters and 24 months for rats [14]. For dermal studies, animals are treated with the COPC for at least 6 h per day on a 7-day per week basis for a period. A minimum of 24 h should be allowed for the skin to recover before the next dosing. The COPC is applied uniformly over a shaved area that is approximately 10% of the total body surface area [14].

The animals are evaluated for an increase in number of tumors, size of tumors, and number of rare tumors seen and/or expressed. Even without toxicity, a high dose may trigger events different from those triggered by low-dose exposures. Also, these bioassays can be evaluated for uncontrolled effects by comparing weight vs time and mortality vs time curves [4]. If there is a divergence between the control group and the experimental group in the weight vs time curve, this indicates that there is a disruption of normal homeostasis due to high-level dosing. If there is a divergence in the mortality vs time curves, this indicates that there is an uncontrollable effect [4]. The National Toxicology Program (NTP) criterion for classifying a chemical as a carcinogen is that it must be tumorigenic in at least one site in one sex of F344 rats or $B_6C_3F_1$ mice.

Validation and application of short-term tests (STT) are important in risk assessment because these assays can be designed to provide information about mechanisms of effects. Short-term toxicity experiments includes in vitro or short-term in vivo tests ranging from bacterial mutation assays to more elaborate in vivo short-term tests such as skin-painting studies in mice and altered rat liver foci assays. These studies determine if COPCs are mutagenic, indicating they have the potential to be carcinogens as well. In general, STT are fast and inexpensive compared with the lifetime rodent cancer bioassays [5]. Positive results of STT have been used to predict potential carcinogenicity. Common STT include the following: Ames Salmonella/microsome mutagenesis assay (SAL); assays for chromosome aberration (ABS); sister chromatid exchange induction (SCE) in Chinese hamster ovary cells; the mouse lymphoma L5178Y cell mutagenesis assay (MOLY). There are several limitations to STT such as: STT cannot replace long-term rodent studies for the identification of carcinogens; the available tests do not detect all classes of COPCs that are active in the carcinogenic process such as hormones; and negative results from STT cannot rule out carcinogenicity [4].

2.2.1.3 Epidemiology Studies for Carcinogens and Noncarcinogens

The most convincing evidence for human risk is a well-conducted epidemiological study where an association between exposure to COPC and a disease has been observed. These studies compare COPC-exposed individuals vs non-COPC-exposed individuals [5]. The major types of epidemiology studies are cross-sectional studies, cohort studies, and case-control studies. Cross-sectional studies survey groups of humans to identify risk factors and disease. These studies are not very useful for establishing a cause-and-effect relationship. Cohort studies evaluate individuals on the basis of their exposure to the COPC under investigation. These individuals are monitored for development of disease. Prospective studies monitor individuals who initially are disease-free to determine if they develop the disease over time. In case-control studies, subjects are selected on the basis of disease status and are matched accordingly.

The exposure histories of the two groups are compared to determine key consistent features. Thus, all case-control studies are retrospective studies [5]. Epidemiological findings are evaluated by the strength of association, consistency of observations, specificity, appropriateness of temporal relationship, dose responsiveness, biological plausibility and coherence, verification, and biological analogy [5]. A disadvantage of epidemiological studies is an accurate measure of concentration or dose that the COPC-exposed individuals receives is not available, so estimates must be employed to quantify the relationship between exposure and adverse effects.

Moreover, the control group is a major determinant of whether or not a statistically significant adverse effect can be detected. The various types of control groups are: regional general population; general population of a state; local general population; and workers in the same or a similar industry who are exposed to lower or zero levels of the toxicant under study [4].

2.2.2 Dose Response

Dose-response assessment is the fundamental basis of the quantitative relationship between exposure to an agent and the incidence of an adverse response. The procedures used to define the dose-response relationship for carcinogens and noncarcinogens differ. For carcinogens, a non-threshold, zero threshold, dose-response relationship is used when there are known or assumed risks of an adverse response at any dose above zero. Non-threshold toxicants include hereditary disease toxicants, genotoxic carcinogens, and genotoxic developmental toxicants. For noncarcinogens, a threshold, nonzero threshold is used to evaluate toxicants that are known or assumed to produce no adverse effects below a certain dose or dose rate. Threshold toxicants include nongenotoxic carcinogens, nongenotoxic developmental toxicants, and organ/tissue toxicants [4]. The two different approaches will be discussed separately in this section.

The toxicity factors used to evaluate oral exposure and inhalation exposure are expressed in different units to account for the unique differences between these two routes of exposure. Cancer slope factors (CSFs), in units of $(mg/kg/day)^{-1}$, and reference doses (RfDs), in units of mg/kg/day, are used to quantify the relationship between dose and effect for oral exposure whereas unit risk factors (URFs), in units of $(\mu g/m^3)^{-1}$, and reference concentrations (RfCs), in units of mg/m^3, are used to describe the relationship between ambient air concentration and effect for inhalation exposure. The URF and RfC methodology accounts for the species-specific relationships of exposure concentration to deposited/delivered doses to the respiratory tract by employing animal-to-human dosimetric adjustments that are different than those employed for oral exposure. The interaction with the respiratory tract and ultimate disposition are considered as well as the physicochemical characteristics of the inhaled agent and whether the exposure is to particles or gases.

Most important is the type of toxicity observed since direct effects on the respiratory tract (i.e., portal of entry effects) must be considered as opposed to toxicity remote to the portal-of-entry [15]. Based on the differences between oral and inhalation exposure, route to route extrapolation of oral toxicity values to inhalation toxicity values may not be appropriate. Please refer to Appendix B of the Soil Screening Guidance [16] for a discussion of issues relating to route-to-route extrapolation.

2.2.2.1 Carcinogenic Dose-Response Assessment

Carcinogenic assessment assumes that exposure to any amount of a carcinogenic substance increases carcinogenic risk. Thus, zero risk does not exist (a non-threshold response) because there is no carcinogen exposure concentration low enough that will not increase risk of cancer. A genotoxic carcinogen alters the information coded in DNA; thus, it is reasonable to assume that these agents do not have a threshold so that a risk of cancer exists no matter how low the dose. There are three stages of genotoxic carcinogenesis: initiation, promotion, and progression. Initiation refers to the induction of an irreversible change in DNA caused by a mutagen. The initiator may be a direct-activating carcinogen or a carcinogenic metabolite. Promotion refers to the possibly reversible replication of initiated cells to form a "benign" lesion. Promoters are not genotoxic or carcinogenic but they enhance the tumorigenic response initiated by a primary or secondary carcinogen when administered at a later time. Complete carcinogens have initiation and promotion properties [4]. Nongenotoxic carcinogenesis does not involve direct interaction of a carcinogen with DNA. Mechanisms of nongenotoxic carcinogenesis include an accelerated replication that may increase the frequency of spontaneous mutations or increase the susceptibility of DNA damage. Cancer may be secondary to organ toxicity and may occur only at high dose rates. Moreover, many nongenotoxic cancer mechanisms are species-specific where the results from certain rodent species may not apply to human [4].

Several approaches and models are used to provide estimates of the upper limit on lifetime cancer risks per unit of dose or unit of ambient air concentration, i.e., the CSF or the URF, respectively. The upper bound excess cancer risk estimates may be calculated using models such as the one-hit, Weibull, logit, log-probit, or multistage models [5, 17]. The linearized multistage model is considered to be one of the more conservative models and is typically used because the mechanism of cancer is not well understood and one model may not be more predictive than another one [7, 17].

Because the risk assessor generally needs to extrapolate beyond the region of the dose-response curve for which experimentally observed data are available, models derived from mechanistic assumptions involve the use of a mathematical equation to describe dose-response relationships that are consistent with biological mechanisms of response [5]. "Hit models" for cancer modeling assume

that i) an infinite number of targets exist, ii) after a minimum of targets have been modified, the host will elicit a toxic response, iii) a critical target is altered if a sufficient number of hits occurs, and iv) the probability of a hit in the low-dose range is proportional to the dose of COPC [18]. The one-hit linear model is the simplest mechanistic model where only one hit or critical cellular interaction is required for cell function to be altered. Multi-hit models describe hypothesized single-target multi-hit events as well as multi-target events in carcinogenesis. Biologically based dose-response (BBDR) modeling reflects specific biological process [5].

Because a large number of subjects would be required to detect small responses at very low doses, several theoretical mathematical extrapolation models have been proposed for relating dose and response in the subexperimental dose range: tolerance distribution models, mechanistic models, and enhanced models. These mathematical models generally extrapolate low-dose carcinogenic risks to humans based on effects observed at the high doses in experimental animal studies. The linear interpolation model interpolates between the response observed at the lowest experimental dose and the origin. Linear interpolation is recommended due to its conservatism, simplicity, and reliance because it is unlikely to underestimate the true-low dose risk [4].

There is no universally agreed upon method for estimating an equivalent human dose from an animal study. However, several methods are currently being used to obtain an estimate of the equivalent human dose. The first method calculates an equivalent human dose from an animal study by scaling the animal dose rate for animal body weight. To derive an equivalent human dose from animal data, the 1999 draft cancer guidelines recommend adjusting the daily applied oral doses experienced over a lifetime in proportion to $BW^{3/4}$ [8]. For noncarcinogens, an uncertainty factor is employed to estimate the equivalent human dose from an animal study if pharmacokinetic data is not available.

2.2.2.2 Noncarcinogenic Dose-Response Assessment

Noncarcinogenic dose-response assessment utilizes a point of effects method which selects the highest dosage level tested in humans or animals at which no adverse effects were demonstrated and applies uncertainty factors or margins of safety to this dosage level to determine the level of exposure where no health effects will be observed, even for sensitive members of the population. Also, benchmark dose modeling may be conducted if the experimental data are adequate. Animal bioassay data are generally used for dose-response assessment; however, the risk assessor is normally interested in low environmental exposures of humans, which are generally below the experimentally observable range of responses seen in the animal assays. Thus, low-dose extrapolation and animal-to-human risk extrapolation methods are required and constitute major aspects of dose-response assessment. Human and animal dose rates

are frequently reported in terms of the following abbreviations, which are defined below:

LOEL Lowest observed effect level in mg/kg·day, which produces a statistically or biologically significant effect

LOAEL Lowest observed *adverse* effect level in mg/kg·day, which produces a statistically or biologically significant *adverse* effect

NOEL No observed effect level in mg/kg·day, which does not produce a statistically or biologically significant effect

NOAEL No observed *adverse* effect level in mg/kg·day, which does not produce a statistically or biologically significant *adverse* effect.

Key factors in determining which NOAEL or LOAEL to use in calculating a reference dose (RfD) is exposure duration. As mentioned previously, acute animal studies are typically conducted for up to 7 days, subacute studies for 7 to 30 days, and subchronic studies for 90 days to 1 year. Chronic studies are conducted for a significant portion of the lifetime of the animal. Animals may experience health effects during short-term exposure which may differ from effects observed after long-term exposure, so short-term animal studies less than 90 days should not be used to develop chronic RfDs except for the development of interim RfDs or developmental RfDs. Exceptionally high quality >90 day oral exposure studies may be used as a basis for developing an RfD whereas the inhalation route is preferred for deriving a RfC [15]. Please note that the same approaches used to develop the RfD are used to develop the RfC, the only difference being the route of exposure, animal-to-human dosimetric adjustments, and the units, (i.e., mg/m^3 for the RfC vs mg/kg/day for the RfD).

The highest dose level that does not produce a significantly elevated increase in an adverse response is the NOAEL. The NOAEL from the critical study should be used for criteria development, i.e., the health effect that occurs at the lowest dose. However, if a NOAEL is not available, then the LOAEL can be used if a LOAEL to NOAEL uncertainty factor (UF) is applied. Significance generally refers to both biological and statistical criteria and is dependent on the number of dose levels tested, the number of animals tested at each dose, and the background incidence of the adverse response in the control groups [5]. NOAELs can be used as a basis for risk assessment calculations such as RfDs and acceptable daily intake values (ADI). ADI and RfD values should be viewed as a conservative estimate of levels below which adverse affects would not be expected; exposures at doses greater than the ADI or RfD are associated with an increase probability (but not certainty) of adverse effects [19]. WHO uses ADI values for pesticides and food additives to define "the daily intake of chemical, which during an entire lifetime appears to be without appreciable risk on the basis of all known facts at that time" [5]. In order to remove the value judgments implied by the words "acceptable" and "safety", the ADI and safety factor (SF) terms have been replaced with the terms RfD and UF/modifying factors (MF), respectively. USEPA publishes RfDs and RfCs in either IRIS or in the USEPA's Health Effects Assessment Summary Tables (HEAST). RfDs and ADI values

(Eqs. 1 and 2, respectively) are typically calculated from NOAEL values divided by the UF and/or MF:

$$RfD = \frac{NOAEL}{UF \cdot MF} \tag{1}$$

$$ADI = \frac{NOAEL}{SFs} \tag{2}$$

The uncertainty factor (UF) may range from 1 to 10,000 depending on the nature and quality of the data and is determined by multiplying different UFs together to account for five areas of scientific uncertainty [20]. The UF is primarily used to account for a potential difference between the animal's and human's sensitivity to a particular compound. The UF_H and UF_A accounts for possible intra- and interspecies differences, respectively. As mentioned previously, an UF_S is used to extrapolate from a subchronic duration study to a situation more relevant for chronic study and an UF_L is used to extrapolate from a LOAEL to a NOAEL. An UF_D is used to account for inadequate numbers of animals, incomplete databases, or other experimental limitations. A modifying factor (MF) can be used to account for additional scientific uncertainties. In general, the magnitude of the individual UFs is assigned a value of one, three, or ten, depending on the quality of the studies used in developing the RfD or RfC. This UF is reduced whenever there is experimental evidence of concordance between animal and human pharmacokinetics and when the mechanism of toxicity has been established.

Recently, benchmark dose modeling has been recommended by USEPA instead of the NOAEL approach. Criticism of the NOAEL approach exists because of its limitations, which include the following: i) the NOAEL must be one of the experimental doses tested; ii) once the dose is identified, the remaining doses are irrelevant; iii) larger NOAELs may occur in experiments with few animals thereby resulting in larger RfDs; iv) the NOAEL approach does not identify the actual responses at the NOAEL and will vary based on experimental design. These limitations of the NOAEL approach resulted in the benchmark dose (BMD) method [21]. The dose-response is modeled and the lower confidence bound for a dose (BMDL) at a specified response level, benchmark response (BMR), is calculated [5]. The $BMDL_x$ (with x representing the x percent BMR) is used as an alternative to the NOAEL value for the RfD calculations. Thus, the calculation of the RfD is shown in Eq. (3):

$$RfD = \frac{BMDL_x}{UF \cdot MF} \tag{3}$$

Advantages of the BMD approach includes: i) the ability to account for the full dose-response curve; ii) the inclusion of a measure of variability; iii) the use of responses within the experimental range; iv) the use of a consistent benchmark response level for RfD calculations across studies [5].

2.2.3
Sources of Toxicity Information

There are numerous informational databases or resources that provide risk assessors essential information. USEPA publishes RfDs, RfCs, CSFs, and URFs in the Integrated Risk Information System (IRIS) or in the Health Effects Assessment Summary Tables (HEAST). The information in IRIS followed by HEAST should be used preferentially before all other sources. A recent review of other available resources was published in a special volume of *Toxicology,* vol 157, 2001. Articles by Poore et al. [22] and Brinkhuis [23] provide a thorough review of U.S. government databases such as USEPA's IRIS at http://www.epa.gov/iriswebp/iris/, National Center for Environmental Assessment (NCEA), ATSDR's chemical-specific toxicology profiles and acute, subchronic, and chronic minimal risk levels (MRLs), and HazDat at http://www.atsdr.cdc.gov/hazdat.html, among many other databases. The reviewers provide advise for effective search strategies as well as strategies for finding the appropriate toxicology information resources.

2.3
Exposure Assessment

Exposure occurs when a human contacts a chemical or physical agent. Exposure assessment examines a wide range of exposure parameters pertaining to the environmental scenarios of people who may be exposed to the agent under study. The information considered for the exposure assessment includes monitoring studies of chemical concentration in environmental media and/or food; modeling of environmental fate and transport of contaminants; and information on different activity patterns of different population subgroups. The principal pathways by which exposure occurs, the pattern of exposure, the determination of COPC intake by each pathway, as well as the number of persons and whether there are sensitive subpopulations that need to be evaluated are also included in the evaluation.

2.3.1
Characterization of Exposure Setting

In this step, the assessor characterizes the exposure setting with respect to the general physical characteristics of the site, the site COPCs, and the characteristics of the populations on or near the site. Hazard identification/evaluation consists of sampling and analysis of soil, ground water, surface water, air, and other environmental media at contaminated sites. A common method used in screening substances at a site is by comparison with background levels in soil or ground/surface water [19], determining if a chemical is detected or not and whether the detection limit for that chemical is less than reference concentrations as well as frequency of detection [24]. Once a list of COPCs have been identified at the site, the availability of chemical characteristics such as struc-

ture, solubility, stability, pH sensitivity, electrophilicity, and chemical reactivity and toxicity data are collected and evaluated to ascertain the nature of health effects associated with exposure to these chemicals. In many cases, toxicity information on chemicals is limited. Knowing the COPC's characteristics can represent important information for hazard identification [5]. Also, SARs are useful in assessing the relative toxicity of chemically related compounds.

2.3.2 Identification of Exposure Pathways

During this phase of exposure assessment, the major pathways by which the previously identified populations may be exposed are identified. Therefore, locations of contaminated media, sources of release, fate and transport of COPCs, pathways and exposure points, routes of exposure (i.e., ingestion of drinking water, dermal contact when showering) and location and activities of the potentially exposed population are explored. For example, the common on-site pathways evaluated when conducting a RCRA remediation baseline risk assessment where unauthorized chemical releases have occurred includes direct contact with soil either by ingestion of soil and/or inhalation of volatile chemicals or contaminated dust [19]. The migration of chemicals off-site can occur via wind-blown dust and vapor emissions from soil, leaching of chemicals to ground water with subsequent movement off-site, and run-off surface water. These off-site chemicals can eventually accumulate in other transport media such that the COPC ends up in vegetation crops, meat, milk, and fish that will eventually be consumed by humans. Therefore, pathways, sources of release, locations of contaminated media, fate and transport of COPCs, and location and activities of the potentially exposed population are explored. Exposure points and routes of exposure (ingestion, inhalation) are identified for each exposure pathway. It is necessary to identify populations likely to receive especially high exposure and populations likely to be unusually sensitive to the chemical's effects. An example of possible point of exposures and exposure routes due to exposure to ground water or surface water (i.e., source medium) used for drinking water is shown in Table 5. Please note that all of these exposure path-

Table 5 Possible points of exposure and exposure routes of ground and surface water used as drinking water

Source medium	Transport of chemical	Point of exposure	Route of exposure
Drinking water	NA	Water	Ingestion
Drinking water	Showering/bathing/etc.	Water	Dermal contact
Drinking water	Showering/bathing/etc.	Air	Inhalation
Drinking water	Washing/cooking	Food	Ingestion
Drinking water	Volatilization from water into enclosed space	Air	Inhalation

ways are typically not evaluated when doing a risk assessment on contaminated drinking water since the techniques and exposure parameters for evaluating these routes of exposure are not well developed. Additional pathways to consider for surface water may include recreational exposures (i.e., swimming, boating), ingestion of contaminated fish, shellfish, etc., and dermal exposure to contaminated sediment.

Finally, an attempt should be made to develop a number of exposure scenarios. Exposure scenarios are a combination of "exposure pathways" to which a single "receptor" may be subjected [25]. For example, a residential adult or child receptor may be exposed to all the exposure routes in Table 5 (i.e., drinking water, showering/bathing, washing/cooking food, and volatilization from ground water or drinking water into an enclosed space). An industrial receptor may only be exposed through the drinking water pathway and volatilization from ground water into an enclosed space and not be exposed through showering/bathing or washing/cooking, because these activities are not allowed at an industrial site. Exposure scenarios are generally conservative and not intended to be entirely representative of actual scenarios at all sites. The scenarios allow for standardized and reproducible evaluation of risks across most sites and land use areas [25]. Conservatism allows for protection of potential receptors not directly evaluated such as special subpopulations and regionally specific land uses.

2.3.3 Quantification of Exposure

The magnitude, frequency and duration of exposure for each pathway are next evaluated. For each potential exposure pathway, the chemical doses received by each exposure route needs to be calculated.

2.3.3.1 Estimation of Exposure Concentrations

Because chemical concentrations can vary, many different studies might be required to get a complete picture of the chemical's distribution patterns within the environment. Off-site sampling and analysis are preferred methods to determine the exposure concentrations in the environmental media at the point of exposure. Because sampling data forms the foundation of a risk assessment, it is important that site investigation activities are designed and implemented with the overall goals of the risk assessment to be performed [19]. For example, it is essential that appropriate analytical methods with proper quality assurance/quality control documentation be employed and that the analytical methods are sensitive enough to detect the COPC at concentrations that are below health protective reference concentrations. After the sampling data is collected and evaluated, then statistical techniques may be used to calculate the representative concentration of COPCs that will be contacted over the exposure area. Different statistical techniques may be required for the determination of

representative concentrations in ground water vs surface water [24]. Fate and transport models can be used to estimate current concentrations in media and/or at locations for which sampling was not conducted. In addition, an increase in future chemical concentrations in media that are currently contaminated or that may become contaminated can be predicted by fate and transport modeling. Detailed discussions of these models are contained elsewhere in this book.

2.3.3.2 Calculation of Intakes

Each scenario described in the exposure assessment should be accompanied by an estimated exposure dose for each pathway. Once the exposure pathway is determined, then the estimated risks and hazards from each exposure pathway can be characterized. Exposure estimates for the oral pathway are expressed in terms of the mass of substance in contact with the body per unit body weight per unit time (i.e., intakes) whereas exposure estimates from inhalation pathways are expressed as mass of substance per unit volume (i.e., inhalation concentrations).

The general equation for calculating intakes (mg/kg/day) is as follows [24]:

$$I = \frac{C \cdot CR \cdot EF \cdot ED}{BW \cdot AT} \tag{4}$$

where

I Intake, the amount of chemical at the exchange boundary (mg/kg body weight-day)
C COPC concentration, average concentration contacted over the exposure period
CR Contact rate, the amount of contaminated medium contacted per unit time or event
EF Exposure frequency (days/year)
ED Exposure duration (years)
BW Body weight, the average body weight over the exposure period (kg)
AT Averaging time or period over which exposure is averaged (days).

Each exposure pathway has slightly different variations of the above basic equation. Please refer to Appendix A for examples of equations used to calculate intakes for the major exposure pathway from ground and surface waters as well as examples of exposure parameters employed to calculate intakes: Appendices A-1 and A-2, ingestion of drinking water; Appendices A-3 and A-4, ingestion of contaminated fish tissue; Appendices A-5 and A-6, dermal contact with contaminated water; and Appendix A-7 inhalation of volatiles from contaminated ground water or surface water. Please refer to Kasting and Robinson [26] and Exposure to Contaminants in Drinking Water [27] for additional information on the various issues involved in the assessment of dermal exposure to water.

The exposure parameters (e.g., CR, EF, ED, BW, and AT) for each pathway are derived after an extensive literature review and statistical analysis [28]. For example, information on water ingestion rates, body weights, and fish ingestion rates for adults, children, and pregnant women used to develop the National Ambient Water Quality Criteria were obtained from the following documents: Exposure Factors Handbook [28]; National Health and Nutrition Examination Survey (NHANES III) [29]; and United States Department of Agriculture (USDA) *1994–1996 Continuing Survey of Food Intakes* [30]. Exposure parameters may represent central tendency or average values or maximum or near-maximum values [24]. Science policy decisions that consider the best available data and risk management judgments regarding the population to be protected are both used to choose appropriate exposure parameters. USEPA emphasizes that exposure assessments should strive to achieve an overall dose estimate that represents a "reasonable maximum exposure (RME)." The intent of the RME is to estimate a conservative exposure scenario that is within the range of possible exposures yet well above the average case (above the 90^{th} percentile of the actual distribution). However, estimates that are beyond the true distribution should be avoided. If near maximum or maximum values are chosen for each exposure parameter, then the combination of all maximum values for each exposure parameter would result in an unrealistic assessment of exposure. Using probabilistic risk assessment, Cullen demonstrated that if only two exposure parameters were chosen at maximum or near maximum values, and other parameters were chosen at medium values, than the risk and hazards estimates represented a RME (>99% percentile level) [31]. Risk assessors should identify the most sensitive parameters and use maximum or near-maximum values for one or a few of those variables. Central tendency or average values should be used for all other parameters [24].

When central tendency and/or maximum values are chosen for exposure parameters used to calculate intake for an exposure pathway, single point estimates of risk and hazard are calculated (i.e., a deterministic technique). However, probabilistic techniques like Monte Carlo analysis can be employed to provide different percentile estimates of risk and hazard (i.e., 50^{th} percentile or 95^{th} percentile estimates) as well as to characterize variability and uncertainty in the risk assessment. Monte Carlo simulation is a statistical technique by which a quantity is calculated repeatedly, using randomly selected values from the entire frequency distribution for an exposure parameter or multiple exposure parameters for each calculation. USEPA recommends using computerized Monte Carlo simulations to provide probability distributions for dose and risk estimates by incorporating ranges for individual assumptions rather than a single dose or risk estimate [19]. Using better estimates for the distribution of contaminant levels is a major focus of recent risk assessment research. To obtain such estimates, several techniques, such as generating subjective uncertainty distributions and Monte Carlo composite analyses of parameter uncertainty, have been applied [5]. These are approaches that can provide a

reality check that is useful in generating more realistic exposure estimates [5]. Also, high-end exposure estimates (HEEEs) and theoretical upper-bound estimates (TUBEs) are now recommended for specified populations as well as calculation of exposure for highly exposed individuals [5]. HEEE represents an estimate of the exposure in the upper ninetieth percentile while TUBEs represent exposure levels that exceed exposures experienced by all individuals in the exposure distribution and assume limits for all exposure variables [5]. Please refer to the *Policy for Use of Probabilistic Analysis in Risk Assessment at the USEPA* and *Guiding Principles for Monte Carlo Analysis* at http://www.epa.gov/ncea/mcpolicy.htm [32].

2.4 Risk Characterization

Risk characterization, the last step in the risk assessment process, links the toxicity evaluation (hazard identification and dose-response assessment) to the exposure assessment. Estimates of the upper-bound excess lifetime cancer risk and noncarcinogenic hazard for each pathway, each COPC, and each receptor identified during the exposure assessment are calculated. Another important component of risk characterization is the clear, transparent communication of risk and hazard estimates as well as an uncertainty analysis of those estimates to the risk manager.

2.4.1 Carcinogenic Risk Characterization (Risk Estimates)

Cancer risk is usually expressed as an estimated rate of excess cancers in a population exposed to a COPC for a lifetime or portion of a lifetime [33]. Oral intakes are multiplied by the CSF (Eq. 5), dermal intakes are multiplied by the CSF adjusted for GI absorption (Eq. 6), and lifetime average inhalation concentrations are multiplied by the URF (Eq. 7) to obtain risk estimates.

For evaluating the risk from oral exposure, the intakes from all ingestion pathways can be summed (i.e., ingestion of drinking water, ingestion of fish, etc.), then the total intake is multiplied by the CSF, as follows:

$$Risk_{oral} = Intake_{oral} \cdot CSF \tag{5}$$

where

$Intake_{oral}$ The combined amount of COPC from all oral pathways at the exchange boundary (mg/kg/day) (Appendices A-1 to A-4)

CSF Cancer slope factor $(mg/kg/day)^{-1}$.

For evaluating dermal exposure, the dermally absorbed dose (DAD) is calculated (Appendices A-5 and A-6) and multiplied by an adjusted CSF, CSF_{dermal}. The CSF is typically derived based on oral dose-response relationships that are based on administered dose, whereas the dermal intake estimates are based on

absorbed dose. Therefore, if the CSF is based on an administered dose, it should be adjusted for gastrointestinal absorption, if gastrointestinal absorption is significantly less than 100% (e.g., <50%) [34]. Therefore, if an estimate of the gastrointestinal absorption fraction (ABS_{GI}) is available for the compound and ABS_{GI} is less than 50% [34, 35], then the oral dose-response factor, based on an administered dose, can be converted to an absorbed dose basis by dividing the CSF by the ABS_{GI} to form a CSF_{dermal}:

$$Risk_{dermal} = DAD \cdot CSF_{dermal} \tag{6}$$

where

DAD Dermally absorbed dose (mg/kg/day) (Appendices A-5 and A-6)
CSF_{dermal} Dermal cancer slope factor $(mg/kg/day)^{-1}$; $CSF_{dermal}=(CSF/ABS_{GI})$.

When ABS_{GI} values are not available from Bast and Borges [35] for a compound, then USEPA Region 4 [36] recommends the following defaults for ABS_{GI}: 80% for volatile organics; 50% for semi-volatile organics and non-volatile organics; and 20% for inorganics.

For evaluation of inhalation exposure, the lifetime average inhalation concentration is multiplied by the URF:

$$Risk_{inh} = C_{inh} \cdot URF \cdot 1000\,(\mu g/mg) \tag{7}$$

where

C_{inh} Concentration of COPC at the exchange boundary (mg/m^3) (Appendix A-7)
URF Unit Risk Factor $(\mu g/m^3)^{-1}$.

To obtain a conservative total risk estimate, the risks for an individual COPC from each pathway is summed and then the risks from all COPCs are summed (Eq. 8):

$$Risk_{total} = \sum R_i \tag{8}$$

where

R_{total} Sum of all risk estimates from all i^{th} COPCs from all pathways.

However, USEPA is still developing approaches to deal with the uncertainties associated with combining risk estimates of chemical mixtures across different routes of exposure (i.e., inhalation, oral, and dermal) since differences in the properties of the cells that line the surfaces of the air pathways and the lungs, the gastrointestinal tract and the skin may result in different intake patterns of chemical mixtures components depending on the route of exposure. Another consideration in dealing with chemical mixtures is the chemicals in a mixture may partition to contact media differently [37]. A risk estimate of 1×10^6, 1×10^5, or 1×10^4 is interpreted to mean that an individual has not more than, and likely less than, a 1 in 1,000,000, 1 in 100,000, or 1 in 10,000 chance, respectively, of developing cancer from the exposure being evaluated. The range of carcinogenic risks acceptable by the USEPA is 10^{-6} to 10^{-4}.

2.4.2 Noncarcinogenic Risk Characterization (Hazard Estimates)

For chronic exposures to noncarcinogens, the intake of a COPC is compared to the appropriate RfD (i.e., oral RfD or RfD_{dermal}) or RfC to form the hazard quotient (HQ)[33]. Oral intakes are compared to the RfD (Eq. 9), dermally absorbed doses (DADs) are compared to the RfD_{dermal} (i.e., RfD adjusted for GI absorption refer to the previous section for a discussion of procedures for adjusting toxicity factors for GI absorption) (Eq. 10), and inhalation intakes are compared to the RfC (Eq. 11) to obtained hazard quotients for each route of exposure:

$$HQ_{oral} = \frac{\sum Intake_{oral}}{RfD} \tag{9}$$

where

$Intake_{oral}$ The combined amount of COPC from all oral pathways at the exchange boundary (mg/kg/day) (Appendices A-1 to A-4)
RfD Oral reference dose (mg/kg/day)

$$HQ_{dermal} = \frac{DAD}{RfD_{dermal}} \tag{10}$$

where

DAD Dermally absorbed dose (mg/kg/day) (Appendices A-5 and A-6)
RfD_{dermal} Dermal reference dose (mg/kg/day); $RfD_{dermal}=(RfD \cdot ABS_{GI})$

$$HQ_{inh} = \frac{C_{inh}}{RfC} \tag{11}$$

where [15]:

C_{inh} Concentration of COPC at the exchange boundary (mg/m^3) (Appendix A-7)
RfC Inhalation reference concentration (mg/m^3).

The total hazard index (HI) for an individual COPC from all routes of exposure is the sum of the HQs from all applicable pathways (oral, dermal, or inhalation) (Eq. 12):

$$HI_i = \sum HQ_i \tag{12}$$

where

HI_i The sum of the hazard quotients from all relevant pathway for the i^{th} COPC.

In order to be conservative, a total HI can be calculated by summing the HIs from each individual COPC. "If the overall HI value is less than one, public health risk is considered to be very low"; however, "if the HI value is equal to

or greater than one, then the exposure assessment and hazard characterization should be investigated more thoroughly." If the HI exceeds one, then the hazard estimates may be refined by grouping the COPCs that affect the same target organ or have the same mechanism of action and adding only the HIs from similar-acting COPCs [37, 38]. Ideally, chemicals would be grouped according to effect-specific toxicity criteria, information on chemicals exhibiting multiple effects would be available, and their exact mechanism of action would be known. Instead, RfDs and RfCs are available for just one of the several possible endpoints of toxicity for a chemical and data are often limited to gross toxicological effects in an organ or an entire organ system. The list of these specific endpoints of toxicity is limited so it is best to consult a toxicologist during this step of the hazard evaluation [16]. Each COPC and exposure pathway needs to be calculated to determine the actual risk. The HI provides a rough estimate of possible toxicity and requires careful interpretation [38]. The HI does not account for the number of individuals who might be affected by exposure or the severity of the effects. USEPA recommends that a HI of 1.0 be used for noncancer health effects.

In the "real world", exposures generally involve complex mixtures of COPCs. There are three basic actions for mixtures: i) independent joint action, which describes COPCs that act independently and have different modes of action and are not expected to affect the toxicity of one another; ii) similar joint action or "dose addition," which describes a mixture where the COPCs produce similar but independent effects; iii) synergistic action, which the effective mixture cannot be assessed from the individual ingredients but depends on knowledge of their combined toxicity [39] (Table 3 and Fig. 1). The total HI can exceed the target hazard level as a result of the presence of either one or more COPCs with an HQ exceeding the target hazard level or the summation of several COPC-specific HQs that are each less than the target hazard level.

2.4.3 Uncertainty Analysis

It is important to mention that the numbers generated by risk assessors should not be viewed as either accurate measures or even predictors of rates of adverse health effects in human populations [33]. The calculated estimates are routinely based on assumptions recognized as being conservative. Thus, these numbers should be used as tools open to interpretation on a site-by-site basis. It is important for the risk manager to be informed of the uncertainties during the risk assessment process.

Significant limitations and uncertainties can exist throughout the entire risk assessment process; thus, it is important that a discussion of uncertainty accompanies risk assessment analysis so that the limitations of the quantitative results are taken into consideration. Both qualitative and quantitative methods have been developed to analyze the uncertainty associated with risk assessment. A quantitative analysis may be conducted using either a sensitivity analysis or

a probability analysis. Listed below are the various reasons why uncertainty exists in a risk assessment analysis [4, 19]:

- Deficient control groups
- Difference in smoking habits between an epidemiology study group and a risk group
- Differences or lack of consideration of pharmacokinetics and/or mechanism of toxicity between species
- Failure to diagnose or misdiagnosis the cause of mortality
- Inappropriate experimental study design
- Lack of knowledge regarding combined biological effects of exposure to multiple toxicants
- Limitation in data regarding nature and magnitude of levels in the environment
- Low-dose extrapolation from high-dose experimental conditions
- Reliance on mathematical models
- Toxicant interaction with another agent
- Use of animal studies in the determination of risk for humans

3 Risk Management

It is important to make clear the distinction between risk assessors and risk management. Risk assessors generate risk estimates but a risk manager considers these risk estimates, other scientific information, and integrates it into societal decisions [40]. For example, risk managers consider data analysis, technical concerns, economic concerns, and social/political concerns in addition to comparing the risk estimates to an acceptable level set by federal or state health agencies [40]. Generally, trade-offs or compromises are made for the lowest possible risk and society's demand for jobs and economic growth. Examples of questions that may be asked by risk managers are: "Is a particularly deadly type of cancer in a narrow population worse or better than widespread effects of a non-lethal nature? Can this decision be successfully defended in court?"

In general, risk management decisions may be based more on political and economic factors than risk factors [40]. Risk assessment and risk management are an integral part of the contemporary regulatory scene. Risk management refers to the selections and implementation of the most appropriate regulatory action based on: i) goals; ii) social and political factors; iii) available control technology; iv) costs and benefits; v) results of risk assessment; vi) acceptable risk; vii) acceptable number of cases [4].

Another aspect to consider is cumulative risk in either the risk assessment or risk management phase. Cumulative risk evaluation considers all "involuntary" risk to which a receptor may be exposed by a variety of environmental

risks such as: i) automobile exhaust emissions; ii) leaking underground storage tanks; iii) untreated sewage; iv) agricultural land runoff; v) industrial process air emissions; vi) conventional combustion-related air emissions [41]. However, at the present time, definite guidance from USEPA regarding the evaluation of cumulative risk is not available.

4
Conducting Refined Site-Specific Risk Assessments vs Calculating Media-Specific Benchmark Values

A refined site-specific risk assessment takes into account the specific characteristics concerning the site, all relevant pathways a receptor is exposed to, and other site-specific information. This represents a "forward" calculation method where risk and hazard estimates are calculated. However, each state or USEPA regional office may utilize slightly different exposure factors, exposure scenarios, target risk and hazard levels or different procedures to account for childhood exposure, cumulative risk, etc. It is a very time- and resource-intensive process, which involves numerous scientific policy decisions. However, risk and hazard estimates from a refined site-specific risk assessment typically provide more realistic estimates than a generic screening level risk assessment.

In contrast, media-specific comparison values can be calculated based on a "backward" calculation method based on standardized equations, USEPA toxicity values, standard exposure pathways or scenarios, default exposure factors, and conservative risk and hazard levels. USEPA Office of Water has derived Drinking Water Standards and Health Advisories to evaluate levels of contaminants in public drinking water supplies. To evaluate levels of contaminants in surface water, USEPA publishes guidance documents [42] as well as National Recommended Water Quality Criteria. State and tribal agencies then develop water quality standards for each water body in the state based on USEPA guidance and the use designation for the individual water body. USEPA must review the proposed state water quality standards before they become legally enforceable standards. If Drinking Water Standards and/or state and tribal water quality standards are available for the COPCs present at the site, these standards generally must be used to evaluate human health impacts to groundwater and/or surface water, respectively.

Water quality standards apply to surface waters of the United States, including rivers, streams, lakes, oceans, estuaries, and wetlands. Water quality standards consist, at a minimum, of three elements: 1) the "designated beneficial use" or "uses" of a water body or segment of a water body; 2) the water quality "criteria" necessary to protect the uses of that particular water body; 3) an antidegradation policy. Typical designated beneficial uses of water bodies include public water supply, propagation of fish and wildlife, recreation, agricultural water use, industrial water use and navigation.

Table 6 Examples of protective media-specific comparison values

Agency	Benchmark comparison values	Web address
USEPA Soil Screening Guidance (USEPA 1996)	Soil screening levels	http://www.epa.gov/superfund/resources/soil/index.htm
USEPA Region 3[a]	Risk based concentrations	http://www.epa.gov/reg3hwmd/risk/riskmenu.htm
USEPA Region 6[b]	Human health medium-specific screening levels	http://www.epa.gov/earth1r6/6pd/rcra_c/pd-n/screen.htm
USEPA Region 9[c]	Preliminary remediation goals	http://www.epa.gov/region09/waste/sfund/prg/index.htm
Texas Risk Reduction Program	Protective concentration levels	http://www.tnrcc.state.tx.us/permitting/trrp.htm

[a] Region 3 – Delaware, district of Columbia, Pennsylvania, Virginia, West Virginia.
[b] Region 6 – Arkansas, Louisiana, New Mexico, Oklahoma, Texas, Pueblo of Acoma, Pueblo of Isleta, Pueblo of Nambe, Pueblo of Picuris, Pueblo of Pojoaque, Pueblo of Sandia, Pueblo of San Juan, Pueblo of Santa Clara, Pueblo of Tesuque.
[c] Region 9 – American Samoa, Arizona, California,Guam, Hawaii, Nevada, White Mountain Apache.

If information concerning COPCs is not present in the drinking water and/or state and tribal water standards databases, or additional exposure pathways need to be included during the site assessment, then media-specific comparison values are available from the *Soil Screening Guidance* [16], several USEPA regional offices, and individual state governments (Table 6). These benchmark values may be used as a tool to perform initial site screenings or as initial cleanup goals, if applicable. The different media-specific comparison values are generic, but can be recalculated using more site-specific information and guidance provided on the applicable web addresses (Table 6). However, they usually do not consider all potential human health exposure pathways or consider ecological concerns. Many of the databases listed in Table 6 also provide COPC concentration in soil calculated with fate and transport models that are protective of ground water and surface water. If information concerning COPCs is not present in these databases, or additional exposure pathways need to be included during the site assessment, then a detailed toxicity evaluation

and risk assessment may need to be conducted based on state or other regulatory agency guidelines.

5
Drinking Water Standards and Health Advisories

USEPA was granted authority to set drinking water standards by the Safe Drinking Water Act (SDWA) of 1974. The SDWA has since been amended in 1986 and 1996. The responsibility for implementing drinking water standards is delegated to states and tribes. USEPA is responsible for identifying contaminants to regulate, establishing priorities for contaminants that are of the greatest concern, and then deriving National Primary Drinking Water Regulations.

The SDWA is applicable to public water systems that provide water for human consumption through at least 15 service connections or regularly serve at least 25 individuals. The standards apply to the water delivered to any user of a public water system. The standards are not applicable to private wells, although state and local governments do set rules to protect users of these wells. Owners are urged to test their wells annually for nitrate and coliform bacteria, to test their wells for other compounds if a problem is suspected, and to take precautions to ensure the protection and maintenance of their drinking water supplies. Even though these drinking water standards do not apply to private wells, many states adopt them as ground water standards or use them to evaluate whether concentrations of contaminants in ground water are above a level of concern.

The Office of Water establishes National Primary Drinking Water Standards, Secondary Drinking Water Regulations, as well as Health Advisories. The derivation of these standards, regulations, and Health Advisories are discussed below. The Drinking Water Standards and Health Advisories tables may be reached from the Office of Science and Technology (OST) home page at http://www.epa.gov/OST. The tables are accessed under the OST Programs heading on the OST Home page.

5.1
National Primary Drinking Water Goals and Standards

National Primary Drinking Water Standards are regulations the USEPA sets to control the level of contaminants in the nation's drinking water. Maximum contaminant level goals (MCLGs) are the maximum level of a contaminant in drinking water at which no known or anticipated chronic adverse effect on the health of persons would occur, and which allows an adequate margin of safety. MCLGs are non-enforceable public health goals. Maximum contaminant levels (MCLs) are enforceable standards that are set as close to MCLGs as possible but take into consideration the availability of technology treatments and techniques

as well as whether reliable analytical methods capable of detecting low concentrations of contaminants are available. The derivation of MCLGs and MCLs are discussed in the following sections.

5.1.1 Maximum Contaminant Level Goals

5.1.1.1 Noncarcinogens

For noncarcinogens (not including microbial contaminants), the MCLG is based on the RfD. The definition and derivation of the RfD has been discussed previously. The RfD is first adjusted for an adult with body weight assumed to be 70 kg and consuming 2 L of water per day to produce the Drinking Water Equivalent Level (DWEL):

$$DWEL(mg/L) = \frac{RfD \cdot 70\ kg}{2\ L/d} \tag{13}$$

The DWEL represents the concentration of a substance in drinking water that is not expected to cause any adverse noncarcinogenic health effects in humans over a lifetime of exposure and assumes the only exposure to the chemical comes from drinking water. However, exposure to the chemical can also occur through other pathways and routes of exposure. Therefore, the MCLG is calculated by reducing the DWEL in proportion to the amount of exposure from drinking water relative to other sources (e.g., food, air). In the absence of actual exposure data, this relative source contribution (RSC) is generally assumed to be 20%. The final value is in mg/L and is generally rounded to one significant figure:

$$MCLG(mg/L) = DWEL \cdot RSC \tag{14}$$

5.1.1.2 Carcinogens

If the chemical is considered to be a Class A or B carcinogen, then it is assumed that there is not a dose below which the chemical is considered safe. Therefore, the MCLG is set at zero. If a chemical is a Class C carcinogen and scientific data provides information that there is a threshold below which carcinogenesis does not occur, then the MCLG is set at a level above zero that is safe. Prior to 1996, the MCLG for Class C carcinogens was based on an RfD approach that applied an additional uncertainty factor of 10 to account for possible carcinogenic potential of the chemical. If there weren't any reported noncancer effects, then the MCLG was based on a nominal lifetime excess cancer risk of 10^{-6} to 10^{-5}, if data were adequate. The Office of Water is now moving toward guidance contained in the 1999 draft cancer guidelines [8, 43] which allows standards for nonlin-

ear carcinogens to be derived based on low dose extrapolation and a mode of action approach.

5.1.1.3 Microbial Contaminants

For microbial contaminants that may present public health risk, the MCLG is set at zero because ingesting one protozoa, virus, or bacterium may cause adverse health effects. USEPA is conducting studies to determine whether there is a safe level above zero for some microbial contaminants. So far, however, this has not been established.

5.1.2 Maximum Contaminant Levels

As mentioned previously, Maximum Contaminant Levels (MCLs) are enforceable standards that are set as close to MCLGs as possible but take into consideration the availability of technology treatments and techniques as well as whether reliable analytical methods capable of detecting low concentrations of contaminants are available. If there is not a reliable analytical method, than a treatment technique (TT) is set rather than an MCL. A TT is an enforceable procedure or level of technological performance, which public water systems must follow to ensure control of a contaminant. In addition, MCLs take into account an economic analysis to determine whether the benefits of enforcing the standard justify the costs. For Group A and Group B carcinogens, MCLs are usually promulgated at the 10^{-6} to 10^{-4} risk level.

5.2 Secondary Drinking Water Regulations

Secondary drinking water regulations are non-enforceable Federal guidelines that take into account whether a chemical produces cosmetic effects such as tooth or skin discoloration or aesthetic effects such as affecting the taste, odor, or color of drinking water. Because there are at least 15 different contaminates (i.e., aluminum, chloride, copper, and fluoride) in drinking water that are not considered to be health threatening, secondary maximum contaminant levels (SMCLs) guidelines have been established for public water systems that voluntarily test the water. These secondary standards give the public water systems guidance on removing the contaminants. In most cases, the state health agencies and public water systems often monitor and treat their drinking water for secondary contaminants.

5.3
Health Advisories (HA)

5.3.1
Health Advisories for the Assessment of Noncarcinogenic Risk

In order to provide information and guidance concerning drinking water contaminants for which national regulations currently do not exist, the USEPA Health and Ecological Criteria Division, Office of Water, in cooperation with the Office of Research and Development prepares Health Advisories (HA). These detailed HAs are used to "estimate concentrations of the contaminant in drinking water that are not anticipated to cause any adverse noncarcinogenic health effects over specific exposure durations" [17]. They include a margin of safety to protect sensitive members of the population (e.g., children, the elderly, and pregnant women). HAs are not legally enforceable in the United States, are only used for guidance by Federal, state and local officials, and are subject to change as new information becomes available. Included in the HAs is information on analytical and treatment technologies. HAs are provided for acute or short-term effects as well as chronic effects. The One-day HA, the Ten-day HA and the Longer-term HA are based on the assumption that all exposures to the contaminant comes from drinking water whereas the Lifetime HA takes into account other sources such as food, air, etc. The following types of HAs have been developed [17].

One-day HA – the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to one day of exposure. A one-day HA is generally based on data from acute human or animal studies involving up to 7 days of exposure. The protected individual is assumed to be a 10-kg child with an assumed volume of drinking water (DI) of 1 L ingested/day.

Ten-day HA – the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to ten days of exposure. A Ten-day HA is generally based on subacute animal studies involving 7–30 days of exposure. Similarly to the One-day HA, the protected individual for the Ten-day HA is assumed to be a 10-kg child with an assumed DI of 1 L ingested/day.

Longer-term HA – the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to approximately seven years (10% of an individual's lifetime) of exposure, with a margin of safety. A Longer-term HA is generally based on subchronic animal studies involving 90 days to 1 year of exposure. The protected individual is assumed to be a 10-kg child with an assumed DI of 1 L ingested/day and a 70-kg adult with an assumed DI of 2 l ingested/day.

Lifetime HA – the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure. A Lifetime HA is generally based on chronic or subchronic

animal studies. The protected individual is assumed to be a 70-kg adult with an assumed DI of 2 L ingested/day. A DWEL is calculated and multiplied by a RSC of 20% to account for exposure to drinking water as well as other sources (food, air, etc.). Therefore, the lifetime HA is derived similarly to the MCLG.

The following general formula is used to derive the One-day, Ten-day, and the Longer-term HAs and the DWEL:

$$HA(mg/L) = \frac{RfD \cdot BW}{DI} \tag{15}$$

5.3.2 Health Advisories for the Assessment of Carcinogenic Risk

If a contaminant is recognized as a human or probable human carcinogen (Groups A or B), a carcinogenic slope factor (CSF) is derived based on techniques discussed above. The slope factor is then used to determine the concentrations of the chemical in drinking water that are associated with theoretical upper-bound excess lifetime cancer risks of 10^{-4}, 10^{-5}, or 10^{-6}. The following formula is used to calculate the concentration predicted to contribute an incremental risk level (RL) of 10^{-4}, 10^{-5}, or 10^{-6}:

$$C_{DW}(mg/L) = \frac{RL \cdot 70\ kg}{CSF \cdot 2L/d} \tag{16}$$

where

C_{DW} Concentration in drinking water at desired RL (mg/L)
RL Desired risk level (10^{-4}, 10^{-5}, or 10^{-6})
70 Assumed body weight of adult human (kg)
CSF Carcinogenic potency factor for humans $(mg/kg/day)^{-1}$
2 Assumed water consumption of an adult human (L/day).

If a DWEL was calculated for a Class A, B, or C carcinogen based on an RfD study, (i.e., noncarcinogen), then the carcinogenic risk associated with lifetime exposure to the DWEL can be calculated to assist the risk manager for comparison in assessing the overall risks. The theoretical upper-bound cancer risk associated with lifetime exposure to the DWEL is calculated as follows:

$$Risk = DWEL \cdot \frac{2L/d \cdot CSF}{70\ kg} \tag{17}$$

6
Ambient Water Quality Criteria (AWQC) and State and Tribal Water Quality Standards

6.1
AWQC for the Protection of Human Health

USEPA is required by the Clean Water Act of 1972 to develop, publish, and revise ambient water quality criteria (AWQC). The AWQC "involves the calculation of the maximum water concentration for a pollutant that ensures drinking water and/or fish ingestion exposures will not result in human intake of that pollutant (i.e., the water quality criteria level) in amounts that exceed a specified level based upon the toxicological endpoint of concern" [20]. In October 2000, USEPA issued new guidelines [20] that replaced the 1980 AWQC National Guidelines [44]. The 2000 AWQS Guidelines incorporated significant scientific advances in the following key areas: cancer risk assessment (1986 cancer guidelines [7] vs the 1999 draft cancer guidelines) [8, 43]; risk assessments for Class C carcinogens using nonlinear low-dose extrapolation; non-cancer risk assessments (benchmark dose approach and categorical regression); exposure assessments (consideration of non-water sources of exposures); bioaccumulation in fish (bioaccumulation factors, BAFs, are recommended for all compounds to calculate concentration in fish tissue). In addition, the procedures for deriving AWQC under the CWA were made more consistent to the procedures for deriving MCLG by the SDWA. This section will discuss guidelines from the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health*, hereafter referred to as the AWQC Methodology Guidance [20], accessible at http://www.epa.gov/ost/humanhealth/method/index.html.

State and tribal environmental agencies are responsible for developing ambient water quality standards (AWQS) for each water body in the state based on guidance provided by USEPA [20] and the uses that water bodies have been designated for (i.e., drinking water supply, recreation, or fish protection, etc.). These designated uses are a part of the water quality standards, provide a regulatory goal for the water body and define the level of protection assigned to it. The Watershed Assessment, Tracking&Environmental Results database (WATERS), accessible at http://www.epa.gov/waters/ provides information on the water body designation for each individual state and tribe.

6.1.1
Noncarcinogens and Cancer Effects Evaluated by Nonlinear Low-Dose Extrapolation

The exposure pathways typically evaluated for AWQC are direct ingestion of drinking water obtained from that water body and the consumption of fish/shellfish obtained from that water body. When an AWQC is set, anticipated exposures from other sources of exposure (e.g., food, air) are taken into account

for noncarcinogenic effects, or carcinogenic effects evaluated by the margin of exposure (MOE) approach (i.e., Class C carcinogens, using the 1986 WOE cancer guideline terminology). The amount of exposure attributed to each source compared to total exposure is called the relative source contribution (RSC) for that source. The RSC is typically set at 20% but if a site-specific assessment is conducted for a particular water body and it can be demonstrated that other sources of exposures are not likely to occur, then the RSC can be set as high as 80%. An Exposure Decision Tree Approach is described in the Methodology Guidance to assist in calculating a site-specific RSC for a water body [20]. The allowable dose (typically, the RfD) is then allocated via the RSC approach to ensure that the criterion is protective enough, given the other anticipated sources of exposure:

$$AWQC = RfD \cdot \left[\frac{RSC \cdot BW}{DI \cdot \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right] \tag{18}$$

where

AWQC Ambient Water Quality Criterion (mg/L)
RfD Reference dose for non-cancer effects (mg/kg-day)
RSC Relative source contribution factor to account for non-water sources of exposure – may be either a percentage (multiplied) or amount subtracted, depending on whether multiple criteria are relevant to the chemical
BW Human body weight (default=70 kg for adults)
DI Drinking water intake (default=2 L/day for adults)
FI_i Fish intake at trophic level (TL) i (i=2, 3, and 4) (defaults for total intake=0.0175 kg/day for general adult population and sport anglers, and 0.1424 kg/day for subsistence fishers). Trophic level breakouts for the general adult population and sport anglers are: TL2=0.0038 kg/day; TL3=0.0080 kg/day; and TL4=0.0057 kg/day
BAF_i Bioaccumulation factor at trophic level i (i=2, 3, and 4), lipid normalized (L/kg).

The following equation is used for deriving AWQC for chemicals evaluated with a nonlinear low-dose extrapolation (margin of exposure) based on guidance in the 1999 draft cancer guidelines:

$$AWQC = \frac{POD}{UF} \cdot \left[\frac{RSC \cdot BW}{DI \cdot \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right] \tag{19}$$

where

POD Point of departure for carcinogens based on a nonlinear low-dose extrapolation (mg/kg/day), usually a LOAEL, NOAEL, or LED10
UF Uncertainty Factor for carcinogens based on a nonlinear low-dose extrapolation (unitless).

6.1.2 Carcinogens

For carcinogens, only two water sources (i.e., drinking water and fish ingestion) are considered when AWQC are derived. AWQC for carcinogens are determined with respect to the incremental lifetime risk posed by a substance's presence in water, and is not being set with regard to an individual's total risk from all sources of exposure [20]. The 1986 cancer guidelines are the basis for IRIS risk numbers that were used to derive the current AWQC, except for a few compounds developed using the revised cancer guidelines [14, 45]. Each new assessment applying the principles of the 1999 draft cancer guidelines [8, 43] will be subject to peer review before being used as the basis of revised, updated AWQC. The cancer-based AWQC was calculated using the risk specific dose (RSD) and other input parameters listed below. The RSD and AWQC for carcinogens was calculated for the specific targeted lifetime cancer risk (i.e., 10^{-6}, 10^{-5}, 10^{-4}), using the following two equations:

$$RSD = \frac{Target\ Cancer\ Risk}{CSF} \tag{20}$$

$$AWQC = \frac{RSD \cdot BW}{DI \cdot \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \tag{21}$$

where

RSD	Risk specific dose (mg/kg/day)
Target Cancer Risk	10^{-6}, 10^{-5}, 10^{-4} (lifetime incremental risk)
CSF	Cancer slope factor $(mg/kg\text{-}day)^{-1}$

6.1.3 Adjustments to AWQC by the States and Tribes

Exposure parameters based on a site-specific or regional basis can be substituted to reflect regional or local conditions and/or specific populations of concern. These include the relative source contribution, fish consumption rate, BAF (including factors used to derive BAFs such as concentration of particulate organic carbon applicable to the AWQC (kg/L) or concentration of dissolved organic carbon applicable to the AWQC (kg/L), percent lipid of fish consumed by target population, and species representative of given trophic levels. States and tribes are encouraged to make adjustments using the information and instructions provided in the AWQC Methodology Guidance [20]. The National Water Quality Standards Database (WQSDB) at the web address, http://www.epa.gov/wqsdatabase/, provides access to several WQS reports that provide information about designated uses, water body names, State numeric water quality standards, and EPA recommended numeric water quality crite-

ria. The WQSDB allows users the ability to compare WQS information across the nation using standard reports.

Some states and tribes use an incidental ingestion value (II) instead of DI value when the water body is used for recreational purposes and not as a source of drinking water. However, an II value is not used to develop National AWQC. The default value for II is 0.01 L/day and is assumed to occur from swimming and other activities. The fish intake value is assumed to remain the same.

6.2
AWQC Based on Criteria Other than Human Health

Besides protection of human health, AWQC are developed based on other criteria such as organoleptic effects; aquatic life protection, sediment quality protection, nutrient criteria, microbial pathogens, biocriteria, excessive sedimentation, flow alterations, and wildlife criteria. For example, the National Recommended Water Quality Criteria table (http://www.epa.gov/ost/standards/wqcriteria.html) lists freshwater or saltwater Criteria Maximum Concentration (CMC) criteria values that are the acute limits for the priority pollutant for the protection of aquatic life in freshwater or saltwater. The freshwater or saltwater Criterion Continuous Concentration (CCC) criteria value is the chronic limit for the priority pollutant for the protection of aquatic life in freshwater or saltwater, respectively. The table also includes criteria for organoleptic effects for 23 pollutants developed to prevent undesirable taste and/or odor imparted by them to ambient water. In some cases, a water quality criterion based on organoleptic effects or aquatic life protection would be more stringent than a criterion based on toxicologic endpoints. Information and links to guidance documents relating to these subjects may be reached from the Office of Water, Water Quality Criteria and Standards Program page at http://www.epa.gov/waterscience/standards/.

7
Recycled Hazardous Waste Materials

As more knowledge is gained about the waste generated and disposed in landfills by our society, there is great concern about the toxic effects that this waste has on our environment as well as animal and human health. Over the past decade, there have been numerous attempts to recycle various waste products generated by our society. This section will review some of the recent literature on recycled hazardous waste materials.

7.1
Pavement

Recycled concrete pavement as aggregate for the construction of highways can produce effluent with a high pH that can enter the underwater drains [46].

When Portland cement is recycled, the concrete consists of limestones and minerals where 60–65% is lime (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). $Ca(OH)_2$ is formed sparingly in water and the saturated solution has a pH of 12.45 at 25 °C. The pH of the water effluent in underdrains is approximately 11–12. At this pH, the $CaCO_3$ precipitates out and forms deposits on the screen [46]. The deposition on the screens produces clogging and scales to form in the underdrain; thereby, causing vegetative kill around the outlet.

In addition to recycled concrete, rubber is recycled for asphalt pavements. Recycling of rubber allows a means of disposal of scrap tires and reduces the quantity of construction materials for the asphalt. Asphalt pavement contains hot mix asphalt with and without crumb rubber modifier. The use of rubber tires reduces the weight of the asphalt and provides good drainage media as well as extending the life of the asphalt [47]. While there is an apparent benefit for recycling rubber, it has been found by the Minnesota pollution control agency that leaching can occur from the use of waste tires in subgrade roadbeds into the run-off water. In acidic conditions, leaching of barium, cadmium, lead, chromium, selenium, and zinc occurred from the asphalt while in basic conditions, there was leaching of polynuclear aromatic hydrocarbons. Thus, the recommended allowable levels (RALs) may be exceeded for drinking water standards in areas where there is recycled rubber in the asphalt.

7.2 Paper

Paper or wood itself does not contain any hazardous chemicals unless the paper undergoes recycling. The recycling process requires de-inking of waste paper prior to recovery of the fiber generating a sludge that contains particles of ink and fibers too short to be converted to a finished paper product [48]. The de-inking chemicals such as sulfur, chlorine, cadmium, and fluorine are present in the sludge generated. A sludge is any solid, semi-solid, or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, water supply treatment plant, or air pollution control facility exclusive of treated effluent from a wastewater treatment plant [48]. Thus, hazardous waste can be generated from the recycling paper process.

7.3 Plastic

A commodity used by numerous industries is plastic. Because of the enormous amount of plastic disposed by consumers on a daily basis, it has become a common recycled item at many facilities. Some metal sites will recycle the plastic insulation generated by their facility. The recycled plastic from such a facility generally includes metals such as lead, copper, manganese, and zinc, as well as dioxins, polychlorinated naphthalene, and polychlorinated biphenols. A leachate, contaminated run-off water, from the plastic "fluff" is formed during

the recycling process. The leachate runs off into the water drains carrying hazardous chemical residue into soil and ground water. The plastic fluff is generally recycled on site into tiles, cushions, traffic cones, fenders, and highway barriers. The non-recyclable material and contaminated soil is generally taken to an off-site landfill. Another common way to recycle plastic is to use the "sink-float" process where paper, fiber, and metal can be separated from the plastics and then recycled. The "sink-float" process uses water where the heavy items sink and the light items float [49].

It has been demonstrated that recycled plastics can be used as construction material as an alternative to lumber. This product is made from used bottles collected at curbside for recycling. The recycled plastics undergo sorting to remove unpigmented polyethylene milk/water jugs and polyethylene terephthalate carbonated beverage bottles. The leftover plastic material is referred to as curbside tailings (CT). CT consists of approximately 80% polyolefin (polyethylene and polypropylene) with the remaining percentages made of polyethylene terephthalate, polystyrene, polyvinyl chloride, and other plastics [50]. The CT product has reasonable strength compared to wood. Weis et al. (1992) evaluated three CT recycled plastic formulations in fiddler crabs, snail, and algae [50]. It was found that limb regeneration of the fiddler crabs was accelerated with all three formulations but had no effect on fertilized eggs or larval developments formulations. There was a significant reduction in the sperm fertilization success rate [50]. Furthermore, all three CT plastic formulation did not have an affect on the survival rate of snails or other algal species.

7.4 Metals

The presence of metals in sludge and wastewater is a current problem. For instance, the use of sludge as a fertilizer of agricultural land generally receives cadmium (Cd^{++}) from aerial deposition and phosphatic fertilizers. Cd^{++} is considered a hazardous chemical and has been shown to produce toxicity of the lung and kidney and to be carcinogenic in rats [51]. The highest concentration of Cd^{++} is found in tobacco, lettuce, spinach, and other leafy products/vegetables. Using crop uptake data from field trials, it is possible to relate potential human dietary intake of Cd^{++} on which hazard depends, to soil concentrations of cadmium [52]. Transfer via farm animals to meat and dairy products for human consumption is thought to be minimal even allowing for some direct ingestion of sludge-treated soil by the animals. Background soil contains 0.1 to 1.0 mg Cd^{++}/kg where 90% of cadmium is found in raw sewage that is converted to sludge. After the formation of sludge, 70% of the 90% Cd^{++} is removed primarily by sedimentation.

In order for Cd^{++} uptake in roots to occur, Cd^{++} must be in its soluble form adjacent to the root membrane for some finite period [52]. Generally, a decrease in pH in soil will enhance the solubility of Cd^{++}, which will increase the crop uptake of Cd^{++}. In 1984, WHO/USEPA agreed that the maximum acceptable

daily uptake of Cd^{++} was 70 μg/day. Where 200 μg Cd^{++}/day over a 50-year period would be necessary to produce toxicity to the kidney. Farm animals fed fodder crops grown on sludge-treated soil will absorb ≤5% of the Cd^{++} ingested [52].

In addition to recycling Cd^{++}, lead (Pb)-EDTA wastewater also undergoes recycling. EDTA a chelating agent used in the soil washing process for the decontamination of Pb contaminated soil. Kim et al. [53] outlines a method to recycle Pb-EDTA wastewater by substituting the Pb-EDTA complex with Fe^{3+} ions at a low pH followed by precipitation of Pb ions with phosphate or sulfate ions. Fe^{3+} ions-EDTA will precipitate at a high pH with NaOH. The recycled EDTA solution can be recycled several times without losing its extractive power [53].

7.5
Miscellaneous

7.5.1
Computers

Recycling computers can be extremely hazardous if not properly disposed. There are many parts of the computer that are toxic. To begin with, the cathode ray tube (CRT) glass may be classified as a hazardous waste due to its high Pb concentration. The liquid crystal display (LCD), which contains benzene material for the liquid crystal, is also considered hazardous. In addition, the mercury switch, mercury relay, lithium battery, Ni-H battery, Ni-Cd battery, and polychlorinated biphenyl (PCB) capacitor are all hazardous materials. Because of this, Taiwan has recently established guidelines for the proper disposal of computer and/or computer parts [54]. The nine guidelines are: i) landfill or incineration of scrap computers shall be avoided; ii) the phosphorescent coatings which have been applied to the glass panel of CRT must be removed; iii) ALL the batteries (Li, Ni-Cd, Ni-H) must be removed by non-destructive means; iv) all the PCB capacitors which have a diameter greater than 1 cm and a height larger than 2 cm must be removed; v) all the mercury containing parts must be removed; vi) CRT must be ventilated before stored inside a building; vii) the high-Pb content funnel glass of the CRT must be properly treated; viii) the LCD of notebook computer must be removed by non-destructive means; and lastly, ix) plastic that contains the flame-retardant, bromine, shall be treated properly. Hopefully, this model can be used in other countries where computer waste is becoming a major issue of environmental concern.

7.5.2
Organic Solvents

Organic solvents have many applications in the industry such as formulation of products, thinning of products prior to use or cleaning of materials by

removal of contaminants. During this application, solvent emission and waste solvent generation occur. Most organic solvents are known to have adverse effects on both human health and the environment. Solvents may affect the body through inhalation and skin contact and lead to either acute or chronic poisoning [55]. The effects of acute poisoning include narcosis, irritation of throat, eyes, or skin, dermatitis, and even death and the effects of chronic poisoning include damage to blood, lung, kidney, and gastrointestinal system and/or nervous system. In addition, many solvents are inflammable in nature. Waste management of organic solvents includes: source reduction, recycling, treatment, and disposal [55]. Case studies indicate that dry cleaning facilities use perchloroethylene (PERC) in which workers around the cleaning machines are subject to high health risks; thus, vapor recovery systems are used to reduce the PERC emissions especially from older machines [55].

7.5.3
Flame Retardants

Riess et al. [56] evaluated the recyclability of flame-retarded polymers that contain brominated flame-retardants from 108 televisions (TV) and 78 personal computers (PCs) obtained from a recycling company. The flame-retardants identified in the TV were: 54% high-impact polystyrene, 24% acrylonitrile butadiene styrene, 15% polystyrene, and 7% polyphenyleneoxide polystyrene. The flame retardants found in PCs were: 43% acrylonitrile butadiene styrene, 35% polyphenyleneoxide polystyrene, 18% high-impact polystyrene, 3% polystyrene, and 1% polyvinyl chloride. Recycling may be practical if 75% *new* material is added to mixture [56].

8
Case Studies

8.1
The Denver Potable Reuse Project

The Denver Potable Reuse Pilot Project began in 1968 to recycle wastewater effluent to achieve potable water quality as well as being economically competitive with conventional technology. Moreover, this project sponsored the first large-scale risk assessment studies using experimental animals [57]. After ten years, this pilot project was converted to a demonstration treatment plant to address many of the technical and non-technical issues. The objectives of the "Reuse Demonstration Project were (i) to establish end product safety, (ii) to demonstrate the reliability of the process, (iii) to generate public awareness, (iv) to generate regulatory agency acceptance, and (v) to provide data for a large-scale implementation" [57]. However, insuring end-product water safety proved to be difficult to demonstrate because the health standards established for

drinking water were not intended to apply to treated waters. Thus, additional criteria were used to prove that the effluent was suitable for human consumption. Below were the criteria used in this project:

- The product was compared with the National Primary and Secondary Drinking Water Regulations values
- The product was compared with federal or state regulated parameters
- Effluent levels were compared with the levels suggested to be hazardous
- Concentrations of product in the water were compared to Denver's current drinking water criteria or other "acceptable" water supplies in the U.S. and/or worldwide
- Whole-animal studies (i.e., chronic toxicity, oncogenicity, and reproductive tests) were conducted using Denver's current drinking water as a comparison standard

8.1.1
Testing Protocols for Chronic Toxicity and Carcinogenicity

The Denver Project used two dosage groups per water sample: reclaimed water from the Demonstration Plant with reverse osmosis treatment (ROT) and Denver drinking water from the Foothills Water Treatment Plant (DWT). RO and DW were administered to Fischer 344 rats and $B_6C_3F_1$ mice at dosages at least 500 times the amount found in the original water samples. Ultrafiltration water treatment samples (UFT) were only administered to rats at the high dose (500×) and distilled water was used as the control in both the rats and mice studies. In addition to the chronic toxicity studies, reproductive toxicity studies were performed to identify potential adverse effects on reproductive performance, intrauterine development, and growth and development of the offspring. The teratology phase will identify potential embryotoxicity and teratogenicity.

8.1.2
Results of Testing Protocols

Administration of RO, UFT, and DW water at 500 times the amount found in the original water samples for 104 weeks in rats did not result in any toxicologic or carcinogenic toxicity [57]. The survival rate was slightly higher among the female rats (64%–84%) compared to the male rats (52%–70%). There were a variety of neoplasms seen in all treatment groups (Table 7). The "C" cell tumors in the thyroids were not considered treatment related because these neoplasms were within the anticipated ranges for the age and strain of the rat.

Similar results were seen with the mouse chronic studies where there was no toxicity or carcinogenicity seen after 104 weeks of high dose treatment and the survival rate was identical to the rats. The organs most affected by the treatment were the hematopoietic system, liver, lung, and pituitary gland [57]. The remarkable finding of the reproductive studies was "the absence of treatment-

Table 7 Percentage of representative neoplasms of rats [57]

Neoplasam Site	Male				Female			
	Con	DWT	ROT	UFT	Con	DWT	ROT	UFT
Pituitary								
Adenoma	39%	22%	45%	38%	38%	44%	38%	40%
Carcinoma	0%	2%	0%	0%	0%	0%	0%	0%
Adrenal medulla								
Benign pheochromocytoma	16%	8%	16%	18%	6%	6%	4%	0%
Malignant pheochromocytoma	0%	0%	0%	0%	0%	2%	2%	0%
Thyroid								
Follicular cell adenoma	10%	2%	6%	6%	4%	0%	4%	4%
Follicular cell carcinoma	0%	2%	4%	6%	2%	0%	0%	0%
"C" cell adenoma	4%	18%	6%	10%	8%	8%	17%	4%
"C" cell carcinoma	6%	8%	2%	10%	4%	6%	2%	4%
Hematopoietic neoplasia								
Leukemia, mononuclear	54%	43%	45%	43%	32%	22%	36%	22%
Pancreas								
Islet cell adenoma	6%	2%	8%	6%	0%	44%	0%	40%
Islet cell carcinoma	2%	2%	0%	4%	0%	2%	0%	0%
Testis								
Benign interstitial cell tumor	94%	94%	76%	90%	–	–	–	–
Malignant mesothelioma	2%	2%	4%	8%	–	–	–	–
Uterus								
Endometrial stromal polyp	–	–	–	–	14%	8%	14%	12%
Endometrial stromal sarcoma	–	–	–	–	2%	0%	2%	0%
Mammary gland								
Fibroadenoma	2%	0%	2%	0%	14%	20%	10%	2%

Con=distilled water treatment control.
DWT=Denver drinking water.
ROT=reverse osmosis treatment.
UFT=ultrafiltration water treatment.

related effects on reproductive performance, growth, mating capacity, survival of offspring, or fetal development in any of the treatment groups" [57]. The Denver Project met the outlined objectives at the start of the project and all three of the toxicity studies demonstrated that concentrations 500 times the original amount seen in sample water did not cause any notable toxicity. Thus, secondary wastewater can be recycled into safe drinking water for human consumption.

8.2 Chemical Mixtures

Chemical mixtures have always been an issue of concern to address/assess the toxicity to the environment and to humans. An interagency agreement between ATSDR and the NTP resulted in participation in a Public Health Service (PHS) activity related to the Superfund Act (CERCLA Comprehensive Environmental Response, Compensation and Liability Act) [58]. Yang was the lead scientist at the National Institute of Environmental Health Sciences (NIEHS)/NTP for the development of the "Superfund Toxicology Program". Particular focus centered on chemical mixtures of environmental concern, especially groundwater contaminants derived from hazardous waste disposal and agricultural activities.

Yang states that obtaining a "representative" sample is practically impossible [58]. A core sample from one location of a site will definitely be different from a core sample from a different location of a site. Also, a core sample taken from the exact location at different times of day and/or different days will be different because weather, activity at the site, and composition of the waste can change and degrade or synthesize new compounds. Thus, Yang proposed a strategy to study chemical mixtures [58]:

1. Study chemical mixtures between binary and complex mixtures to avoid duplication of earlier studies that evaluated the two extremes
2. Study chemically defined mixtures to make determination and mechanistic studies manageable
3. Study chemical mixtures related to groundwater contamination because groundwater contamination is among the most critical environmental issue
4. Study chemical mixtures at environmentally realistic concentrations to access the potential health effects of environmental pollution of long-term, low-level exposure
5. Study chemical mixtures with potential for life-time exposure.

A chemical mixture of groundwater contaminants from hazardous waste sites and agricultural activities were created. This formulation mixture contained 25-chemicals that simulated groundwater contamination as shown in Table 8. The concentrations selected represent the average survey values of 180 hazardous waste disposal sites representing all 10 USEPA regions. Even though such a mixture may never exist in reality, new insights may be gained to elucidate potential health effects from laboratory animals to human. For most of the

Table 8 Chemical mixture and the average USEPA survey results in parts per million (ppm) for the studies in the National Toxicology Program Chemical Mixture Program[a]. Adapted from Yang [58]

Chemical (CAS No.)	Average EPA survey values (ppm)
Acetone (67-64-1)	6.9
Arochlor 1260 (11096-82-5)	0.21
Arsenic (7440-38-2) (trioxide)[b]	30.6
Benzene (71-43-2)	5.0
Cadmium (7440-43-9) (acetate hydrate)	0.85
Carbon tetrachloride (56-23-5)	0.54
Chlorobenzene (108-90-7)	0.1
Chloroform (67-66-3)	1.46
Chromium[b] (7440-47-3) (chloride hexahydrate)	0.69
DEHP[c] (117-81-7)	0.13
1,1-Dichloroethane (75-34-3)	0.31
1,2-Dichloroethane (107-06-2)	6.33
1,1-Dichlorothylene (75-35-4)	0.24
1,2-*trans*-Dichloroethylene (156-60-5)	0.73
Ethylbenzene (100-41-4)	0.65
Lead[b] (7439-92-1) (chloride)[b]	37.0
Mercury (7439-97-6)	0.34
Methylene chloride (75-09-2)	11.2
Nickel[b] (7440-02-0) (acetate hydrate)[b]	0.5
Phenol (108-95-2)	3.27
Tetrachloroethylene (127-18-4)	9.68
Toluene (108-88-3)	5.18
1,1,1-Trichloroethane (71-55-6)	1.25
Trichloroethylene (79-01-6)	3.82
Xylenes (1330-20-7)	4.07

[a] The values are average concentrations for each of these chemicals in groundwater samples in and around hazardous waste disposal sites all of the US.

[b] The concentrations (ppm) shown are for the ionic forms of the metal; the respective salts forms are shown in parentheses. CAS numbers are for the ionic forms.

[c] DEHP, Di-(2-ethylhexyl)-phthalate.

end-points examined in this study, the results were negative. The negative results of this study were significant because various mixtures were tested at 10- to 100-fold or several orders of magnitude higher than potential human exposure levels [58].

Insights gained from Yang's project were: i) the effects will be subtle and marginal; ii) toxicologic interactions are possible at the environmentally realistic levels of exposure; iii) toxic responses may be from unconventional toxicologic end-point (immunosuppression, myelotoxicity); iv) possibility of subclinical residual effects may become more interactive with subsequent insults from chemical, physical, and/or biological agents; and v) negative results *do not* in-

dicate safety for humans because the studies were done on rodents. Subsequent work on this mixture at low doses increased the acute toxicity of high doses of known hepatic and renal toxicants [59]. Recently, NIEHS has begun to focus on simpler mixtures of chemicals that share common mechanisms of action rather than complex mixtures.

9
Conclusions

Over the past several decades, much effort has been made to establish national guidance on proper waste handling disposal techniques such that there are many local, state, national and federal agencies that provide guidelines to protect the surface and ground waters for humans. These guidelines also provide methods and approaches used to evaluate potential health effects and assess risks from contaminated source media, (i.e., soil, air, and water) as well as establish standards of exposure or health benchmark values in the different media, which are not expected to produce environmental or human health impacts. The use of the risk assessment methodology by various regulatory agencies using the following steps: i) hazard identification; ii) dose-response assessment; iii) exposure assessment; and iv) risk characterization balances the risks and benefits and sets the "acceptable" target levels of exposure to ground water and surface water.

Appendix A-1. Ingestion of Chemicals in Drinking Water

$$\text{Intake} = \frac{CW \cdot IR \cdot EF \cdot ED}{BW \cdot AT \cdot (365\ days/yr)}$$

Intake =The amount of COPC at the exchange boundary (mg/kg/day)
CW =Chemical concentration in water (mg/L)
IR =Ingestion rate (L/day)
EF =Exposure frequency (days/year)
ED =Exposure duration (years)
BW =Body weight (kg)
AT =Averaging time in years (period over which exposure is averaged)

Exposure parameters[a]

Residential adult	Residential child	Industrial/commercial worker
IR =2 L/day	IR =0.64 L/day	IR =1.4 L/day
EF =350 days/year	EF =350 days/year	EF =250 days/year
ED =30 years	ED =6 years	ED =25 years
BW =70 kg	BW =15 kg	BW =70 kg
AT_c =70 years	AT_c =70 years or age adjusted[b]	AT_c =70 years
AT_{nc} =30 years	AT_{nc} =6 years	AT_{nc} =25 years

[a] The exposure parameters for the residential adult, the residential child, and the industrial/commercial worker were taken from the Texas Risk Reduction Program Rule [60] and are provided as examples only. Different regulatory or state agencies may recommend different exposure parameters based on scientific policy or risk management decisions.

[b] See age adjusted ingestion of carcinogens in drinking water (Appendix A-2).

c=carcinogen, nc=noncarcinogen.

Appendix A-2. Age Adjusted Ingestion of Carcinogens in Drinking Water[a]

$$Intake = \frac{CW \cdot IR_{age\text{-}adjusted} \cdot EF}{AT \cdot (365\ days/yr)}$$

Intake	=The amount of COPC at the exchange boundary (mg/kg/day)
CW	=Chemical concentration in water (mg/L)
$IR_{age\text{-}adjusted}$	=Age adjusted ingestion rate (L-yr/kg-day)
EF	=Exposure frequency (days/year)
AT	=Averaging time in years (period over which exposure is averaged)

Exposure parameters[b]	
IR(age-adjusted)	=0.8 L-yr/kg-day
EF	=350 days/year
AT_c	=70 years

[a] A number of studies has shown that an age-adjusted approach should be used to calculate intakes for children for carcinogens to take into account the difference in ingestion rates, body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 31 years [16].

[b] The exposure parameters were taken from the Texas Risk Reduction Program Rule [60] and are provided as examples only. Different regulatory or state agencies may recommend different exposure parameters based on scientific policy or risk management decisions.

Appendix A-3. Ingestion of Contaminated Fish

$$Intake = \frac{CF \cdot IR \cdot FI \cdot EF \cdot ED}{BW \cdot AT \cdot (365\ days/yr)}$$

Intake =Intake (mg/kg/day)
CF =Chemical concentration in fish (mg/kg) (See Appendix A-4)
IR =Ingestion rate (kg/day) fresh weight (FW)
FI =Fraction ingested from contaminated source (unitless)
EF =Exposure frequency (days/year)
ED =Exposure duration (years)
BW =Body weight (kg)
AT =Averaging time in years (period over which exposure is averaged)

Exposure parameters[a]

Adult recreational fisher and pregnant women		Child recreational fisher		Subsistence fisher	
IR	=17.5 g/day FW	IR_{child}	=156.3 g/day FW[c]	IR	=142.4 g/day FW
IR_{women}	=165.5 g/day FW[b]				
FI	=1	FI	=1	FI	=1
EF	=350 days/year	EF	=350 days/year	EF	=350 days/year
ED	=30 years	ED	=14 years	ED	=30 years
BW	=70 kg	BW	=30 kg	BW	=70 kg
AT_c	=70 years	AT_c	=70 years or age-adjusted[d]	AT_c	=70 years
AT_{nc}	=30 years	AT_{nc}	=14 years	AT_{nc}	=30 years

[a] Fish ingestion rates and body weights are from the *Methodology for deriving ambient water quality criteria for the protection of human health* [20] and are provided as examples only. Different regulatory or state agencies may recommend different exposure parameters based on scientific policy or risk management decisions.

[b] Use only when a RfD is based on developmental toxicity [20].

[c] Use only when a RfD is based on health effects in children [20].

[d] The Office of Water is in the process of preparing an Exposure Assessment Technical Support Document in which an age-adjusted approach will be used to calculate fish intakes for children for carcinogens to take into account the difference in ingestion rates, body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 31 years [20].

Appendix A-4. Calculation of Chemical Concentration in Fish[a]

For COPCs whose log K_{ow}<4.0
$CF = CW \cdot BCF$

For COPCs whose log K_{ow}>4.0
$CF = CW \cdot BAF$

For dioxins, furans, and polychlorinated biphenyls
$CF = C_{sed} \cdot BSAF$

CF =Chemical concentration in fish (mg/kg), fresh weight (FW)
CW =Chemical concentration in water (mg/L)
BCF =Bioconcentration factor (L/kg FW)[b]
BAF =Bioaccumulation factor (L/kg FW)[b]
C_{sed} =Chemical concentration in sediment (mg/kg)
BSAF =Biota-sediment accumulation factor (unitless)[c]

---

[a] Please refer to reference [25] for a detailed discussion of procedures used to calculate chemical concentration in fish. Different regulatory or state agencies may recommend different procedures based on scientific policy or risk management decisions [20, 44].

[b] Please refer to Appendix A-3 of reference [25] for BCF, BAF, and BSAF values and procedures for calculating these values. Also, please refer to [20, 44].

[c] BSAFs are used to account for the transfer of COPCs from the bottom sediment to the lipid in fish [25, 61–63].

Appendix A-5. Dermal Exposure to Compounds in Water

$$DAD = \frac{DA_{event} \cdot EV \cdot EF \cdot ED \cdot SA}{BW \cdot AT \cdot (365\ days/year)}$$

DAD =Dermally absorbed dose (mg/kg/day)
DA_{event} =Absorbed dose per event (mg/cm^2-event) (see Appendix A-6)
A =Skin surface area available for contact (cm^2)
EV =Event frequency (events/day)
EF =Exposure frequency (days/year)
ED =Exposure duration (years)
BW =Body weight (kg)
AT =Averaging time (years)[a]

Showering[b]

	Central	RME Scenario
Event and exposure frequency	1 event/day 350 days/year	1 event/day 350 days/year
Exposure duration	adult – 9 years child – 6 years	adult – 30 years child – 6 years
Skin surface area	adult – 18,000 cm^2 child – 6,600 cm^2	adult – 18,000 cm^2 child – 6,600 cm^2

Swimming[b]

	Central	RME scenario
Event and exposure frequency	Site-specific	Site-specific
Exposure duration	Adult – 9 yrs Child – 6 yrs	Adult – 30 yrs Child – 6 yrs
Skin surface area	Adult – 18,000 cm^2 Child – 6,600 cm^2	Adult – 18,000 cm^2 Child – 6,600 cm^2

[a] For noncarcinogenic effects AT=ED; for carcinogenic effects AT=70 years.
[b] Exhibit 3-2 of the interim dermal guidance document [34]. Different regulatory or state agencies may recommend different exposure parameters based on scientific policy or risk management decisions.

Appendix A-6. Calculation of DA_{event} for Organic and Inorganic Compounds

Organic compounds

Non-steady state[a]

Not applicable for inorganics

If $t_{event} < t^*$, then $DA_{event} = 2FA \cdot K_p \cdot C_v \cdot \sqrt{\frac{6 \cdot \tau \cdot t_{event}}{\pi}}$

Steady state

If $t_{event} > t^*$, then $DA_{event} = FA \cdot K_p \cdot C_v \cdot \left[\frac{t_{event}}{1 + B} + 2\tau\left(\frac{1 + 3B + 3B^2}{(1 + B)^2}\right)\right]$

Inorganic compounds

$DA_{event} = K_p \cdot C_v \cdot t_{event}$

DA_{event} =Absorbed dose per event (mg/cm^2-event)
FA =Fraction absorbed water (dimensionless) [b]
K_p =Dermal permeability coefficient of compound in water (cm/h)[b,c]
C_v =Chemical concentration in water (mg/cm^3)
τ =Lag time per event (h/event)[b]
t_{event} =Event duration (h/event) [d]
t^* =Time to reach steady state (h)[b]
B =Dimensionless ratio measuring the permeability of the stratum corneum relative to the epidermis[b]

---

[a] Short contact times such as swimming, bathing, and showering. Not applicable for inorganics.

[b] Appendix B of the interim dermal guidance document [34] provides chemical-specific values for FA, B, K_p, τ, and t^* for common pollutants and detailed procedures for deriving these values for other organics.

[c] Exhibit 3-1 of the interim dermal guidance document [34] provides K_p values for inorganics. For other inorganics, use a default value of 10^{-3} cm/h.

[d] Central tendency t_{event} values for showering/bathing for the adult and child residential receptor are 0.25 and 0.33 h/event, respectively. RME scenario t_{event} values for showering/bathing for adult and child residential receptors are 0.58 and 1 h/event, respectively [34]. For swimming t_{event} values are determined on a site-specific basis.

Appendix A-7. Calculation of Air Intake

$$C_{inh} = \frac{CW \cdot VF \cdot EF \cdot ED}{AT \cdot (365\ days/year)}$$

Where:
C_{inh} =The concentration of COPC at the exchange boundary (mg/m^3)
CW =Chemical concentration in water (mg/L)
VF =Volatilization factor [$(mg/m^3)/(mg/L\text{-}H_2O)$][a]
EF =Exposure frequency (days/year)[b]
ED =Exposure duration (years)[b]
AT =Averaging time in years (period over which exposure is averaged)[b]

[a] Specific fate and transport models are used to derive volatilization factors to quantify the transfer of volatile COPCs from ground water into an enclosed space, from ground and surface waters into ambient air, etc. These fate and transport models are discussed elsewhere in this book.

[b] The exposure parameters for EF, ED, and AT from Appendix A-1 can be used for the residential adult, residential child, and commercial/industrial worker for some pathways, but site-specific exposure parameters may need to be developed for other pathways.

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Chemodynamics and Multicontaminant Joint Toxicity Modeling of Organic Leachates from Recycled Solid Wastes

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Abstract Chemodynamics (the fate and transport) of leachates from recycled solid waste materials (SWMs) of complex organic mixtures (COMs) is a basic need in environmental planning, restoration and engineering management. Sorption/desorption, an important chemodynamic behavior of leachates, can greatly influence the mobility and bioavailability of compounds from recycled wastes in the multimedia environment. Similar to all interphase mass-transfers, the sorption/desorption process can be defined by the final-phase equilibrium of the contaminant at the aqueous-solid phase interface and the time required to approach final equilibrium. Accordingly, aqueous-solid phase interfaces are significant in determining: (1) the route and rates by which organic contaminants can transfer to and/or from these interfaces, (2) the chemodynamics of contaminants, and (3) their toxicity, genotoxicity and bioavailability to the ambient microorganisms. When the rates of such processes are known, environmental fate modeling can provide an educated estimate and prediction of the accessibility and bioavailability of a target contaminant leached from SWMs to a specific transport mechanism in the environment. Therefore, the present chapter is an attempt to assess fate (in terms of contaminant mobility using predictive sorption or desorption coefficients), as well as effects (in terms of bioavailability) of various contaminants, and to correlate these observations for development of predictive relationships.

To fulfill this general objective, the following interdisciplinary approaches are covered in the present chapter: (1) a review of the most widely used models analyzing sorption/desorption data generated for leachates from recycled SWMs, discussion of their chemical kinetics, and estimates of their transport parameters from laboratory studies; (2) a discussion of the fundamentals of both quantitative structure-activity and structure-property relationships (QSARs and QSPRs, respectively), with special emphasis on using molecular connectivity indices as useful properties to predict contaminant mobility and bioavailability, and (3) a review of the multicomponent (multicontaminant) joint toxic/genotoxic effect models (additivity, synergism, antagonism) used to predict the bioavailable fraction and action of organic contaminants at aqueous-solid phase interfaces. The applicability of these interdisciplinary approaches is discussed and evaluated using a group of toxic and carcinogenic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), which are frequently characterized in most recycled solid wastes of complex organic mixtures.

Keywords Organic contaminants · Desorption · Kinetics · PAHs · QSAR · QSPR · Multicomponent joint effect · Modeling · Highway materials · Leachates

Abbreviations

AI	Additivity index
BET	Brunauer-Emmett-Teller
COMs	Complex organic mixtures
EC_{50}	Ecological concentration at which 50% growth inhibition of *Selenastrum capricornutum* occurs
HOMO	Highest occupied molecular orbital
IAS	Ideal adsorbed solution
K_{OC}	Organic carbon partition coefficient
K_{OW}	Octanol-water partition coefficient
LFER	Linear free energy relationships
LUMO	Lowest unoccupied molecular orbital
MCI	Molecular connectivity index
MOLCONN	Molecular connectivity
MTI	Mixture toxicity index
PAHs	Polycyclic aromatic hydrocarbons

PCA	Principal component analysis
QSAR	Quantitative structure-activity relationship
QSPR	Quantitative structure-property relationship
SAR	Structure-activity relationship
SCAM	Simplified competitive equilibrium adsorption model
SCS	Single component system
SWMs	Solid waste materials
TU	Toxic unit

1 Introduction

Chemodynamics studies of contaminants leached from recycled/disposed solid waste materials (SWMs) of complex organic mixtures (COMs) can investigate the fate and transport of these contaminants in various environmental compartments. Many of these contaminants have been shown to be toxic, genotoxic and/or carcinogenic in both surface/subsurface and aquatic environments [1]. During SWM leachate transport through surface/subsurface environments, physical/chemical processes can result in the accumulation of contaminants on the solid (soil, sediments) phase constituents. The degree to which this accumulation renders the trapped contaminants immobile is of vital interest in considerations for modeling the proposed contaminant fate and transport.

The behavior of organic contaminants in the aqueous-solid phase environment is governed mainly by both physical/chemical properties of such compounds and a variety of complex processes, the most important of which are sorption and desorption (leaching). Sorption/desorption processes can influence the mobility and biological activity (the bioavailability) of many contaminants leached from SWMs. Degradation, another chemodynamical behavior, can either be enhanced or impeded by sorption/desorption depending on the exact nature of the degradation process. Accordingly, sorption/desorption investigations have received remarkable attention.

The present chapter is an attempt to introduce an advanced modeling approach which combines the physical and chemical properties of contaminants, quantitative structure-activity and structure-property relationships (QSARs and QSPRs, respectively), and the multicomponent (multicontaminant) joint toxic effect in order to predict the sorption/desorption coefficients, and to determine the bioavailable fraction and the action of various organic contaminants at the aqueous-solid phase interface.

The goals of the present chapter are to: (1) review the most widely used models used for analyzing sorption/desorption data generated for leachates from recycled SWMs, discuss their chemical kinetics, and estimate their transport parameters from laboratory data; (2) discuss the fundamentals of QSARs and QSPRs, with special emphasis on using molecular connectivity indices as useful properties to predict contaminant mobility and bioavailability; (3) review

different multicomponent joint action models which cover additivity, synergism, and antagonism that help predict the bioavailable fraction and action of organic contaminants at aqueous-solid phase interfaces, and (4) apply, use and evaluate these interdisciplinary approaches on a group of toxic and carcinogenic organic contaminants (PAHs) frequently characterized and identified in most SWMs of COMs.

2
Sorption/Desorption Chemodynamics

A number of models (see other chapters in the present book) have been developed to reflect the actual sorption/desorption processes that occur in the natural environment [1–6]. Some models have a sound theoretical basis; however, they may have only limited experimental utility because the assumptions involved in the development of the relationship apply only to a limited number of sorption/desorption processes. Other models are more empirical in their derivation, but tend to be more generally applicable. In the latter case, the theoretical basis is uncertain.

2.1
Single Component System Models

Single component system (SCS) sorption models actually mean one contaminant component in an aqueous system or in a SWM leachate [34]. Since water is simply assumed to be inert, and the contaminant/leachate sorption is assumed to be unaffected by water, the system is therefore treated as a SCS. To represent the equilibrium relation for SCS sorption, a number of models reported in the literature [2–10] and discussed in various chapters of the present book are summarized in Table 1 (see Eqs. 1 to 11).

2.2
Multicomponent Equilibria Models

Multicomponent contaminants in leachates from of SWMs of COMs usually consist of more than one contaminant in the exposed environment [1, 11–14]. Multicomponent adsorption involves competition among contaminants to occupy the limited adsorbent surface available and the interactions between different adsorbates. A number of models have been developed to predict multicomponent adsorption equilibria using information from SCS adsorption isotherms (Sect. 2.1, Table 1). For simple systems considerable success has been achieved but there is still no established method with universal proven applicability, and this problem remains one of the more challenging obstacles to the development of improved methods of process design [15–17]. Table 2 summarizes the different

Table 1 Single component system isotherm models

Model	Description	Final equation
Langmuir	– The model describes the equilibrium between aqueous and solid phase systems as a reversible chemical equilibrium between species – The model assumes the following: (a) the adsorption energy is constant and independent of the extent of surface coverage, (b) adsorption is on localized sites with no interaction between adsorbed molecules, and (c) the maximum adsorption possible is a complete monolayer – The adsorbent surface (solid phase) is made up of fixed individual sites where molecules of adsorbate (the organic contaminant of interest) may be chemically bound	$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q}$ (1) Where: C = the equilibrium concentration in solution q = the number of moles of adsorbate per mass adsorbent at equilibrium Q = the maximum number of moles of a contaminant adsorbed per mass adsorbent when the surface sites are saturated with an adsorbate b = an equilibrium constant
Double-reciprocal Langmuir	– The model is an adaptation of the traditional equation for elemental sorption of solid phases exhibiting two primary adsorbing surface sites – The basic assumptions for application of graphic isotherm and regression equations are that the data: (a) be derived under equilibrium conditions, constant temperature, and minimal fixation effects, and (b) can be modeled as a regression function	$\frac{q}{Q} = \frac{k_1 \cdot b_1 \cdot C}{(1 + k_f \cdot C)} + \frac{k_2 \cdot b_2 \cdot C}{(1 + k_2 \cdot C)}$ (2) Where: q, Q, and C are defined earlier (see Langmuir model) k_f = constant = $[(q/Q)/C]$ k_1 and k_2 are constants, and b_1 and b_2 are constants (the maximum quantities of the compound that can be sorbed by two surfaces

Table 1 (continued)

Model	Description	Final equation
Brunauer-Emmett-Teller	– The BET model describes multi-layer Langmuir adsorption, which occurs in physical or van der Waals bonding of gases or vapors to solid phases [7] – The model has been applied to the description of adsorption from solid solutions (Eq. 3) – The adsorption of molecules to the surface of particles forms a new surface layer to which additional molecules can adsorb – The main assumption is that the energy of adsorption on all successive layers is equal (see Eq. 4)	$\frac{q}{Q} = \frac{A_m \cdot K_B \cdot C}{(C_s - C) \cdot \left[1 + (K_B \cdot C) \cdot \left(\frac{C}{C_s}\right)\right]}$ (3) Where: A_m = maximum adsorption density of first layer K_B = a dimensionless constant related to the free energy difference between adsorbate on the first and successive layers, and C_s = the saturation concentration of the adsorbate in solution When $K_B \gg 1$ and $(C/C_s) \ll 1$, Eq. 4 may be rearranged to a linear form as: $\left(\frac{C}{C_s - C}\right) = \left(\frac{1}{K_B \cdot A_m}\right) + \left(\frac{K_B - 1}{K_B \cdot A_m}\right)\left(\frac{C}{C_s}\right)$ (4)

Table 1 (continued)

Model	Description	Final equation
Freundlich	– The Langmuir and BET models incorporate an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage – Since in reality the energy of adsorption may vary because real surfaces are heterogeneous, the Freundlich adsorption model attempts to account for Eq. 5 [8] – If log$q$ is plotted as a function of log$C$, a straight line should be obtained with an intercept on the ordinate of log$K$ and slope n	$q = K_f \cdot C^n$ (5) where: C = the equilibrium concentration of the chemical compound of interest in solution K_f = an equilibrium constant indicative of sorption strength n = the degree of non-linearity (when >1, there is no limit to the amount sorbed other than its solubility, which is not expected with a true adsorption process) A linear form of Eq. 5 can be presented as: $\log q = \log K_f + n \cdot \log C$ (6)
Langmuir-Freundlich	– Sips [9] modified the Langmuir adsorption model by introducing a power law expression of the Freundlich Eq. 6 to Eq. 7 – This reduces to the Freundlich equation for low concentrations and exhibits saturation for high concentrations	$q = \frac{Q \cdot b \cdot C^n}{(1 + b \cdot C^n)}$ (7)

Table 1 (continued)

Model	Description	Final equation
Linear	– When the Freundlich isotherm n values approximate one, it indicates a linear relationship between the amount sorbed and the equilibrium concentration in solution – Thus, the distribution of any organic contaminant in the aqueous-solid system can be defined by a simple proportionality constant, as shown in Eq. 8 – A variation of the relationship shown in Eq. 9 is used to account for the contribution of the solid phase organic matter – The relation between the two distribution constants (Eqs. 8 and 9) can be expressed as Eq. 10	$q = K_d \cdot C$ (8) Where: K_d is a simple measure of the distribution of an organic contaminant between the two phases. $q = K_{om} \cdot C$ (9) Where: the amount of the sorbed organic contaminant is expressed per unit of organic matter on the solid phase rather than per unit mass of solid phase $K_{om} = \frac{(K_d) \cdot (100)}{(\%\ \text{Organic Matter})}$ (10)

Table 1 (continued)

Model	Description	Final equation
Toth	- The model has only considered adsorption of gases but it can be extended to adsorption of solutes from dilute aqueous solution [10] - The model has the form shown in Eq. 11 - The Toth model reduces to Henry's law at very low concentrations and exhibits saturation at high concentrations	$q = \frac{QC}{(b + C^M)^{1/M}}$ (11) Where: C = the equilibrium concentration of the chemical compound of interest in solution Q = the maximum number of moles of a contaminant adsorbed per mass adsorbent Q = the number of moles of adsorbate per mass adsorbent at equilibrium

Table 2 Multicomponent equilibria models

Model	Description	Final equation
Multicomponent Langmuir	– The model [18] is based on the same assumptions as the Langmuir model for single adsorbates, assuming that the rate of adsorption of a species at equilibrium is equal to its desorption rate (Eq. 12) – Because of its mathematical simplicity, the multicomponent Langmuir model is wi dely used [19–24] – The extension of the Langmuir theory to adsorption from binary adsorbate systems is thermodynamically consistent only in the special case where $Q_1=Q_2$ – The thermodynamic consistency is of secondary importance if Eq. 12 provides the correct analytical description of the adsorption phenomena	$q_i = \frac{Q_i \cdot b_i \cdot C_i}{1 + \sum_{i=1}^{n} b_i \cdot C_i}$ (12) Where: Q_i and b_i are the Langmuir constants determined from the single solute adsorption isotherm of species i (Eq. 1).

Table 2 (continued)

Model	Description	Final equation
Modified multicomponent Langmuir	- The Langmuir model for competitive adsorption satisfactorily predicts the extent of adsorption from a bi-solute system when $Q_1 \neq Q_2$, probably due to the competition for all available sites [25] - The modified multicomponent Langmuir model was developed to predict the extent of adsorption of each species from a bi-solute solution if a portion of the adsorption occurs without competition [25] - The model is based on the hypothesis that adsorption without competition occurs when $Q_1 \neq Q_2$ [22–24] - The main assumption is that the number of sites on solid phases for which there is no competition is equal to the quantity $(Q_1 - Q_2)$, where $Q_1 > Q_2$ (see Eqs. 13 and 14)	$q_1 = \left[\frac{(Q_1 - Q_2) \cdot b_1 \cdot C_1}{1 + b_1 \cdot C_1} + \frac{Q_2 \cdot b_1 \cdot C_1}{1 + b_1 \cdot C_1 + b_2 \cdot C_2} \right]$ (13) $q_2 = \left[\frac{Q_2 \cdot b_2 \cdot C_2}{1 + b_1 \cdot C_1 + b_2 \cdot C_2} \right]$ (14) Where: - The first term on the right side of Eq. 13 is the Langmuir expression for the number of moles of species 1 which adsorb without competition on the surface area proportional to $(Q_1 - Q_2)$ - The second term represents the number of moles of species 1 adsorbed on the surface area proportional to Q_2 under competition with species 2 and is based on the Langmuir model for competitive adsorption - The number of moles of species 2 adsorbed on the surface area proportional to Q_2 and under competition with species 1 can be calculated from Eq. 14

Table 2 (continued)

Model	Description	Final equation
Multi-component Langmuir-Freundlich	– The Sips [9] model (Table 1, Eq. 7) can easily be extended to binary or multicomponent systems (Eq. 15 [15, 17]) – The simple formula makes this method very attractive – Although not thermodynamically consistent, Eq. 15 has been shown to provide a reasonably good empirical correlation of binary equilibrium data for a number of simple gases on molecular sieve adsorbents [15, 17]	$q_i = \frac{Q_i \cdot b_i \cdot C_i^{n_i}}{1 + \sum b_i \cdot C_i^{n_i}}$ (15)

Table 2 (continued)

Model	Description	Final equation
Ideal adsorbed solution	- The ideal adsorbed solution (IAS) model relies on the assumption that the adsorbed phase forms an ideal solution and hence the name IAS model has been adopted (Eqs. 16 and 17) - The application of the IAS model necessitates only single-solute data and the model is flexible in that multi-component calculations can be performed using several different single-solute isotherm relationships - The model has a solid theoretical foundation, providing a useful understanding of the thermodynamic approach to adsorption - The IAS model is most reliable for those systems where solute adsorption loading is moderate (if solute adsorption loading is large, the deviations of the predictions from experimentally observed data may be significant) [5, 15, 26, 27]	- The IAS model relates the concentration of solute i in a complex mixture (C_1) to a corresponding concentration of this solute in an single solute system (C^o): $C_i = (\prod, T, Z_i) = Z_i C_i^o (\prod, T)$ (16) Where: Z_i = the mole fraction of surface coverage by component i, $\prod$ = the spreading pressure on the surface, and T = the absolute temperature - The spreading pressure defines the lowering of surface tension at the aqueous-solid phase (adsorbate-solution) interface: $\prod = \gamma^o - \gamma$ (17) Where: γ^o = the surface tension of the pure solvent (water), and γ = the surface tension created by the mixture of solvent and solutes

Table 2 (continued)

Model	Description	Final equation
Simplified competitive equilibrium	– A simplified competitive equilibrium adsorption model (SCAM) is based on the Freundlich isotherm, assuming that single-solute isotherms of all the components are equal and it utilizes average isotherm constants when this assumption is not valid – This model (Eq. 18) significantly simplifies the computations of the IAS model, although it does not improve its accuracy [27]	$q_i = K'^{\left(\frac{n'-1}{n'}\right)} = [K_i C_i^{n_i}]^{1/n'} \left[\sum_{i=1}^{N} \left(\frac{K_i}{K} C_i^{n_i}\right)^{1/n'}\right]^{(n'-1)}$ (18) Where: q_i = the solid-phase equilibrium concentration of solute i; n_i, K_i are the empirical Freundlich constants for single solute i; C_i = the liquid-phase equilibrium concentration of solute i; n' = the average value of n_i; and K' = the average value of K_i.

multicomponent equilibria models and includes the following models: Multicomponent Langmuir, Modified Multicomponent Langmuir, Multicomponent Langmuir-Freundlich, Ideal Adsorbed Solution, and Simplified Competitive Equilibrium (see Eqs. 12 to 18 [15–27]).

2.3 Kinetics Processes

Most of the sorption/desorption transformation processes of various solid phases are time-dependent. To understand the dynamic interactions of organic contaminants leached from SWMs and to predict their fate with time, knowledge of the kinetics of these processes is important [1, 28, 29]. There are four main processes (bulk transport, chemical reaction, and film and particle diffusion) that can affect the rates of SWM chemical reactions and can broadly be classified as transport and chemical reaction processes [4, 30–35]. The slowest of these will limit the rate of a particular reaction. A bulk transport process of a certain contaminant(s), which occurs in the aqueous phase, is very rapid and is normally not rate limiting. In the laboratory, it can be eliminated by rapid mixing. The actual chemical reaction at the surface of a solid phase is also rapid and usually not rate limiting. The two remaining transport or mass transfer processes (i.e., film and particle diffusion processes), either singly or in combination, are normally rate-limiting. Film diffusion involves transport of a contaminant through a boundary layer or film (water molecules) that surrounds the solid particle surface. Particle diffusion (intra-particle diffusion) involves transport of a contaminant along pore-wall solid surfaces and/or within the pores of the solid particle surface.

Kassim [1] studied the characterization, chemodynamics and environmental impact assessment of organic leachates from complex mixtures. An important factor in controlling the rate of SWM leaching reactions was reported to be the type and quantity of SWM components as well as the time period (short vs long) over which the organic contaminant has been in contact with the SWM phase.

The main reasons for investigating the rates of SWM leaching processes are to: (1) determine how rapidly reactions attain equilibrium, and (2) infer information on leaching reaction mechanisms. One of the important aspects of chemical kinetics is the establishment of a rate law.

There are four types of rate laws that can be determined for SWM leaching processes [28–29]: mechanistic, apparent, transport with apparent, and transport with mechanistic rate laws, as follows:

- *Mechanistic rate laws* assume that only chemical kinetics is operational and transport phenomena are not occurring. Consequently, it is difficult to determine mechanistic rate laws for most SWM systems due to the heterogeneity of the SWM phase system.
- *Apparent rate laws* include both chemical kinetics and transport-controlled processes. The apparent rate laws and rate coefficients indicate that diffusion and other microscopic transport processes affect the reaction rate.

- *Transport with apparent rate laws* emphasize transport phenomena and assume first-order or zero-order reactions.
- *Transport with mechanistic rate laws* describe simultaneous transport-controlled and chemical kinetics phenomena and explain accurately both the chemistry and the physics of the solid phase system.

To interpret the kinetics experimental data of leachates from COMs, it is necessary to determine the sorption/desorption process steps in a given experimental system which govern the overall adsorption/desorption rate. For instance, the adsorption process of an organic compound leached from recycled SWMs by a porous adsorbent can be categorized into three consecutive steps:

Step 1. The contaminant transport across the boundary layer or surface film to the exterior surface of the adsorbent solid phase particle.
Step 2. The contaminant transport within the pores of the adsorbent solid phase particle, from the exterior of the particle to the interior surfaces of the particle.
Step 3. The physical or chemical binding of the organic contaminant to the interior surface of the adsorbent.

While first-order models have been widely used to describe the kinetics of solid phase sorption/desorption processes, a number of other models have been employed. These include various ordered equations such as zero-order, second-order, fractional-order, Elovich, power function or fractional power, and parabolic diffusion models. A brief discussion of these models is given in Table 3 (see Eqs. 19 to 38 [28, 29, 31, 36, 37]).

2.4 Transport Parameters

Generally, there is no simple and easy theoretical procedure which can provide exact or nearly precise quantitative predictions of what and how much will be sorbed/desorbed by any solid phase over a period of time [9, 38–40]. Understanding sorption/desorption characteristics of any solid phase material requires two main laboratory experimental techniques: (a) batch equilibrium test, and (b) continuous solid phase column-leaching test. These are two completely different kinds of experimental tests, and the sorption characteristics determined from either one should not be confused with the other (see other chapters in the present book). Sorption isotherms are obtained by carrying out batch equilibrium tests and are applied to solid phase suspensions. The physical model that is assumed with this experiment is a system with completely dispersed solid phase particles, where all the solid particle surfaces are exposed and available for interaction with the contaminant of interest. On the other hand, column-leaching tests are performed with intact solid phase samples that have a definite matrix and solid structure. The sorption/desorption characteristics obtained from these tests are required in order to: (a) study soil sorp-

Table 3 Kinetics modeling techniques

Model	Description	Final equation
Zero order	– The relationship between the rate of a chemical reaction, the concentration of a contaminant and the reaction order, n, (in other words, 0, 1, 2), is given by Eq. 19 – Zero order (Eq. 20) is defined where the rate of reaction is independent of the contaminant concentration (the minus sign indicates that the concentration of A is reduced with time) – Half life time of a contaminant is the time it takes the contaminant to react/adsorb to 50% completion or half its initial concentration (Eq. 21)	$r = C^n$ and $\log r = n \log C$ (19) Where: r = rate of the reaction n = order of the reaction C = concentration of contaminant If C represents the concentration of A at any time t, and k_0 is the reaction rate constant then: $-\frac{d[C]}{dt} = k_0$ (20) Integrating: $C = -k_0 t$ + constant when $C = C_0$ at time $t = 0$ $C - C_0 = -k_0 t$ or $C = C_0 \cdot e^{(-k_0 t)}$ (21)

Table 3 (continued)

Model	Description	Final equation
First order	– First order is defined where the rate is directly proportional to the concentration (Eqs. 22–24) – The rate of reaction of a contaminant A for first-order kinetics is as shown in Eq. 22, while the half-life constant is shown in Eqs. 25–26	$-\frac{d[C]}{dt} = k_1 \cdot C$ (22) Where k_1 is the first-order rate constant and C the concentration at any time t. Integrating: $\ln\left(\frac{C_0}{C}\right) = k_1 t$, or (23) $\log\left(\frac{C_0}{C}\right) = \frac{k_1 t}{2.3}$ (24) $\ln\left(\frac{C_0}{C_0/2}\right) = k_1 t_{0.5}$ then (25) $t_{0.5} = \frac{\ln(2)}{k_1} = \frac{0.69}{k_1}$ (26)

Table 3 (continued)

Model	Description	Final equation
Second order	- Second order is defined where the rate is proportional to the square of the concentration (Eqs. 27 and 28) - The rate of reaction of a contaminant A for second-order kinetics is described by Eq. 28, while the half-life constant is shown in Eq. 29	$-\frac{d[C]}{dt} = k_2 \cdot C^2$ (27) Where k_2 is the second-order reaction rate constant. Integrating: $\frac{1}{C} - \frac{1}{C_0} = k_2 t$ (28) $\frac{1}{C_0/2} - \frac{1}{C_0} = k_2 t_{0.5}$ then $t_{0.5} = \frac{1}{k_2 C_0}$ (29)
Elovich	- The Elovich model (Eq. 30) was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surfaces [30, 31] - It describes a number of reaction mechanisms including bulk and surface diffusion, as well as activation and deactivation of catalytic surfaces - A plot of (q_t) vs (ln t) should give a linear relationship if the Elovich model is applicable, with a slope of ($1/\beta$) and an intercept of [($1/\beta$). ln ($\alpha\beta$)]	$q_t = \left(\frac{1}{\beta}\right) \ln\left(\frac{\alpha}{\beta}\right) + \left(\frac{1}{\beta}\right) \ln(t)$ (30) Where: q_t = the amount of sorbate per unit mass of sorbent at time t, and α and β are constants during any one experiment.

Table 3 (continued)

Model	Description	Final equation
Parabolic diffusion	– The parabolic diffusion model (Eq. 31) is used to indicate that diffusion controlled phenomena are rate limiting – It was originally derived based on radial diffusion in a cylinder where the chemical compound concentration on the cylindrical surface was constant, and initially the chemical compound concentration throughout the cylinder was uniform – It was also assumed that the diffusion of the compound of interest through the upper and lower faces of the cylinder was negligible – From Eq. 31, if the parabolic diffusion law is valid, a plot of (q_t/q_∞) versus ($t^{1/2}$) should yield a linear relationship	$\frac{q_t}{q_\infty} = \left(\frac{4}{\pi^{1/2}}\right)\left(\frac{Dt^{1/2}}{r^2}\right) - \left(\frac{Dt}{r^2}\right)$ (31) Where: r = the average radius of the solid particle, q_t = defined earlier, q_∞ = the corresponding quantity of sorbate at equilibrium, and D = the diffusion coefficient.
Fractional power or power function	– The fractional power or power function model can be expressed as shown in Eq. 32 – The model is empirical, except for the case where v=0.5	$q = k\,t^v$ (32) Where: q = the amount of sorbate per unit mass of sorbent, k = constant, t = time, and v = positive constant (<1)

Table 3 (continued)

Model	Description	Final equation
Internal surface diffusion	– An adsorbate can diffuse by two mechanisms within the adsorbent (by pore and surface diffusion). For pore diffusion, the adsorbate is transported within the pore fluid. For surface diffusion, the adsorbate continues to move along the surface of the adsorbent to available adsorption sites as long as it has enough energy to leave its present site – Surface diffusion, in general, is the dominant mechanism, so the contribution of pore diffusion is neglected – The partial differential equation for this model is written in spherical coordinates, as in Eq. 3	$\frac{\partial q(r,t)}{\partial t} = D_S \cdot \left[\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial q(r,t)}{\partial t}\right]$ (33) Where: $q(r,t)$ = the solid-phase concentration along the inner particle surface; r = the radial coordinate with an origin at the particle center; and D_s = the surface diffusion coefficient.
Linear-driving-force approximation	– The surface diffusion model is usually approximated by the linear-driving-force relation (Eq. 34) – If the adsorption isotherm can be expressed by the Langmuir model, i.e, $q^* = \frac{QbC}{(1+bC)}$ and the mass balance $q = \frac{(C_0 - C)}{M}$ is used, Eq. 34 becomes as shown in Eq. 35	$\frac{dq}{dt} = K_p \cdot a(q^* - q)$ (34) Where: $K_p a$ = the mass transfer coefficient, and q = is the solid-phase concentration in equilibrium with the instantaneous fluid-phase concentration outside the particle. $-\frac{dC}{dt} = K_p \cdot a \cdot \left[\frac{MQbC}{(1+bC)}\right] + (C - C_0)$ (35)

Table 3 (continued)

Model	Description	Final equation
Surface reaction	– For the case where surface reaction is the rate controlling step, the rate of adsorption can be expressed as shown in Eqs. 36–38 – The process can be described as molecules leaving a solution and being held on the solid surface by chemical and physical bonding – If the bonds that form between the adsorbate and adsorbent are very strong, the process is almost always irreversible [36, 37], and chemical adsorption (chemisorption) is said to have occurred – On the other hand, if the bonds that are formed are weak, as is characteristic of bonding by dispersion interactions or hydrogen bonding, then physical adsorption (physisorption) has occurred – The molecules adsorbed by physisorption are easily removed or desorbed by a change in the solution concentration of the adsorbate, and for this reason, the process is reversible	$q_{avg} = \left[\frac{3}{(d_p/2)^3}\right] \cdot \int_0^{dp/2} q(r,t) \cdot r^2 \cdot dr$ (36) $\frac{dq}{dt} = K_a \cdot \left[C \cdot (Q - q) - \frac{q}{b}\right]$ (37) Where: K_a =the surface reaction rate constant, and Q and b are the Langmuir adsorptive capacity and equilibrium constant, respectively. Using the mass balance $q = \frac{(C_0 - C)}{M}$, Eq. 33 changes to: $-\frac{dC}{dt} = K_a\left[C \cdot (QM - C_0 + C) - \frac{1}{b}(C - C_0)\right]$ (38)

tion and desorption of contaminants in complex mixtures and/or leached from SWMs, (b) estimate pore volume numbers required to achieve a specific organic contaminant breakthrough curve, (c) provide information necessary for the retardation parameter calculation required in the contaminant transport equation, and (d) determine the transport parameters that control contaminant migration through the subsurface environment (diffusion/dispersion and diffusion coefficients).

In order to predict contaminant chemodynamics of COMs and/or their leachates, the transport parameters involved in the governing sets of equations that describe the transport process need be defined accurately [1]. In general, methods used to calculate the transport parameters fall into two broad categories: steady and transient states. Steady state methods used to estimate transport parameters [41, 42], require the use of the general fate and transport equations, which include three different techniques: (a) decreasing source concentration, (b) time-lag method, and (c) root time method (see Table 4, which contains Eqs. 39 to 47, and refers to Figs. 1, 2 and 3).

On the other hand, the two most common transient methods of experimentation used to obtain test data for calculations of the transport coefficient (the column-leaching cell and diffusion function) are shown and discussed in Table 5 (which contains Eqs. 48 to 51 and refers to Figs. 4 and 5).

3
Mobility and Bioavailability Modeling

The present section presents an advanced modeling approach which can be applied to predict and determine both the mobility and bioavailability of organic contaminants leached from SWMs. Many physical and chemical properties of organic contaminants can control the relationships between contaminant chemical structures and their properties (QSPR modeling) or their toxic/genotoxic effect (QSAR modeling).

3.1
Physical and Chemical Properties of Contaminants Leached from COMs

Understanding environmental partitioning at aqueous-solid phase interfaces of organic contaminants leached from complex mixtures requires the complete knowledge and analysis of most of the important physical and chemical properties of such compounds. This includes properties such as solubility, equilibrium vapor pressure, Henry's law constant, partition coefficient, as well as pK_a and pK_b values [1]. Such properties can initially help determine, for instance, the sorption-desorption behavior of organic contaminants once they are released, directly and/or indirectly, to the aqueous environment and are then in direct contact with solid phases (see other chapters in the present book for complete discussion).

Table 4 Estimation of transport parameters using steady state methods

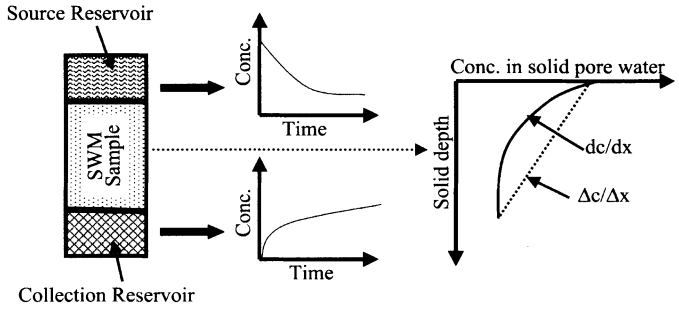
Method	Description	Equation
Decreasing source concentration	– Figure 1 illustrates the decreasing source method for diffusion transport determination of any organic contaminant in solution or leached from COMs. The COM sample is contained between two reservoirs, a source reservoir containing the complex mixture contaminants of interest, and a collection reservoir from which samples are withdrawn for further organic analyses (Fig. 1a). The initial test condition establishes the contaminant concentration to be higher in the source reservoir than in the collection reservoir (Fig. 1b). In this manner, this results in a chemical concentration gradient across the solid phase sample and contaminant diffusion across the sample (Fig. 1c). The test condition does not require replenishment of the contaminants in the source reservoir. Only the solution volumes are kept constant in both source and collection reservoirs. – When the contaminant concentration difference between the source and collection reservoir becomes smaller, the flux rate of contaminants decreases, and a near steady state flux (J_s) is obtained (Fig. 1c). At this time, the diffusion parameter (D) can be calculated using Fick's model as expressed in Eq. 39	 **(a) Column Setup** **(b) During the test** **(c) After the test** **Fig. 1a–c** Schematic diagram illustrating the decreasing source method for diffusion transport determination of any organic contaminant in solution or leached from complex mixtures, as follows: (a) column setup, (b) contaminant concentration versus time in source and collection reservoirs during the test, and (c) contaminant concentration in solid pore water with depth from source after the test

Table 4 (continued)

Method	Description	Equation
Decreasing source concentration	– The use of the difference operator in Eq. 40 implies that the concentration gradient across the sample is linear. However, due to coupled flow processes, the concentration gradient within the sample is non-linear. As a result, the calculated diffusion parameter using the total (across the sample length) concentration gradient may not be the same as that determined using the incremental (along the sample length) distribution of concentration, as might be directly deduced from (c) in Fig. 1c – Since the quantity $\frac{L}{A \cdot \Delta c}$ in Eq. 40 can be measured or set independently of the test, only the change in mass with respect to time $\frac{\Delta m}{\Delta t}$ is measured during the test – At steady state, Eq. 41 can be obtained	$J_s = -D \cdot \frac{\partial c}{\partial x}$ (39) Hence Eq. 40 $D = -\left(\frac{\Delta x}{\Delta c}\right) \cdot J_s = -\left(\frac{L}{\Delta c}\right)\left(\frac{\Delta m}{A \cdot \Delta t}\right) = -\left(\frac{L}{A \cdot \Delta c}\right)\left(\frac{\Delta m}{\Delta t}\right)$ (40) Where: J_s = mass flux D = diffusion parameter L and A are length and cross-sectional area of the soil sample, respectively Δm = change in contaminant mass in an increment of time (Δt). $-\left(\frac{\Delta m}{\Delta t}\right) = \left(\frac{\Delta m_2}{\Delta t}\right) = \left(\frac{\Delta m}{\Delta t}\right)$ (41) Where: Δm_1 = the decrease in mass of the chemical species in the source reservoir; Δm_2 = the increase in mass of the chemical species in the collection reservoir.

Table 4 (continued)

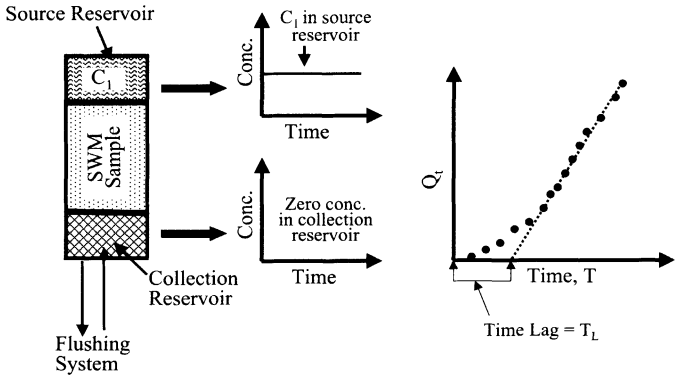
Method	Description	Equation
Time-lag	– This method is used to obtain the diffusion coefficient through porous membranes (Fig. 2) – As in the test set-up shown in Fig. 2a, the SWM sample is contained between the source and collection reservoirs. Using this technique for diffusion coefficient determination of contaminants requires that the following conditions are satisfied: – The concentrations of the organic contaminant species should be higher in the source reservoir than the collection reservoir. – The organic contaminant species diffusing from the source reservoir must be continuously replenished while the mass of the organic contaminant species diffusing into the collection reservoir is continuously removed in order to maintain a constant concentration difference across the sample. This is shown as the contaminant flushing system in Figs. 2a,b. – The total amount of diffusing substance per cross-sectional area (Q_t) that has passed through the solids approaches a steady state value as (t) approaches infinity [43]. Equation 42 yields a straight line on a plot of Q_t versus time, as shown in Fig. 2c. – The diffusion coefficient (D) can be calculated using Eq. 43 by plotting Q_t versus time and determining the value for the intercept T_L.	 **(a) Column Setup** **(b) During the test** **(c) After the test** **Fig. 2a–c** Schematic diagram illustrating the time-lag method for determination of diffusion transport of organic contaminants, as follows: (**a**) column setup, (**b**) contaminant concentration versus time in source and collection reservoirs during the test, and (**c**) Σ amount of contaminants (Q_t) transported through solid particles with time after the test

Table 4 (continued)

Method	Description	Equation
Time-lag		$Q_t = \left(\frac{Dc_1}{L}\right)\left(t - \frac{L^2}{6D}\right)$ (42) Where: L = length of test sample, C_1 = concentration in the source reservoir, which is maintained at a constant value with time.The intercept on the time axis is the time lag (T_L), which is given by: $T_L = \left(\frac{L^2}{6D}\right)$ (43)
Root time	- The procedure used for computing the diffusion coefficient utilizes the analytical solution of the differential equation of solute transport in solids (the diffusion-dispersion equation) as given by Eq. 44 [44] - Equation 44 is converted first to a non-dimensional form and the Fourier Transform Series is used to solve the differential equation for specified initial and boundary conditions. The final solution of Eq. 44 in a non-dimensional form is given by Eq. 45, while the relative change in concentration is given by Eq. 46	$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) - v_x\left(\frac{\partial c}{\partial x}\right)$ (44) Where v_x=the advective velocity. $c^*(\zeta, \tau) \sim (1 - \zeta) - \frac{1}{\pi} e^{-\pi^2 \tau} \cdot \sin(\pi\zeta)$ (45)

Table 4 (continued)

Method	Description	Equation
Root time	– The test, theoretical relationship between the non-dimensional relative concentration (c^*_{RC}) and the root time factor (τ) is shown in Fig. 3. – Data analyses of results were obtained from the diffusion experiment shown in Figs. 3a,b, using the information from solution of Eq. 46. The theoretical correlation in Fig. 5c shows a linear relationship up to a relative concentration of 0.2 (80% equilibrium). At a relative concentration of 0.1 (90% equilibrium), the abscissa is used to determine the point on the experimental curve corresponding to a relative concentration of 0.1 (90% of the steady state equilibrium time). – When the data obtained from the experimental system shown in Fig. 3 are reduced in terms of relative concentrations of specific ions in the collected effluent versus square-root time, the experimental curve obtained shows a linear portion, followed by a curve (Fig. 3d). The point (D) corresponding to the initial condition is obtained by projecting the linear part of the curve to zero time. A straight line (DE) is then drawn having abscissa 1.055 times the corresponding abscissa on the linear portion of the experimental plot. The intersection of the line (DE) with the experimental plot locates the point (t_{90}) corresponding to a relative concentration of 0.1 and the corresponding value t_{90} can be obtained.	Where: $t = \left(\frac{Dt}{L^2}\right)$; $c^* = \left(\frac{c - c_2}{c_1 - c_2}\right)$; and $\zeta = \frac{x}{L}$ $c^*_{RC} = e^{-\pi^2 \tau}$ (46) where: τ = non-dimensional time factor, ζ = non-dimensional distance; c^* = non-dimensional concentration; c = concentration at specific time and distance; c_1 = concentration at x=0; c_2 = concentration at x=L, and L = length of soil specimen.

Table 4 (continued)

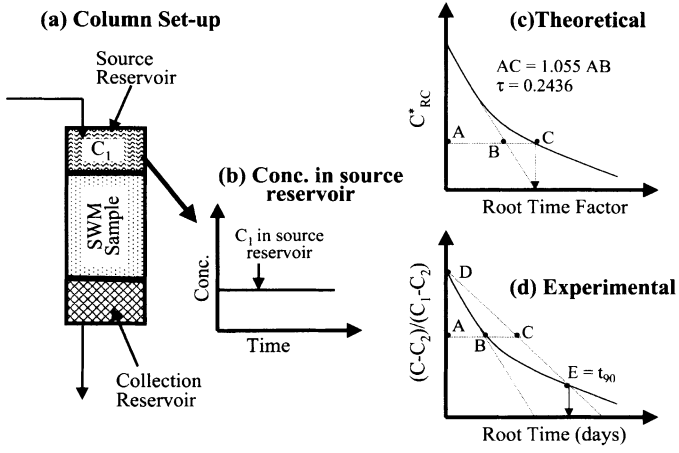
Method	Description	Equation
Root time	– The value of τ corresponding to c^*_{RC}=0.1 is 0.2436 and the diffusion coefficient (D) is given by Eq. 47 – The method is applicable for the situation where adsorption and desorption occur, and for various pH values of the influent. The closer (DE) is to (DB) in Fig. 3d, the greater the accuracy of the D coefficient	

Fig. 3 The theoretical relationship between the nondimensional relative concentration (c^*_{RC}) and the root time factor (τ)

$$D = 0.2436\left(\frac{L^2}{t_{90}}\right) \tag{47}$$

Table 5 Estimation of transport parameters using transient methods

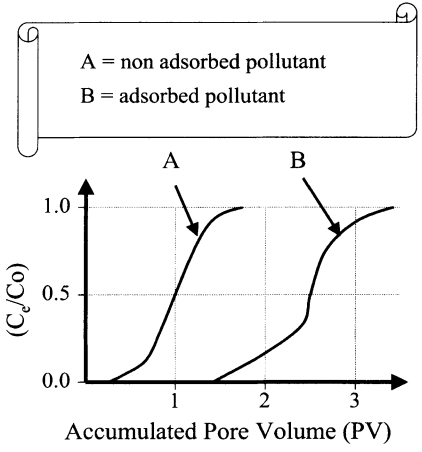
Method	Description	Equation
Column-leaching cell	- During the performance of the leaching experiment, a steady-state flow through the solid phase sample will be established using distilled water as the influent fluid (Fig. 4). - After steady-state flow has been established, the fluid in the influent reservoir is changed to the test solution (the contaminant of interest or leachate), with known and constant concentrations (C_o's) of the various contaminant constituents of the COMs to be tested as a mix leachate. - The effluent concentration (C_e) is determined as a function of time and pore volumes (PV), and the data reduced in the form of breakthrough curves, of relative concentration (C_e/C_o) versus time or pore volumes of flow (Fig. 4). - Breakthrough curves such as those illustrated in Fig. 6 are typically analyzed using the following analytical solution for Eq. 48 [44]	

Fig. 4 General column-leaching cell methods, with their breakthrough curves

Table 5 (continued)

Method	Description	Equation
Column-leaching cell		$\left(\frac{c_e}{c_0}\right) = 0.5\left[erfc\left(\frac{L - vt}{2 \cdot (Dt)^{0.5}}\right) + \exp\left(\frac{vL}{D}\right) erfc\left(\frac{L + vt}{2 \cdot (Dt)^{0.5}}\right)\right]$ (48)
		Where: L = the length of the soil column, v = advective velocity, t = time, and erfc = the complementary error function.
		For any argument z, the erfc is given by Eq. 49: $erfc(z) = 1 - erfc(z) = 1 - \frac{2}{(\pi)^{0.5}} \int_0^z e^{-u^2} du$ $= 1 - \frac{2}{\pi}\left(z - \frac{z^3}{3X1!} - \frac{z^5}{5X2!} - \frac{z^7}{7X3!} + \ldots\right)$ (49)
		Where: erf(z)=the error function of the argument (z). The diffusion coefficient can then be calculated once C_e, C_o, v, L and t are known

Table 5 (continued)

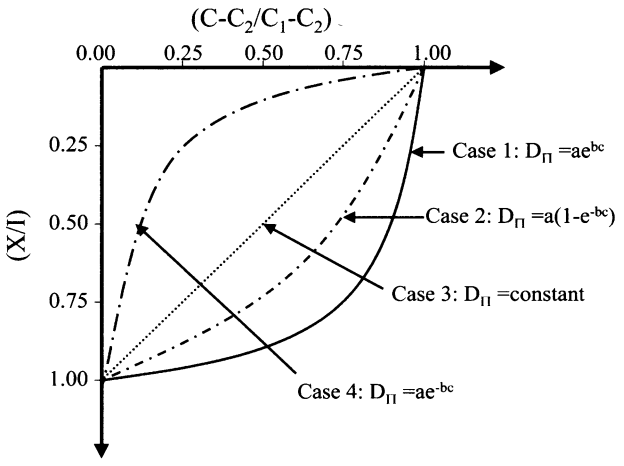
Method	Description	Equation
Diffusion function	– The diffusion coefficient (D_X) can be expressed as a function of the concentration of the specific constituent in the pore fluid [45]. – Figure 5 shows four relationships between the non – dimensional contaminant concentration and D_π (the molecular diffusion coefficient). These show the strong influence from both in characterizing the shape of the relative contaminant concentration profile. Leaching-column test information shows that case (4) in Fig. 5 is the more likely profile ($D_\pi = ae^{-bc}$). Using this function, the final governing equation for $(X)^+$ will be: as given by Eq. 50 – The input data required for parameter determinations are the concentration profiles at all time steps. These data can be obtained from leaching cell experiments. Therefore, for example, in the case of desorption analysis, the concentration of the absorbed contaminants considered in the hypothetical example, at all time steps, should first be obtained to determine $\frac{\partial C_j}{\partial t}$. Concentrations of $(X_1)^{2+}$ and $(X_2)^{2+}$ should be determined at all time steps. Following this, their derivatives with respect to time $\frac{\partial C_2}{\partial t}$ and $\frac{\partial C_3}{\partial t}$ at all time steps should be calculated	

Fig. 5 Relationships between the non-dimensional contaminant concentration and molecular diffusion coefficient

Table 5 (continued)

Method	Description	Equation
Diffusion function	– If the measured and calculated concentrations are designated as $C_{exp}(x,t)$ and $C_{calc}(x,t)$ respectively, then the best choice of parameters (A, B, a, b, and K_{hc}) are those which minimize the function expressed in Eq. 51	$$[1 - A_1B_1 e^{-A_1C_1}]\left(\frac{\partial C_1}{\partial t}\right) = ae^{-bC_1}\left(\frac{\partial^2 C_1}{\partial x}\right) - abe^{-bC_1}\left(\frac{\partial C_1}{\partial x}\right)^2 - R_i v_x \frac{\partial C_1}{\partial x} - R_\pi \frac{\partial^2 C_1^2}{\partial x^2} - R_\pi \frac{\partial^2 C_1^2}{\partial x^2} - \frac{\rho_s}{n}\left[A_2B_2 e^{-A_2C_2}\frac{\partial C_2}{\partial t} + A_3B_3 e^{-A_3C_3}\frac{\partial C_3}{\partial t}\right]$$ (50)
		$$\sigma = \sum_{i=1}^{m} ABC\left\|C_{exp}(x,t) - C_{calc.}(x,t)\right\|$$ (51)
		Where: m=number of measured concentrations in the experiments.

In general, definitive experimental values for these parameters are required before any organic compound can be used and applied in environmental modeling; however, partitioning of complex organic mixtures (COMs) will result in an inadvertent release of some intermediates or by-products into the environment. Chances are that no experimental values are available for these intermediates or by-products, and decisions concerning their environmental behavior and partitioning are required before the necessary data could be generated. Even though predicted values may be less accurate than experimental values in this situation, they are better than no values at all.

3.2 Quantitative Structure-Property and Structure-Activity Relationships

The section presents an overview of the fundamentals of quantitative structure-activity relationships (QSARs [46–56]) and quantitative structure-property relationships (QSPRs [57–60]). It also shows how such an approach can be used in order to estimate and predict sorption/desorption coefficients of various organic contaminants leached from SWMs of COMs.

QSARs are defined as the systematic categorization of atoms or molecules according to common features called structure, and they relate these assignments to the values of measured properties [61–70]. A property or activity of a molecule is a characteristic that can be determined or measured. By subjecting a target compound to a form of energy, numerical values can be obtained. Repeated subjection of a molecule to such an assault yields numerical measurements that are highly reproducible. By defining the physical events underway in such a process, we can define the observations as a property. A profile of measured properties is characteristic to that atom or molecule under investigation. Therefore, every organic compound has a boiling point, molar refraction, partition coefficient, density, and so on. Information about its form or structure is not self evident from physical property measurements. The structure is inferred from these measurements because it is known that properties are a consequence of structure [71].

QSAR/QSPR analyses describe the dependence of activity on structure and typically include several physical-chemical parameters, such as electronic (σ, pK_a), hydrophobic (π, P_{ow}, K_{ow}), and steric (E_s, MR) properties [68–69]. Since the properties of a molecule are dependent on the nature of the independent atoms and their chemical bonds, a fixed relationship exists between topological indices conveying information on bond types and bond characteristics and properties exhibited by a molecule [72–74]. These topological or structural indices may be defined as a count of selected topological features such as the number of skeletal atoms or bonds, the number of bonds or atoms of a given type, the number of double bonds, the number of rings, and other structural parameters. Molecular topology provides a rationale for correlating interactions between a molecule and its environment through molecular connectivity indices, which are based on the graphical depiction of molecular

structure and may be described by a set of numerical values [47, 68, 69]. In line with the main objective of the present chapter, the next section discusses structure-activity relationships (SAR), such as molecular connectivity indices, and how these can be used to predict contaminant mobility and bioavailability.

3.2.1 Molecular Connectivity

At the molecular level, the structure of an organic contaminant is characterized by: (1) the total number of atoms, (2) the number of different kinds of atoms, and (3) the linking pattern or bonding scheme of the atoms. These three elements of structural information depict a molecule as a graphic structural formula [75–76]. There are two general approaches to structure description, including:

- The identities of atoms and their connections which form one set of information about molecular structure called the "*topology*" of the molecule [46–49, 71, 75–76].
- Various three-dimensional (3-D) aspects called "*molecular topography*".

Characteristics, such as size, shape, volume, and surface area can be directly explained by 3-D molecular topography [77].

Generally the properties of a molecule are dependent upon the 3-D topography of the molecule, and the geometry which in turn depends on molecular topology (the nature of the individual atoms and the bonded connections between them). Because of the relationship between bond types and characteristics (for example, bond strength, length and polarity), there are relationships between topology and properties. Hence, it is most useful to express molecular structure in terms of its molecular topology [47, 78]. The starting point in representing molecular structure is the molecular skeleton that in chemical graph theory is defined as the hydrogen suppressed graph. The most basic element in the molecular structure is the existence of a connection or a chemical bond between a pair of adjacent atoms. The whole set of connections can be represented in a matrix form called the connectivity matrix [79]. Once all of the information is written in the matrix form, relevant information can be extracted. The number of atoms connected to a skeletal atom in a molecule, called the vertex degree or valence, is equal to the number of σ bonds involving that atom, after hydrogen bonds have been suppressed.

For molecular connectivity indices (MCIs) with orders higher than 2, it is also necessary to specify the subclass of index. There are four subclasses of higher order indices, including: (a) path, (b) cluster, (c) path/cluster, and (d) chain. These subclasses are defined by the type of structural subunits they are describing, a subunit over which the summation is to be taken when the respective indices are calculated.

3.2.2 Nomenclature of MCIs

The most successful of all topological indices at present is the MCI or a system of MCIs. Their numerous applications in various areas of physics, chemistry, biology, pharmacology (drug design), and environmental sciences outnumber all of the other existing topological indices [52, 80–84] because: (1) these indices are based on sound chemical, structural (topologic and geometrical), and mathematical grounds, and (2) they were developed with the idea of paralleling important physico-chemical properties (like boiling point, mobility on chromatographic columns, enthalpies of formation, and total molecular surface areas).

The concept of the MCI was originally introduced by Randic [85], and uses in its calculation the number and type of atoms and bonds as well as the numbers of total valence electrons. All MCIs are calculated only for the non-hydrogen part of the molecule [86–87]. Each non-hydrogen atom is described by its atomic δ value, which is equal to the number of adjacent non-hydrogen atoms.

Table 6 discusses the nomenclature used to designate various MCIs (Eqs. 52 to 58 [85]). The Greek letter chi (χ) is used to represent the index itself. Two superscripts and one subscript are used to specify a particular index. The left-side superscript (zero or a positive integer) is used to designate the order of index. The right-side superscript (letter v) differentiates between valence- and nonvalence-type indices. The right-side subscript (P, C, PC, or CH) specifies the subclass of molecular connectivity index, which may be a path, cluster, path/cluster, or chain-type index. If no subscript is indicated, a path-type index is assumed.

In summary, molecular structure and topological indices aid in identifying structural features responsible for toxic organic compound chemodynamics at the molecular level which have influenced their use in developing relationships that accurately predict a broad range of physico-chemical and biological responses, resulting recently in more consistent statistically relevant and reliable models. The MCIs have been shown to be rich in structural information related to topological, geometric and spatial attributes. Information about different topological and geometric properties of a chemical structure is encoded in different MCIs. The relative degree of branching of a molecule is encoded in the ${}^{1}\chi$ index when compared to other structural isomers. This translates into encoding molecular bulk or volume and surface area. The ${}^{0}\chi$ index encodes information about atoms; the ${}^{2}\chi$ index carries information about three atom fragments which are the minimum number necessary to describe a plane, while the ${}^{3}\chi_{p}$ index encodes information about three dimensional attributes such as conformation. The ${}^{3}\chi_{pc}$ index encodes information useful to the structural analysis of substituted rings. Information such as degree of substitution, length and heteroatom content of these groups is contained in ${}^{4}\chi_{p}$ and ${}^{4}\chi^{v}_{pc}$ indices.

Table 6 Types of molecular connectivity indices

MCIs	Description	Equation

The path-type	- The path-type MCIs [46, 47, 50–53, 55] is divided into two subgroups:
	  - the first contains the zero-, first-, and second- order indices (describing global molecular properties, like size, surface, volume), and
	  - the second contains all other higher order indices (describing more and more local structural properties and possibly long-range interactions)
	- The first-order ($^1\chi$) MCI is calculated from the atomic δ values [88, 89] using Eq. 52
	- The first-order ($^1\chi^v$) valence MCI is calculated from the non-hydrogen part of the molecule and was suggested by several authors [47]. In the valence approximation, non-hydrogen atoms are described by their atomic valence δ^v values, which are calculated from their electron configuration using Eq. 53
	- By analogy with Eq. 52, the $^1\chi^v$ index is then calculated from the atomic δ^v values using Eq. 54
	- The zero-order ($^0\chi$) and second-order ($^2\chi$) MCIS are the closest members to the $^1\chi$ index described in Eq 54 [102–104, 107–109, 113–115, 120, 125], which are calculated from the same input information (atomic δ values) using Eqs. 55 and 56, respectively.
	- The zero-order valence and the second-order valence MCIs are useful in modeling and estimation of acute and chronic toxicity and of fish bioconcentration factors, respectively
		$^1\chi = \sum(\delta_i \cdot \delta_j)^{-0.5}$ (52)
		Where:
		i and j correspond to the pairs of adjacent non-hydrogen atoms and summation is over all bonds between non-hydrogen atoms
		$\delta^v = \left(\frac{Z^v - h}{Z - Z^v - 1}\right)$ (53)
		Where:
		Z^v = the number of valence electrons in the atom,
		Z = its atomic number, and
		h = the number of hydrogen atoms bound to the same atom.
		$^1\chi^v = \sum(\delta_i^v \cdot \delta_j^v)^{-0.5}$ (54)
		$^0\chi = \sum(\delta_i)^{-0.5}$ (55)
		$^2\chi = (\delta_i \cdot \delta_j \cdot \delta_k)^{-0.5}$ (56)

Table 6 (continued)

MCIs	Description	Equation
The path-type	– The $^{0}\chi^{v}$ index is a simple and sound approximation for the molecular volume, correlating strongly with many molecular properties where molecular bulk plays an important role	where *i*, *j*, and *k* correspond to three consecutive non-hydrogen atoms and summations are over all non-hydrogen atoms and over all pairs of adjacent bonds between non-hydrogen atoms, respectively. Their valence analogs are defined identically as for the first-order valence MCI
The cluster- and path/cluster-type	– For cluster-type indices, all bonds are connected to the common, central atom (a star-type structure) – The third-order cluster MCI ($^{3}\chi_{c}$) is the first, simplest member of the cluster-type indices where three bonds are joined to the common central atom. The simplest chemical structure it refers to is the non-hydrogen part of *tert*-butane (Eq. 57) – The fourth-order path/cluster MCI ($^{4}\chi_{pc}$) is the first, simplest member of the path/cluster-type indices. It refers to sub-graphs consisting of four adjacent bonds between non-hydrogen atoms, three of which are joined to the same non-hydrogen atom [90–91]. Structurally (chemically) this sub-graph corresponds to the non-hydrogen part of iso-pentane (Eq. 58) – For path/cluster-type indices, orders higher than six do not have much chemical and structural sense either. In addition, it becomes very difficult to understand what the structural and physical meaning of higher order path/cluster-type indices is	$^{3}\chi_{c} = \sum(\delta_i \cdot \delta_j \cdot \delta_k \cdot \delta_l)^{-0.5}$ (57) Where *i*, *j*, *k*, and *l* correspond to the individual non-hydrogen atoms that form the subgraph, and the summation is over all *tert*-butane-type subgraphs in a molecule. For cluster-type indices, orders higher than four do not have much chemical and structural sense for organic compounds. $^{4}\chi_{pc} = \sum(\delta_i \cdot \delta_j \cdot \delta_k \cdot \delta_l \delta_m)^{-0.5}$ (58) Where *i*, *j*, *k*, *l*, and *m* correspond to the individual non-hydrogen atoms that form the subgraph and the summation is over all iso-pentane-type subgraphs in a molecule. The second structural property described by the $^{4}\chi_{pc}$ index is the substitution pattern on the benzene ring. The value of the $^{4}\chi_{pc}$ index increases sharply with the degree of substitution, while in the isomeric classes of substituted benzenes it increases with the proximity of substituents.

Table 6 (continued)

MCIs	Description	Equation
The cluster- and path/ cluster-type	- The cluster and path/cluster indices describe mainly local structural properties (for instance, the extent or degree of branching in a molecule). They are highly sensitive to changes in branching, and their value rapidly increases with the degree of branching. They may be useful as steric descriptors. From these two classes of MCIs the most interesting and commonly used are the third-order cluster and fourth-order path/cluster indices	
The chain-type	- It describes the type of rings that are present in a molecule as well as the substitution patterns on those rings, in other words it describes more local-type properties [66, 71, 90] - Their specificity is that they describe the same number of non-hydrogen atoms and bonds - For all other classes of MCIs, the corresponding subgraphs always contain more atoms than bonds	- The lowest order for the chain-type index is third-order and increases up to the largest ring in any particular molecule - In this class of MCIs, the most interesting and commonly used are the sixth-order (${}^{6}\chi_{CH}$) and seventh-order (${}^{7}\chi_{CH}$) chain-type indices since they are related to benzene rings - The ${}^{7}\chi_{CH}$ index corresponds to monosubstituted benzene rings. The latter index was found to be very useful in describing the chromatographic behavior of chlorinated benzenes [47, 74, 75]

3.2.3 Modeling Techniques

The molecular shape of organic compounds influences biological activity, especially where enzymes and receptors are evolved. Several research studies have been conducted to address the problem of finding a mathematical means to express differences in geometric features such as those evidenced in the measurement of both size (a bulk measure) and shape (vectorial quantity) of molecules. The first has been to find parameters suitable for use in the Hansch equation. Taft's E_s parameter, or its variants derived from the acid and base hydrolysis rates of aliphatic esters, have been most widely used [46–48]. Kier and Hall [47] have adapted the molecular connectivity index χ for QSAR correlations, a number derived originally by Randic [85] from graph theoretical principles to express the relative topology of variously branched hydrocarbon isomers. Many χ terms can be calculated for a given molecule, differing in the number of atoms taken together ($^n\chi$), and these may include or ignore the valence weighted indices ($^n\chi_v$) for the specific atoms or bond types present. The various terms for the molecules of a series may be tested as parameters in the usual multiple regression correlation model [47, 49–52, 85].

Other approaches to expressing topological differences include treating the problem of directionality of steric effects by the direct expedient of modeling a substituent and calculating its extension in five orthogonal directions (such as the minimal steric difference method). Other approaches include the use of quantum mechanical methods and molecular modeling techniques [55, 90].

A brief discussion about different modeling techniques commonly used and the various aspects of statistical analysis associated with multivariate data analysis for model development are presented in Table 7.

In summary, the QSAR and QSPR approaches, as well as their modeling techniques, are important and are a basic requirement for environmental planning and engineering management. MCIs are a sensitive property for many organic contaminants. Such MCIs can be used to predict the partitioning of contaminants at interfaces.

4 Multicontaminant Joint Toxic Effect Modeling

Various joint action models of contaminants are presented in Table 8 in order to predict the combined toxic effects of such compounds leached from SWMs of complex mixtures. The modeling approach presents how and why a mixture of toxic and/or carcinogenic compounds can exhibit greater impacts in the environment than the individual constituents themselves. Such an impact, called the joint toxic effect of multiple chemicals, has been recognized as an important consideration in environmental chemodynamics. An understanding and ability to predict joint effects of chemical mixtures is beneficial to provide

Table 7 QSARs modeling techniques

Type	Description	Equation
Free energy model	- Hansch and co-workers [46–54, 66, 92] used early observations of the importance of relative lipophilicity to biological potency to create the useful formalism of Linear Free Energy Relationships (LFER) to provide a general QSAR model in biological contexts - As a measure of lipophilicity, the partition coefficient ($\log K_{OW}$) between *l*-octanol and water was proposed. - $\log K_{OW}$ was roughly an additive and constitutive property and hence calculable in principle from molecular structure - Using a probabilistic model for transport across biological membranes, Hansch proposed Eqs 59 and 60 (also called the Hansch Equation) - The reciprocal of the concentration reflects that higher potency is associated with lower dosage, and the negative sign for the π^2 or $(\log K_{OW})^2$ term reflects the expectation of an optimum lipophilicity - The applicability of Eq. 59 to a broad range of biological (toxic, genotoxic) structure-activity relationships has been demonstrated convincingly by Hansch and associates [46–54, 69–70, 92, 93]	$\log\left(\frac{1}{C}\right) = -k\pi^2 + k'\pi + \rho\sigma + k''$ (59) $\log\left(\frac{1}{C}\right) = -k(\log K_{OW})^2 + k'(\log K_{OW}) + \rho\sigma + k''$ (60) Where: C = molar concentration (or dose) for a constant biological response (EC_{50}, LC_{50}, genotoxic π = substituent lipophilicitylog induction value) K_{OW} = partition coefficient σ = Hammett value for substituent electronic effect k, k', ρ and k'' are regression coefficients derived from statistical curved fitting A number of statistics are derived from such a calculation, which allow the statistical significance of the resulting correlation to be assessed, the most important of these are: - the standard error of the estimate (standard deviation) - r^2, the coefficient of determination, - F, a statistic for assessing the overall significance of the derived equation, and - t values (also compared with statistical tables) and confidence intervals (usually 95%) for the individual regression coefficients in the equation.

Table 7 (continued)

Type	Description	Equation
Free Wilson mathematical model	– Free and Wilson demonstrated a general mathematical method for assessing both the occurrence of additive substituent effects and quantitatively estimating their magnitude [68, 92] – The molecules of a drug series can be structurally partitioned into a common moiety or core which has various substituents in multiple positions (see Eq. 61) – The attractiveness of this model is as follows: – any set of quantitative biological data may be employed as the dependent variable, – no independently measured substituent constants are required, – the molecules of a series may be structurally partitioned in any convenient manner, and – multiple sites of variable substitution are easily accommodated. – The limitations of the model are [92]: – a substantial number of compounds with varying substituent combinations is required for a meaningful analysis – the derived substituent contributions give no reasonable basis for extrapolating predictions beyond the substituent matrix analyzed – the model will break down if non-linear dependence on substituent properties is important or if there are interactions between the substituents	$B'A_i = \sum_j a_j X_{ij} + \mu$ (61) Where: BA = biological activity X_j = jth substituent with a value of 1 if present and 0 if not a_j = contribution of the jth substituent to BA μ = average overall activity All contributions at each position of substitution should sum to zero. The series of linear equations thus generated is solved by the method of least squares for terms a_j and μ. There must be several more equations than unknowns and each substituent should appear more than once at a position in different combinations with substituents at other positions

Table 7 (continued)

Type	Description	Equation
Principal components analysis (PCA) model	– Theoretically, PCA corresponds to a mathematical decomposition of the descriptor matrix, X, into means (x_k), scores (t_{ia}), loadings (p_{ak}) and residuals (e_{ik}), which can be expressed as Eq. 62 – In the case of PCA, the following points should be considered: – Principal components (PCs) 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 [1] – One of the statistical concerns in PCA is cross correlation between independent variables under consideration	$x_{ik} = x_k + \sum_{a=1}^{A} t_{ia} \cdot p_{ak} + e_{ik}$ (62) Where: x_{ik} = data elements used to describe the structural variation within the class of compounds t_{ia} = location of the ith compound along the ath principal component (PC) p_{ak} = loadings describe how much and in what way the kth chemical descriptor contributes to a certain PC

Table 7 (continued)

Type	Description	Equation

Pattern recognition model	- Pattern recognition is an ensemble of techniques that utilizes Artificial Intelligence to predict biological response or chemical characteristics [1, 94]
	- This method examines structural features and/or chemical properties for underlying patterns which are associated with different biological effects
	- The primary goal is to accurately classify the untested compounds in two stages:
	  - a set of compounds, designated the training set, is chosen for which the correct classification is known, and
	  - a set of molecular or property descriptors is generated for each compound.
	- A suitable classification algorithm is then applied to find some combination and weight of the descriptors that allows perfect classification [94–95]. The derived classification is then applied to compounds not included in the training set to test predictability
	- Performance is judged by the percentage of correct predictions
	- Repeating the training procedure several times with slightly altered but randomly varied training sets usually tests the robustness of the classifications
	- The most widely used pattern recognition systems in QSAR work are called ARTHUR and ADAPT [46–49, 92]	

Table 7 (continued)

Type	Description	Equation
Discriminant analysis model	- Discriminant analysis has been proposed to deal with QSAR research by several workers [1, 96] - This method seeks a linear combination of parameters called a linear discriminant function that will successfully classify the observations into their observed or assigned categories (Eq. 63) - Parameters are added or deleted to improve discrimination and the results are judged by the number of observations correctly classified.	$Group = a + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + \ldots + b_m \cdot x_m$ (63) Where: a is a constant, and b_1 through b_m are regression coefficients. The variables with the largest (standardized) regression coefficients are the ones that contribute most to the prediction of group membership

Table 7 (continued)

Type	Description	Equation
Cluster analysis model	– Cluster analysis is a way to group entities, for which a number of properties or parameters exist, by similarity – Various distance measurements are used, including: – *Euclidean:* It simply is the geometric distance in the multidimensional space (Eq. 64) – *Squared Euclidean:* One may want to square the standard Euclidean distance in order to place progressively greater weight on objects that are further apart (Eq. 65) – *City-block (Manhattan):* This distance is simply the average difference across dimensions. In most cases, this distance measure yields results similar to the simple Euclidean distance. However, the effect of single large differences (outliers) is dampened (since they are not squared) (Eq. 66) – *Chebychev:* This distance measure may be appropriate in cases when one wants to define two objects as "different" if they are different on any one of the dimensions (Eq. 67) – *Power:* It increases or decreases the progressive weight that is placed on dimensions on which the respective objects are very different (Eq. 68) – Cluster analysis is performed in a sequential manner reducing the number of clusters at each step.	*Euclidean distance:* $\text{Distance}(x,y) = \left\{\sum_i (x_i - y_i)^2\right\}^{1/2}$ (64) *Squared Euclidean distance:* $\text{Distance}(x,y) = \sum_i (x_i - y_i)^2$ (65) *City-block (Manhattan) distance:* $\text{Distance}(x,y) = \sum_i \left\|(x_i - y_i)\right\|$ (66) *Chebychev distance:* $\text{Distance}(x,y) = \textit{Maximum}\left\|x_i - y_i\right\|$ (67) *Power distance:* $\text{Distance}(x,y) = \left\{\sum_i \left\|x_i - y_i\right\|^p\right\}^{1/r}$ (68) where r and p are user-defined parameters

Table 8 Multicomponent joint toxic effect models

Model	Description	Equation
Toxic unit concept	- In quantifying the joint actions of PAHs in mixtures, for instance, the concept of toxic unit (TU) is expressed as shown in Eq. 69 - In fresh water algal toxicity, this response could be 50% inhibition of the algal growth - If the TUs of all PAHs in a mixture are equal, then the PAH mixture is referred to as an equitoxic or a uniform mixture - Using the TU concept, alternative schemes have been proposed to characterize the degree of joint action of multiple compounds acting together - Generally, the sum of the TUs of the components M is used as an index to categorize the type of joint action as shown in Eq. 70	$TU_i = \left(\frac{z_i}{Z_i}\right)$ (69) Where z_i = concentration of compound i in a mixture that causes a certain response; and Z_i = its concentration causing the same response when acting singly $M = \sum TU_i$ (70) - If M=1, the components are simply additive (also referred to as concentration *addition*); - If M<1, they are more than additive (also referred to as *synergism*); and - If M>1, they are less than additive (also referred to as *antagonism*)

Table 8 (continued)

Model	Description	Equation
Additive index	- This scheme was proposed by Marking [99] - The additive index (AI) is expressed in Eq. 71	$AI = \frac{1}{M} - 1$; if $M = \leq 1$ (71) Where: $AI = 1 - M$; if $M = > 1$ (72) - If AI=0, components are simply additive - If AI>0, then they are more than additive, and - If AI<0, they are less than additive
Mixture toxicity index	- The mixture toxicity index (MTI) scheme was proposed by Konemann [100] - Equation 73 defines the MTI	$\mathrm{MTI} = 1 - \frac{\log M}{\log M_o}$ (73) Where: $M_o = \left(\frac{M}{\text{the largest } \mathrm{TU_i} \text{ in the mixture}} \right)$ (74)

meaningful inputs in managing the environmental hazards of synthetic compounds. This prediction of mixture toxicity/carcinogenicity can provide an insight about the bioavailable fraction of contaminants at aqueous-solid phase interfaces, and greatly enhance the decision-making processes in optimizing, limiting or preventing the disposal and/or recycling of solid wastes until they meet certain environmental criteria.

The study of joint toxic effects originated with the analysis of the effect of two compounds in binary mixtures. Plackett and Hewlett [98] identified four types of joint effects as follows:

- *Similar versus dissimilar*, depending on whether the sites of action and modes of primary action of the two compounds are the same or different; and
- *Interactive versus non-interactive*, depending on whether one compound does or does not influence the biological action of the other.

If the response of an organism is produced by a combination of the two compounds, then they are said to exert joint action. This joint action can be further classified into simply additive, more than additive (synergistic), and less than additive (antagonistic). When this scheme is applied to multicomponent mixtures present in leachates of solid wastes, the analysis becomes more complex because the joint actions of different compound pairs may fall into different types of joint action.

In Table 8, three different modeling schemes are presented and discussed that include the following: Toxicity Unit Concept, and Additive Index and Mixture Toxicity Index (Eqs. 69 to 74). The use of these models to analyze the joint effect of a group of toxic and carcinogenic organic compounds, such as polycyclic aromatic hydrocarbons, will be presented and evaluated in Sect. 5.

5
Organic Leachates from Recycled SWMs: a Case Study

This section presents a case study that explains how physical and chemical properties, QSAR and QSPR approaches, and multicomponent toxic effect models can be used to predict the mobility and bioavailability of organic contaminants leached from SWMs. These interdisciplinary approaches are applied here to the main group of toxic and carcinogenic compounds characterized in various SMWs of COMs. More detailed information and discussions about the problem statement, project approaches, types of solid waste materials tested, types of soil and sediment samples studied, leachate preparations (for example, 24 hr batch, short/long-term batch, column and flat plate leaching), and solid sorption experiments can be found in other chapters of this book (see the chapter on "Recycling Solid Wastes as Road Construction Materials", Sect. 6; and the chapter on "Forensic Investigation of Leachates from Recycled Solid Wastes", Volume 1, Sect. 4).

5.1 Data Modeling

5.1.1 Batch Leaching

Batch leaching tests, conducted for different types of waste materials, resulted in data that were modeled as shown in Eq. 75:

$$C = C_a(1 - e^{-kt}) \tag{75}$$

where:

C =concentration of either individual leached organic compound;
t =time of leaching;
C_a =asymptotic concentration; and
k =rate coefficient (1/time).

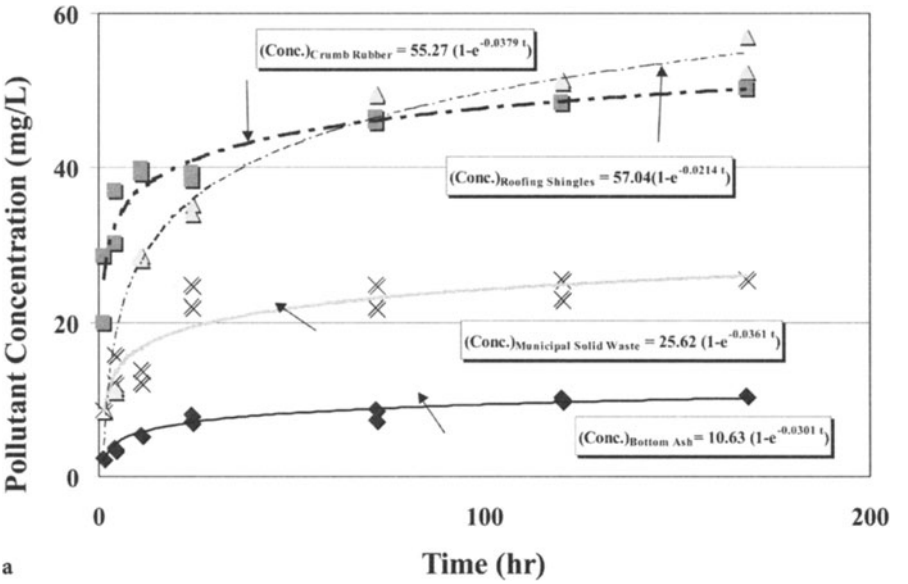
In general, the leaching of organic compounds from SWMs/COMs involved an initial rapid release, followed by a slower release over longer time periods (Fig. 6a). For solid waste materials, disposed in landfills or used as highway construction materials and subjected to long-term environmental exposure, the rate of leaching of constituents at large t values may best represent actual field conditions. As such, accurate modeling of the release near t equal to zero may not be important.

Equation 75 for SWM leaching has the advantage of utilizing only two fitting coefficients (C_a and k) [11–12]. The *flux* or leaching rate is proportional to the derivative (slope) of the concentration vs time, that is flux~dC/dt (Fig. 6a). When the C vs t formulation is nonlinear (Eq. 75), the flux is not constant and gradually decreases with increasing time (Fig. 6a). On the other hand, the modeled leaching data for all waste material leachates are shown in Fig. 6b, where a linear fit could be made to any time segment to obtain an approximate constant leaching rate during that time segment, in units of mg/L per hour.

5.1.2 Column Leaching

The concentration of any contaminant(s) from road construction and repair (C&R) materials appearing in the effluent from the column was measured over time and the results of leachate desorption breakthrough curves [11–12] are shown schematically in Fig. 7. The effluent concentrations of contaminants for three different flow rates were determined to follow a first-order model as shown in Eq. 76, with the coefficients fitted by the linear regressions given in Table 9.

$$C = C_0 e^{-kt} \tag{76}$$



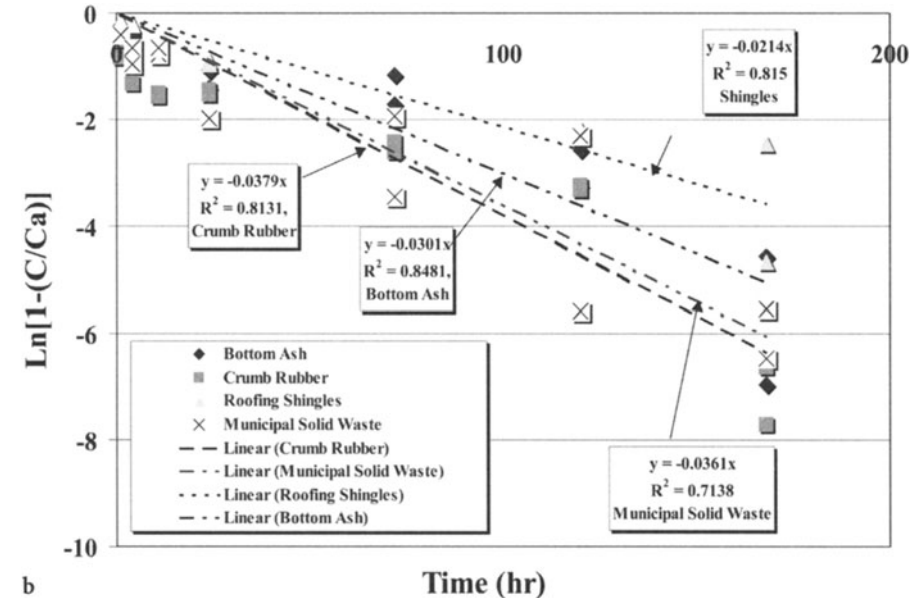


Fig. 6a–b Dynamic batch leaching experiment data for various solid waste material leachates (**a**) before modeling, and (**b**) after modeling

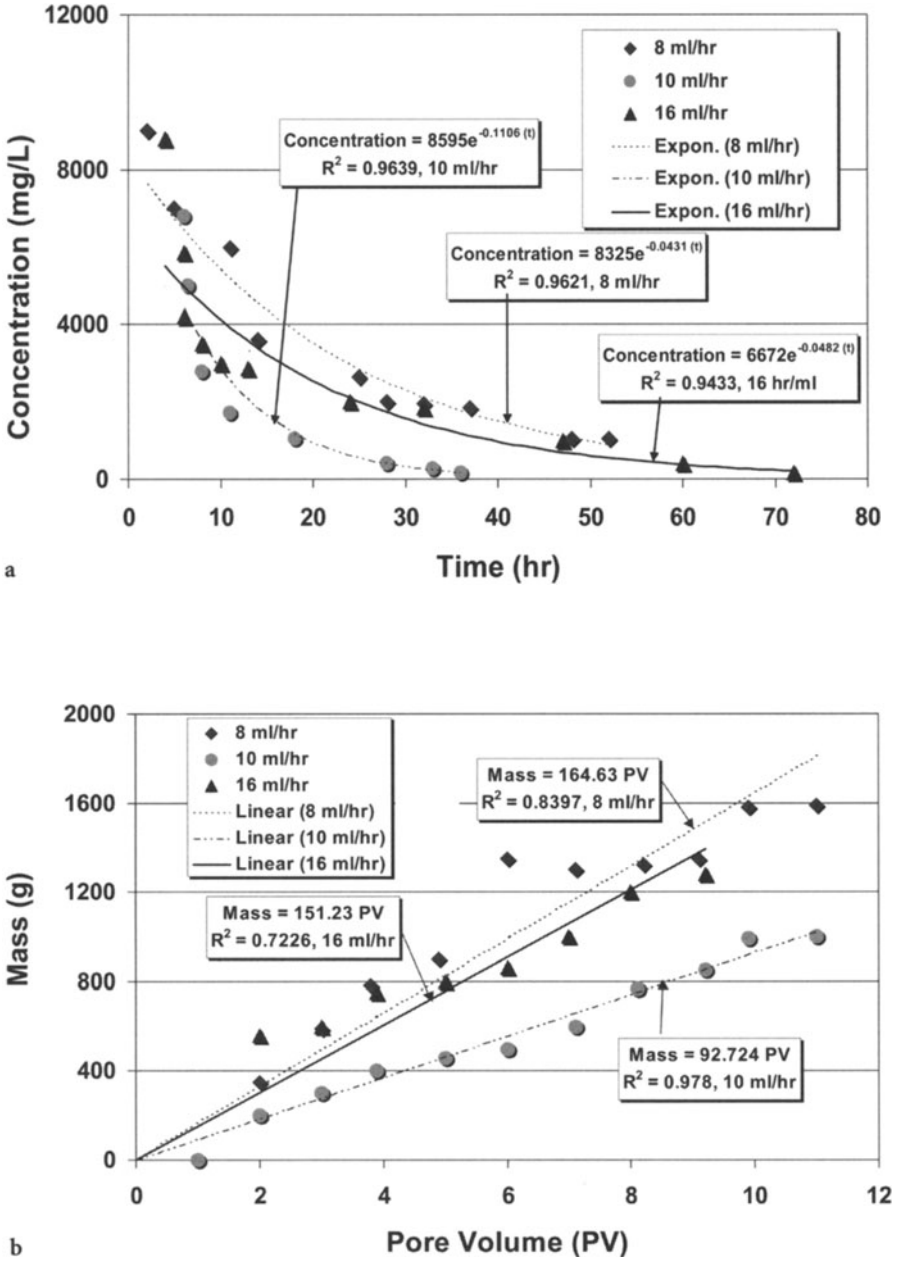


Fig. 7a–b Column experiments using different flow rates, first order model TOC concentration released versus (**a**) time, and (**b**) pore volume

Table 9 First order regression coefficients for columnleaching of TOC at ambient pH (pH≡7) and pore volumes

Flow rate (mL/hour)	C_o (mg/L)	k (L/hour)	R^2	Pore volume V_p (mL)
8	8,325	0.0431	0.96	265
10	8,595	0.1106	0.97	256
16	6,672	0.0482	0.94	243

where:

C =concentration at time t,
C_o =initial concentration at time 0,
t =time, and
k =first-order rate constant.

Leaching of contaminant(s) (expressed as TOC) clearly shows the most rapid decrease in concentration is for the highest flow rate (Fig. 7).

Additional data analyses were performed in a variety of ways, which can be used to compute the cumulative mass of a certain contaminant, as shown in Eq. 77:

$$M = \int CQ\, dt \tag{77}$$

where:

M =cumulative mass leached (mg),
C =concentration in leachate (mg/L),
Q =flow rate (mL/hr), and
t =time (hr).

For a constant flow rate through the column, and using the concentration versus time relationship of Eq. 77, the integration yields the familiar exponential form:

$$M = M_a(1 - e^{-kt}) \tag{78}$$

where:

M_a=total asymptotic mass leached (mg), and may be evaluated as a constant of integration, as shown in Eq. 79:

$$M_a = \left(\frac{QC_0}{k}\right) \tag{79}$$

This leads to a method for computing the total mass leached, for instance, to receiving water.

In column sorption/desorption tests, a dimensionless time is often used and termed pore volume. One pore volume (V_p) is the volume of pores (for instance, voids) present in the column that may be filled with water. The number of pore volumes passed through the column is thus:

$$PV = \left(\frac{V}{V_p}\right) = \left(\frac{Q_t}{V_p}\right) \tag{80}$$

where:

PV =number of pore volumes,
V_p =the volume of pores for a given column,
V =cumulative flow volume, and
Q =flow rate.

The results of total contaminant concentrations appearing in the effluent from the column are plotted versus pore volume (Fig. 7b). Pore volumes for the SWM column experiments are given in Table 9. Time may be normalized to pore volumes for additional analysis, leading to interferences about the trade-off between the mass leaching rate increasing with faster flow rates, but decreasing with longer times. This can be seen from the derivative of Eq. 78:

$$\frac{dM}{dt} = QC_0 e^{-kt} = QC_0 e^{\left[-k\left(\frac{V_p}{Q}\right)PV\right]} \tag{81}$$

where:

$\frac{dM}{dt}$ = mass flux (mg/hr).

The significance of cumulative mass (M) is that this may lead to a method for determining the loading which results from intermittent rainfall. A loading based strictly on time may not suffice when runoff starts, stops and starts again.

5.1.3 Flat Plate Leaching

Results of the SWM/COM experiments reported by Eldin et al [11–12] are shown schematically in Fig. 8. Assuming zero order kinetics, the increase in contaminant concentration is given from the fitted line on the figure as:

$$Y = at \tag{82}$$

where:

Y =contaminant concentration (mg/L),
a =intercept, and
t =leaching time (hr).

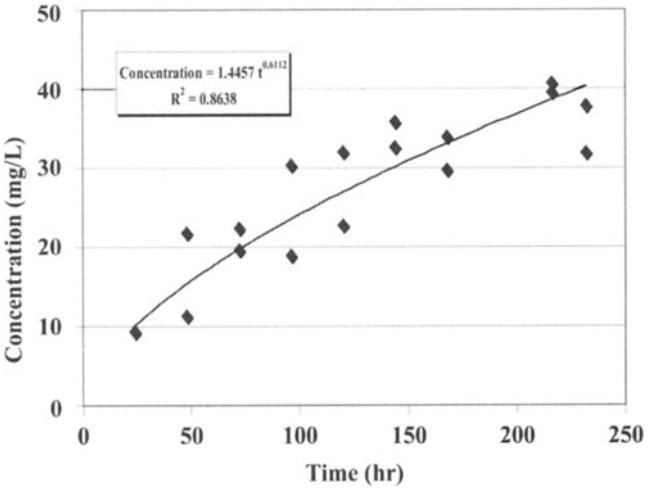


Fig. 8 Flat plate leaching test: TOC concentration in leachate as a function of time

Knowing the average surface area of the SWM/COM flat plate and the volume of the leaching solution, the constant flux, F (for zero-order kinetics) of organic compounds from the SWM/COM is calculated as:

$$F = \left(\frac{V}{A}\right)\frac{dC}{dt}h = \frac{dC}{dt} \tag{83}$$

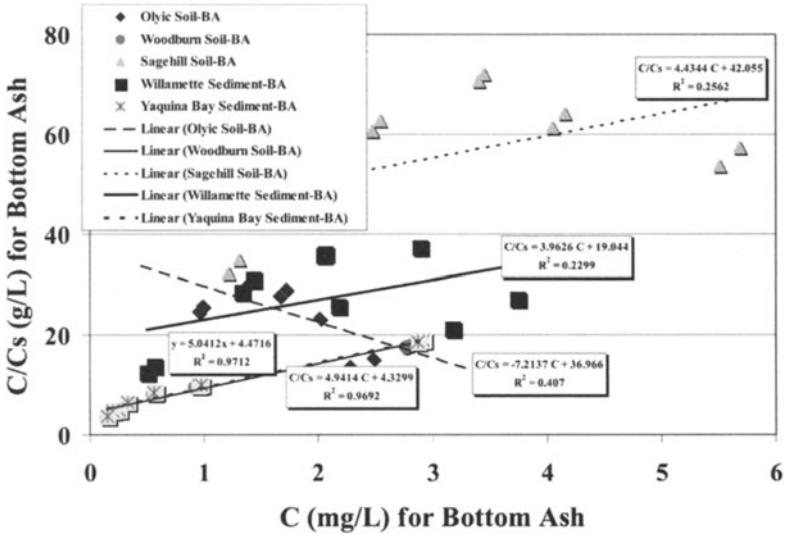
where:

F =flux (mg/cm^2 hr),
V =eluate volume (cm^3),
A =surface area (cm^2), and
h $= \frac{V}{A}$ =depth (cm).

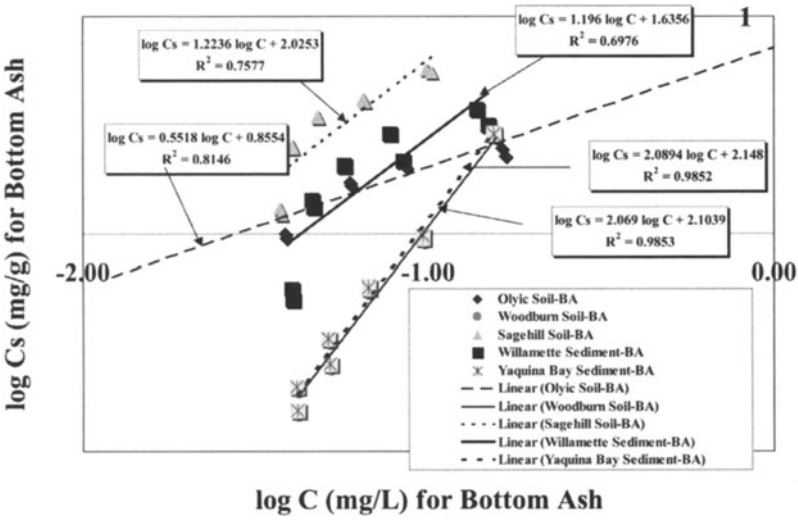
5.1.4 Solid Phase Sorption

Since TOC, for some solid wastes, was used as a criterion to measure leachate sorption for organic compounds, TOC by itself is considered as a single component system (in other words SCS, see Sect. 2.1). To represent the SCS equilibrium system for various waste materials, the sorption characteristics of different soils and sediments were analyzed and evaluated using three different sorption isotherms: Langmuir, Freundlich and linear model (see Table 1).

Isotherm plots of TOC data for only bottom ash solid waste and isotherm equations for the different solid phases are shown in Fig. 9, and the isotherm parameters determined from statistical regression analyses with their coefficients are given in Table 10.

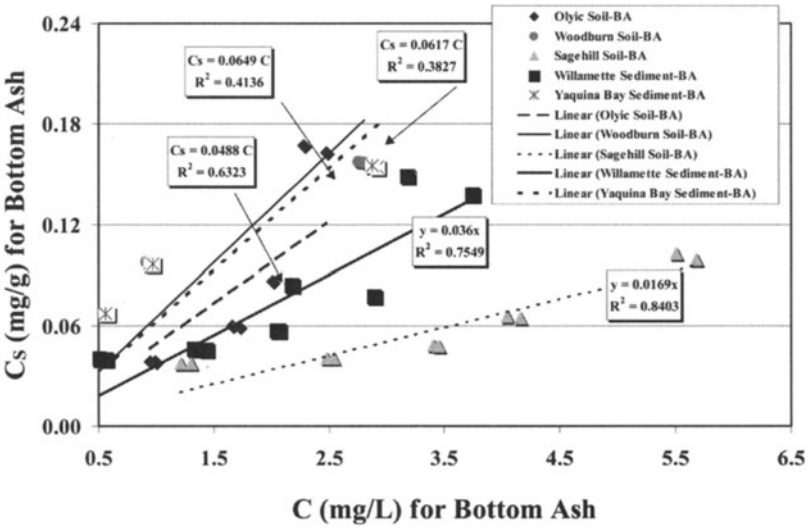


a



b

Fig. 9 Isotherm sorption models for bottom ash solid waste, representing **a** Langmuir (C/C_s vs C), **b** Freundlich ($\log C_s$ vs $\log C$), and **c** linear (C_s vs C) models



c

Fig. 9 (continued)

Both the Langmuir and Freundlich equations automatically pass through the origin, but the linear model is forced through the origin. For the three soil and two sediment samples, most of the three isotherm models yielded statistically significant regressions, with the Freundlich isotherm giving the "best" model, based on a criterion of maximum coefficient of determination (R^2). However, even the linear isotherm model would be reasonable for some of these solid samples.

In summary, the present case study involved sorption/desorption processes with distilled water of a variety of hazardous solid wastes and road C&R materials which are complex organic mixtures. The following are some of the findings:

- The water quality of the leachates was quantified in terms of both chemical constituents and toxicity.
- Sorption and/or desorption processes, an important chemodynamics behavior for chemical constituents in leachates, were determined by a testing methodology using a series of laboratory simulations.
- Leachate chemical constituents (expressed as either individual organic compound or TOC content) were specifically identified and determined by laboratory instrumental methods.
- The potential impacts of organic leachates from complex mixtures on surface and ground waters appear to be of environmental concern, so the testing methodology provides a systematic approach for such evaluations.

Table 10 Summary regression equation constants for various solid waste material leachates on different solid phases (note: base 10 logs)

Waste type	Solid phase type	Model isotherm	Y axis	Intercept	Slope	X axis	R^2
Bottom ash	Olyic soil	Linear	C_s	0.0000	0.0488	C	0.6323
		Langmuir	C/C_s	36.9660	−7.2137	C	0.4070
		Freundlich	logC_s	0.8554	0.5518	log$C$	0.8146
	Woodburn soil	Linear	C_s	0.0000	0.0649	C	0.4136
		Langmuir	C/C_s	4.3299	4.9414	C	0.9692
		Freundlich	logC_s	2.1039	2.0690	log$C$	0.9853
	Sagehill soil	Linear	C_s	0.0000	0.0169	C	0.8403
		Langmuir	C/C_s	42.0550	4.4344	C	0.2562
		Freundlich	logC_s	2.0253	1.2236	log$C$	0.7577
	Willamette River sediment	Linear	C_s	0.0000	0.0360	C	0.7549
		Langmuir	C/C_s	19.0440	3.9626	C	0.2299
		Freundlich	logC_s	1.6356	1.1960	log$C$	0.6976
	Yaquina Bay sediment	Linear	C_s	0.0000	0.0617	C	0.3827
		Langmuir	C/C_s	4.4716	5.0412	C	0.9712
		Freundlich	logC_s	2.1480	2.0894	log$C$	0.9852
Crumb rubber	Olyic soil	Linear	C_s	0.0000	0.4710	C	0.7120
		Langmuir	C/C_s	38.4770	−1.4355	C	0.6030
		Freundlich	logC_s	1.2053	0.5852	log$C$	0.8933
	Woodburn soil	Linear	C_s	0.0000	0.0413	C	0.2690
		Langmuir	C/C_s	4.8269	1.3492	C	0.8398
		Freundlich	logC_s	1.725	2.5408	log$C$	0.8963
	Sagehill soil	Linear	C_s	0.0000	0.0161	C	0.8618
		Langmuir	C/C_s	41.3570	0.9107	C	0.4591
		Freundlich	logC_s	1.9436	1.3515	log$C$	0.8564

Table 10 (continued)

Waste type	Solid phase type	Model isotherm	Y axis	Intercept	Slope	X axis	R^2
Crumb rubber	Willamette River sediment	Linear	C_s	0.0000	0.0124	C	−0.0881
		Langmuir	C/C_s	33.2820	1.7783	C	0.8899
		Freundlich	$\log C_s$	2.2068	1.6759	$\log C$	0.8155
	Yaquina Bay sediment	Linear	C_s	0.0000	0.0106	C	−1.1394
		Langmuir	C/C_s	23.631	2.5079	C	0.8909
		Freundlich	$\log C_s$	2.9569	2.8739	$\log C$	0.7882
Roofing shingles	Olyic soil	Linear	C_s	0.0000	0.0490	C	0.7104
		Langmuir	C/C_s	37.2260	−1.3999	C	0.6096
		Freundlich	$\log C_s$	1.1947	0.5828	$\log C$	0.8938
	Woodburn soil	Linear	C_s	0.0000	0.0431	C	0.3031
		Langmuir	C/C_s	4.7090	1.2861	C	0.8356
		Freundlich	$\log C_s$	1.6713	2.5099	$\log C$	0.8972
	Sagehill soil	Linear	C_s	0.0000	0.0171	C	0.8865
		Langmuir	C/C_s	40.7510	0.7882	C	0.3998
		Freundlich	$\log C_s$	1.8922	1.3079	$\log C$	0.8577
	Willamette River sediment	Linear	C_s	0.0000	0.0133	C	0.1806
		Langmuir	C/C_s	34.024	1.5448	C	0.8637
		Freundlich	$\log C_s$	2.1254	1.5989	$\log C$	0.8372
	Yaquina Bay sediment	Linear	C_s	0.0000	0.0114	C	−0.5408
		Langmuir	C/C_s	24.6480	2.2350	C	0.8594
		Freundlich	$\log C_s$	2.7341	2.6092	$\log C$	0.7893

Table 10 (continued)

Waste type	Solid phase type	Model isotherm	Y axis	Intercept	Slope	X axis	R^2
Municipal solid waste incinerator bottom ash	Olyic soil	Linear	C_s	0.0000	0.0247	C	0.9402
		Langmuir	C/C_s	34.073	0.8461	C	0.1295
		Freundlich	$\log C_s$	1.6939	1.1269	$\log C$	0.8448
	Woodburn soil	Linear	C_s	0.0000	0.0254	C	ND
		Langmuir	C/C_s	7.8078	3.5670	C	0.8358
		Freundlich	$\log C_s$	2.7351	2.7742	$\log C$	0.8439
	Sagehill soil	Linear	C_s	0.0000	0.0067	C	ND
		Langmuir	C/C_s	13.614	9.1697	C	0.9771
		Freundlich	$\log C_s$	6.2770	5.1310	$\log C$	0.5725
	Willamette river sediment	Linear	C_s	0.0000	0.0288	C	0.1626
		Langmuir	C/C_s	8.2438	3.1175	C	0.8872
		Freundlich	$\log C_s$	2.5497	2.6051	$\log C$	0.9128
	Yaquina Bay sediment	Linear	C_s	0.0000	0.0298	C	0.5329
		Langmuir	C/C_s	14.553	2.2335	C	0.9769
		Freundlich	$\log C_s$	1.9516	1.7056	$\log C$	0.9827

ND=not determined.

5.2 Modeling Multicomponent Effects of PAHs

In this part, a case study representing PAH-containing leachates from SWMs is presented in terms of the joint toxic/carcinogenic actions of such PAHs in mixtures. Therefore, different schemes discussed in Table 8 (the toxic unit, TU; the additivity index, AI; and the mixture toxicity index, MTI) for analyzing joint effects of multicontaminant on the fresh water alga *Selenastrum capricornutum* chronic 96-hr toxicity due to PAH mixtures are presented and discussed. MOLecular CONNectivity-Quantitative Structure-Activity Relationship (MOLCONN-QSAR) techniques are then used to develop a predictive model to estimate the concentrations of PAH components in organic mixtures in an aqueous system and/or derived from SWM leachate, which would jointly cause 50% inhibition of the *Selenastrum capricornutum* toxicity. The application of this multicomponent mixture chronic toxicity approach is demonstrated based on the experimental ecotoxicity data of eleven "eight-component" PAH mixtures on the alga *Selenastrum capricornutum*, as was reported [1].

5.2.1 Model Development

If the joint effects of a set of organic compounds in a mixture can be accepted to be simply additive, then their concentrations in any mixture that would result in a certain response can be readily estimated from their respective individual concentrations causing the same response when acting singly. The practical utility of this deduction was further enhanced by Kassim [1] by incorporating QSAR models to estimate the individual 50% inhibition concentration (EC_{50}) values directly from the molecular structures of the PAH components themselves. The integration of both single and joint effects PAHs-QSAR models can be used to predict PAH mixture joint toxicity.

However, when it was decided to use the aforementioned schemes to determine whether PAH compounds would act together by simple addition or not, statistically valid acceptance limits had to be assigned to the indices: TU, AI, and MTI. These limits should account for the variances due to experimental errors and the reproducibility associated with the z_i and Z values (Table 8, Eq. 69). This would help to analyze and estimate multicomponent PAH mixture-combined toxicity with a known degree of reliability. Accordingly, the main approach used to assign acceptable ranges of data is that the 95% confidence intervals for the EC_{50} values are substituted in the formulae for determining AI (Table 8, Eqs. 71 and 72). The lower and upper limits of EC_{50} values are used to get a range, and if that range included zero, additive toxicity is assumed to be valid.

Table 11 Toxicity values (EC_{50}) and molecular connectivity indices for various PAH compounds

Compound tested		CAS #	Chemical formula	MW (g/mol)	EC_{50} (mg/L)	$^{3}\chi^{p}$	$^{6}\chi^{v}_{p}$	$^{2}\chi^{v}$
Name	Symbol							
Naphthalene	NP	91-20-3	$C_{10}H_8$	128.2	19.536	3.47	0.30	2.35
1-Methylnaphthalene	1-MN	90-12-0	$C_{11}H_{10}$	142.2	19.000	4.10	0.41	2.84
2-Methylnaphthalene	2-MN	91-57-6	$C_{11}H_{10}$	142.2	12.000	4.30	0.42	2.54
2,6-Dimethylnaphthalene	DMN	581-40-2	$C_{12}H_{12}$	156.2	14.122	4.50	0.55	2.84
Acenaphthylene	ACY	208-96-8	$C_{12}H_8$	150.2	9.7016	4.84	0.67	3.13
Phenanthrene	PH	85-01-8	$C_{14}H_{10}$	178.2	6.0000	5.39	0.74	3.51
Anthracene	AN	120-12-7	$C_{14}H_{10}$	178.2	2.5000	5.34	0.73	3.55
Fluoranthene	FLU	206-44-0	$C_{16}H_{10}$	202.3	0.0644	6.73	1.23	4.25
Benzo[*a*]pyrene	BaP	50-32-8	$C_{20}H_{12}$	252.3	0.0008	8.62	1.74	5.45
Benzo[*e*]pyrene	BeP	192-97-2	$C_{20}H_{12}$	252.3	0.0028	8.74	1.78	5.74
Perylene	PER	198-55-0	$C_{20}H_{12}$	252.3	0.0001	10.0	2.38	6.20

5.2.2 PAHs and Algal Toxicity Testing

A total of 11 polycyclic aromatic hydrocarbons (PAHs, Table 11) were assayed in non-equitoxic ratios in eleven eight-component mixtures. These PAHs were selected based on their presence in most of the waste materials studied [1], covering a whole range of PAH chemical and physical properties. The organic contaminants assayed and their respective EC_{50} are listed in Table 11. The different PAHs, prepared singly or in mixtures, and the fresh water alga *Selenastrum capricornutum* culture assay were determined according to Kassim [1].

5.2.3 Chronic 96-hr Toxicity Measurement

For each PAH mixture, two reactors were used as controls and the remaining reactors were dosed with PAH mixtures. Chronic 96-hr algal toxicity of the dosed reactors was compared against those of the control reactors to determine

the percent inhibition. The EC_{50} values were obtained from percent inhibition versus PAH concentration plots. In the study by Kassim [1], non-uniform PAH mixtures (eleven different "eight-PAH" mixtures) were assayed. For each PAH component test mixture, two PAH components were added at 0.08 TU (TU_1=0.08, TU_2=0.08); two more at 0.09 TU (TU_3=0.09, TU_4=0.09); three more at 0.1 TU (TU_5=0.1, TU_6=0.1, TU_7=0.1); and the eighth PAH component was added at various TUs (0.1, 0.2, 0.3, 0.4, and 0.5) to determine the TU_8 at which it would induce 50% growth inhibition. If all the eight PAHs in that mixture acted by simple addition, then 50% growth inhibition would occur at a TU_8 of 0.36 since the other seven PAH components together add up to ΣTU_i of 0.64. The experimental TU that would cause 50% growth inhibition due to different PAHs could be found from a plot of percent inhibition versus TU of the eighth PAH compound, and compared against the expected value of TU_8 of 0.36 to verify simple addition.

5.2.4 Molecular Connectivity-QSAR Model for PAH Chronic Toxicity Prediction

A QSAR is a mathematical model between a property (activity) of a certain compound, in this case the chronic toxicity value of a certain PAH compound, and the descriptors of that PAH. The descriptors are chemical or physical characteristics obtained experimentally or from the structure of the compound itself. In order to develop the MOLCONN-QSAR model, Kassim [1]: (1) prepared a training data set of chronic toxicity measurements to statistically establish the relationship between chronic toxicity and PAH descriptors of interest, and (2) used a QSAR modeling technique to predict the chronic toxicity of untested PAH compounds for which the descriptors are known.

Here, molecular connectivity (MOLCONN) models were used as descriptors of PAHs. It is a method of describing molecular structure based solely on the molecule's bonding and branching patterns. Using a simple algorithm, a series of indices called zero order ($^0\chi$), first order ($^1\chi$) and so forth, based on increasingly larger molecular fragments (called subgraphs) were computed for PAH compounds, as follows:

- Simple indices encode information on sigma bonded electrons that can be observed directly from bonding patterns in structural formulae of PAHs,
- Valence indices (denoted with a "v" superscript) encode sigma, pi and lone electrons and so include more information about the specific elements included in the PAH compound.
- Indices of order greater than two can be computed as either path, cluster, path/cluster or chain depending upon the configuration of the molecular fragments.

Simple and valence indices up to sixth order were computed for all the PAHs used in the present study database. The program MOLCONN2 [58, 60, 66] performed these calculations using the chemical structural formula as input. SAS

software was used on a mainframe computer to perform statistical analyses. First, indices were selected which explained the greatest amount of variance in the data (the R^2 procedure). These indices were then used in a multiple linear regression analysis (REG procedure).

Using the 96-hr chronic toxicity data of the different PAHs and their molecular connectivity indices (MCIs), the following MOLCONN-QSAR models were developed:

$$\log EC_{50}(\text{mg/L}) = 4.9861 - 0.888\,(^{3}\chi^{p}) \tag{84}$$

$$\log EC_{50}(\text{mg/L}) = 2.4784 - 2.8352\,(^{6}\chi_{v}^{p}) \tag{85}$$

$$\log EC_{50}(\text{mg/L}) = 5.1341 - 1.4212\,(^{2}\chi^{v}) \tag{86}$$

Here $^{3}\chi^{p}$, $^{6}\chi_{v}^{p}$ and $^{2}\chi^{v}$ are MCIs, listed in Table 11 and shown in Fig. 10. All the relationships were significantly correlated; however, Eq. 61 (EC_{50} vs $^{6}\chi_{v}^{p}$) was used to develop the MOLCONN-QSAR model. The rationale behind that is: (1) it has the highest correlation coefficient (R^2=0.9740) among the MCIs, (2) the inclusion of higher order indices, such as the sixth order index used here, indicates that a critical dimension or number of atoms in a chain is influential. As shown in Fig. 11, the negative coefficient on $^{6}\chi_{v}^{p}$ reflects the fact that beyond a critical dimension, the increasing size, particularly increasing chain size, reflected by $^{6}\chi_{v}^{p}$ decreases a molecule's EC_{50} value (increases its chronic toxicity).

The MOLCONN-QSAR model represented by Eq. 85 (Fig. 10) was used to predict concentrations of the components in the PAH mixtures that would jointly cause 50% growth inhibition. The individual concentrations of the components in the PAH mixture C_i were determined by multiplying the EC_{50} values

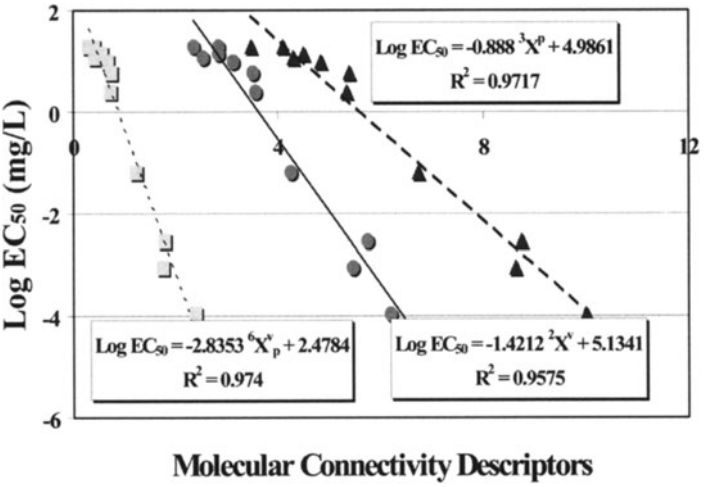


Fig. 10 Concentration of the Molecular Connectivity-QSAR toxicity model for PAHs

by their respective TU_i values. The TU_i value for the eighth component (TU_8) is taken as 0.36 assuming the simple additivity model ($\Sigma TU_i=1$). The simple additivity model was then verified, and these calculations are illustrated in Table 12 for the eleven "eight-component" PAH mixtures tested.

Table 12 Experimental and predicted toxicity values for PAH mixtures of eleven compounds

PAH mixture ID	PAH compounds in mixtures	Experimental values			MOLCONN-QSAR predicted values		
		EC_{50} (mg/L)	TU_i	Conc. (mg/L)	EC_{50} (mg/L)	TU_i	Conc. (mg/L)
8-C1	Naphthalene	19.537	0.08	1.563	42.446	0.08	3.396
	1-Methylnaphthalene	19.000	0.08	1.520	20.700	0.08	1.656
	2-Methylnaphthalene	12.000	0.09	1.080	19.392	0.09	1.745
	2,6-Dimethylnaphthalene	14.122	0.09	1.271	8.299	0.09	0.747
	Acenaphthylene	9.702	0.10	0.970	3.792	0.10	0.379
	Phenanthrene	6.000	0.10	0.600	2.401	0.10	0.240
	Anthracene	2.500	0.10	0.250	2.563	0.10	0.256
	Fluoranthene	0.064	0.21	0.009	0.098	0.36	0.035
	Total TU_i		0.85			1.00	
8-C2	1-Methylnaphthalene	19.000	0.08	1.520	20.700	0.08	1.656
	2-Methylnaphthalene	12.000	0.08	0.960	19.392	0.08	1.551
	2,6-Dimethylnaphthalene	14.122	0.09	1.271	8.299	0.09	0.747
	Acenaphthylene	9.702	0.09	0.873	3.792	0.09	0.341
	Phenanthrene	6.000	0.10	0.600	2.401	0.10	0.240
	Anthracene	2.500	0.10	0.250	2.563	0.10	0.256
	Fluoranthene	0.064	0.10	0.006	0.098	0.10	0.010
	Benzo[*a*]pyrene	0.001	0.14	0.000	0.004	0.36	0.001
	Total TU_i		0.78			1.00	
8-C3	2-Methylnaphthalene	12.000	0.08	0.960	19.392	0.08	1.551
	2,6-Dimethylnaphthalene	14.122	0.08	1.130	8.299	0.08	0.664
	Acenaphthylene	9.702	0.09	0.873	3.792	0.09	0.341
	Phenanthrene	6.000	0.09	0.540	2.401	0.09	0.216
	Anthracene	2.500	0.10	0.250	2.563	0.10	0.256
	Fluoranthene	0.064	0.10	0.006	0.098	0.10	0.010
	Benzo[*a*]pyrene	0.001	0.10	0.000	0.004	0.10	0.000
	Benzo[*e*]pyrene	0.003	0.17	0.000	0.003	0.36	0.001
	Total TU_i		0.83			1.00	
8-C4	2,6-Dimethylnaphthalene	14.122	0.08	1.130	8.299	0.08	0.664
	Acenaphthylene	9.702	0.08	0.776	3.792	0.08	0.303
	Phenanthrene	6.000	0.09	0.540	2.401	0.09	0.216
	Anthracene	2.500	0.09	0.225	2.563	0.09	0.231
	Fluoranthene	0.064	0.10	0.006	0.098	0.10	0.010
	Benzo[*a*]pyrene	0.001	0.10	0.000	0.004	0.10	0.000

Table 12 (continued)

PAH mixture ID	PAH compounds in mixtures	Experimental values			MOLCONN-QSAR predicted values		
		EC_{50} (mg/L)	TU_i	Conc (mg/L)	EC_{50} (mg/L)	TU_i	Conc (mg/L)
8-C4	Benzo[*e*]pyrene	0.003	0.10	0.000	0.003	0.10	0.000
	Perylene	0.000	0.07	0.000	0.000	0.36	0.000
	Total TU_i		0.71			1.00	
8-C5	Acenaphthylene	9.702	0.08	0.776	3.792	0.08	0.303
	Phenanthrene	6.000	0.08	0.480	2.401	0.08	0.192
	Anthracene	2.500	0.09	0.225	2.563	0.09	0.231
	Fluoranthene	0.064	0.09	0.006	0.098	0.09	0.009
	Benzo[*a*]pyrene	0.001	0.10	0.000	0.004	0.10	0.000
	Benzo[*e*]pyrene	0.003	0.10	0.000	0.003	0.10	0.000
	Perylene	0.000	0.10	0.000	0.000	0.10	0.000
	Naphthalene	19.537	0.21	4.103	42.446	0.36	15.281
	Total TU_i		0.85			1.00	
8-C6	Phenanthrene	6.000	0.08	0.480	2.401	0.08	0.192
	Anthracene	2.500	0.08	0.200	2.563	0.08	0.205
	Fluoranthene	0.064	0.09	0.006	0.098	0.09	0.009
	Benzo[*a*]pyrene	0.001	0.09	0.000	0.004	0.09	0.000
	Benzo[*e*]pyrene	0.003	0.10	0.000	0.003	0.10	0.000
	Perylene	0.000	0.10	0.000	0.000	0.10	0.000
	Naphthalene	19.537	0.10	1.954	42.446	0.10	4.245
	1-Methylnaphthalene	19.000	0.24	5.320	20.700	0.36	7.452
	Total TU_i		0.88			1.00	
8-C7	Anthracene	2.500	0.08	0.200	2.563	0.08	0.205
	Fluoranthene	0.064	0.08	0.005	0.098	0.08	0.008
	Benzo[*a*]pyrene	0.001	0.09	0.000	0.004	0.09	0.000
	Benzo[*e*]pyrene	0.003	0.09	0.000	0.003	0.09	0.000
	Perylene	0.000	0.10	0.000	0.000	0.10	0.000
	Naphthalene	19.537	0.10	1.954	42.446	0.10	4.245
	1-Methylnaphthalene	19.000	0.10	1.900	20.700	0.10	2.070
	2-Methylnaphthalene	12.000	0.23	2.880	19.392	0.36	6.981
	Total TU_i		0.87			1.00	
8-C8	Fluoranthene	0.064	0.08	0.005	0.098	0.08	0.008
	Benzo[*a*]pyrene	0.001	0.08	0.000	0.004	0.08	0.000
	Benzo[*e*]pyrene	0.003	0.09	0.000	0.003	0.09	0.000
	Perylene	0.000	0.09	0.000	0.000	0.09	0.000
	Naphthalene	19.537	0.10	1.954	42.446	0.10	4.245
	1-Methylnaphthalene	19.000	0.10	1.900	20.700	0.10	2.070
	2-Methylnaphthalene	12.000	0.10	1.200	19.392	0.10	1.939
	2,6-Dimethylnaphthalene	14.122	0.18	2.542	8.299	0.36	2.988
	Total TU_i		0.82			1.00	

Table 12 (continued)

PAH mixture ID	PAH compounds in mixtures	Experimental values			MOLCONN-QSAR predicted values		
		EC_{50} (mg/L)	TU_i	Conc (mg/L)	EC_{50} (mg/L)	TU_i	Conc (mg/L)
8-C9	Benzo[*a*]pyrene	0.001	0.08	0.000	0.004	0.08	0.000
	Benzo[*e*]pyrene	0.003	0.08	0.000	0.003	0.08	0.000
	Perylene	0.000	0.09	0.000	0.000	0.09	0.000
	Naphthalene	19.537	0.09	1.758	42.446	0.09	3.820
	1-Methylnaphthalene	19.000	0.10	1.900	20.700	0.10	2.070
	2-Methylnaphthalene	12.000	0.10	1.200	19.392	0.10	1.939
	2,6-Dimethylnaphthalene	14.122	0.10	1.412	8.299	0.10	0.830
	Acenaphthylene	9.702	0.23	2.134	3.792	0.36	1.365
	Total TU_i		0.87			1.00	
8-C10	Benzo[*e*]pyrene	0.003	0.08	0.000	0.003	0.08	0.000
	Perylene	0.000	0.08	0.000	0.000	0.08	0.000
	Naphthalene	19.537	0.09	1.758	42.446	0.09	3.820
	1-Methylnaphthalene	19.000	0.09	1.710	20.700	0.09	1.863
	2-Methylnaphthalene	12.000	0.10	1.200	19.392	0.10	1.939
	2,6-Dimethylnaphthalene	14.122	0.10	1.412	8.299	0.10	0.830
	Acenaphthylene	9.702	0.10	0.970	3.792	0.10	0.379
	Phenanthrene	6.000	0.29	1.740	2.401	0.36	0.864
	Total TU_i		0.93			1.00	
8-C11	Perylene	0.000	0.08	0.000	0.000	0.08	0.000
	Naphthalene	19.537	0.08	1.563	42.446	0.08	3.396
	1-Methylnaphthalene	19.000	0.09	1.710	20.700	0.09	1.863
	2-Methylnaphthalene	12.000	0.09	1.080	19.392	0.09	1.745
	2,6-Dimethylnaphthalene	14.122	0.10	1.412	8.299	0.10	0.830
	Acenaphthylene	9.702	0.10	0.970	3.792	0.10	0.379
	Phenanthrene	6.000	0.10	0.600	2.401	0.10	0.240
	Anthracene	2.500	0.30	0.750	2.563	0.36	0.923
	Total TU_i		0.94			1.00	

5.2.5 Data Interpretation

The experimental results and the procedure used in determining the TU of the eighth PAH compound (TU_8) that would induce 50% growth inhibition for the fresh water alga *Selenastrum capricornutum* are detailed in Fig. 11 for only a single test on the eighth component PAH mixture (8-C1, see Table 12 for the mixture composition).

In general, three separate runs were conducted for each PAH mixture. A plot of % growth inhibition (% EC_{50}) versus TU_8, generated from three different

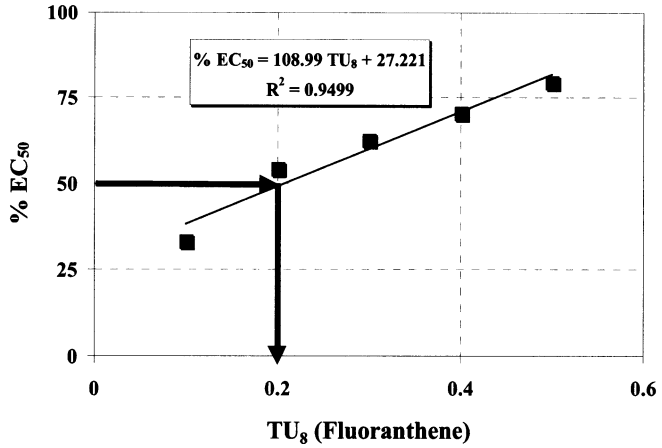


Fig. 11 Procedure for analyzing and determining the TU of the eighth PAH compound in mixture 8-C1 (TU_8 for fluoranthene, Table 9) that would induce 50% growth inhibition for the fresh water alga *Selenastrum capricornutum*

runs on PAH mixture 8-CI, is shown in Fig. 12. The correlation coefficient (R^2) in such plots for all of the eleven PAH mixtures assayed exceeded 0.8.

The ΣTU_i, AI, and MTI values found for the eleven "eight-PAH" mixtures are summarized in Table 13 along with the experimentally determined values for TU_8 (see Fig. 12). In the case of the ΣTU_i (Table 13) joint toxic effect model,all of the observed values were below 1 (indicating synergism rather than a simple additivity model), with a low value of 0.71 for PAH mixture 8-C4 (the mixture causing highest synergism) and a high value of 0.94 for PAH mixture 8-C11 (close to simple addition). For the AI joint toxicity model, none of the TU_8 values of the different PAH mixtures recorded a zero value (Table 13), with a high value of 0.29 (for mixture 8-C2) and a low of 0.07 (for mixture 8-C11). On the other hand, for the MTI all PAH mixtures recorded values over 1.00 (Table 13), with an average of 1.09.

Therefore, when Kassim [1] demonstrated synergism rather than simple additivity using the PAH MOLCONN-QSAR models (Table 8, Eqs. 84 to 86), the concentrations of the PAH components in mixtures that would cause 50% inhibition by joint action were accurately predicted. This can be easily seen from the associations of data points representing predicted vs experimental concentrations along the line of perfect prediction (Fig. 13).

In summary, all of the values observed by the use of different joint toxic effect modeling procedures indicated synergism rather than simple additive effects of the different PAH mixtures. Such a finding can have a big effect when measuring the bioavailable fraction of organic compounds at aqueous-solid phase interfaces. This is due to the fact that measured bioavailable fractions might be either overestimated because of synergism, or underestimated because of antagonism.

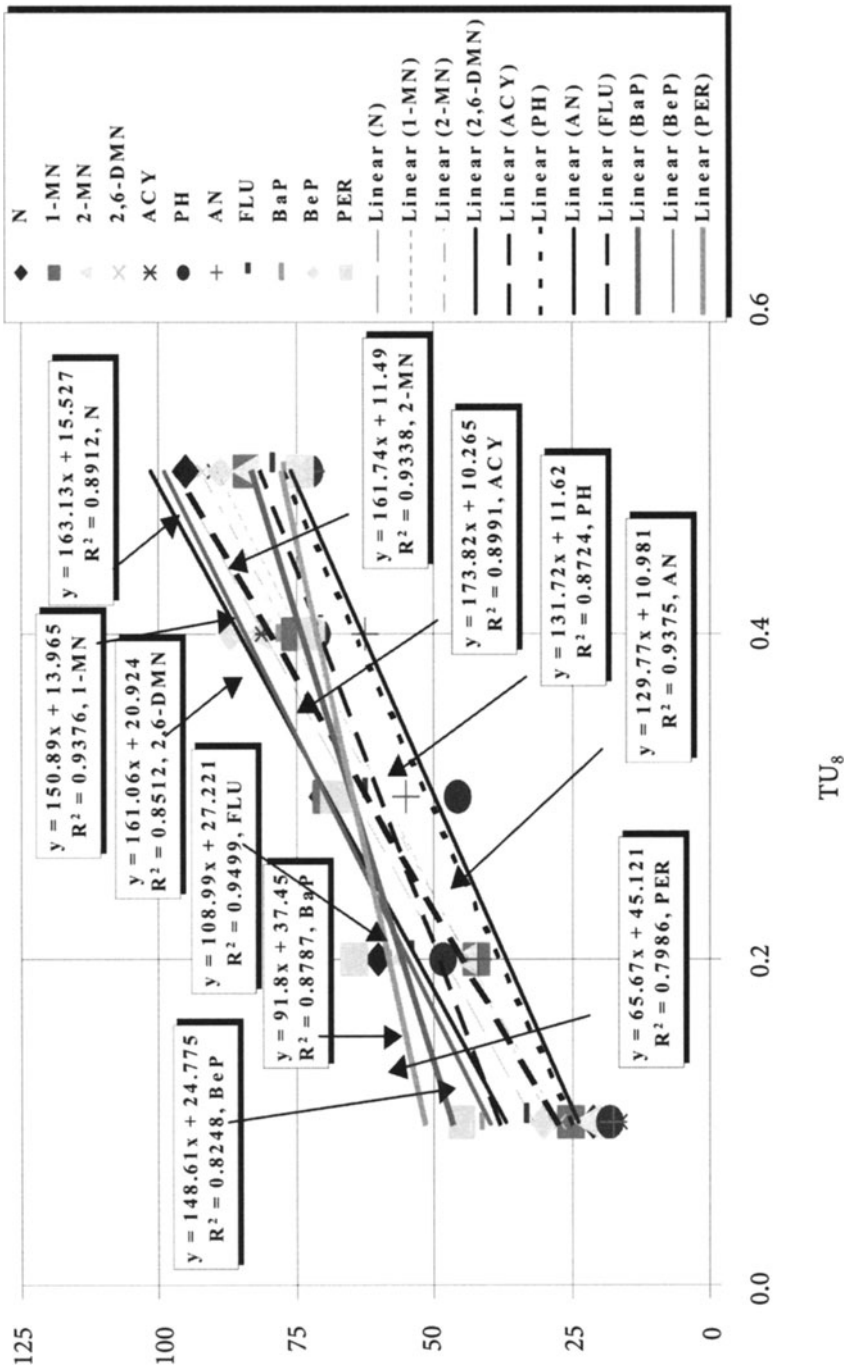


Fig. 12 Determination of TU_8 in non-uniform PAH mixture tests

Table 13 Summary of mixture toxicity results

PAH mixtures	Indicators of synergism*							
	ΣTU_i		AI		MTI		TU_8	
	Exp	Obs	Exp	Obs	Exp	Obs	Exp	Obs
8-C1	1.00	0.85	0.00	0.18	1.00	1.08	3.66	0.21
8-C2	1.00	0.78	0.00	0.29	1.00	1.13	3.66	0.14
8-C3	1.00	0.83	0.00	0.21	1.00	1.09	3.66	0.17
8-C4	1.00	0.71	0.00	0.41	1.00	1.20	3.66	0.07
8-C5	1.00	0.85	0.00	0.18	1.00	1.08	3.66	0.21
8-C6	1.00	0.88	0.00	0.14	1.00	1.06	3.66	0.24
8-C7	1.00	0.87	0.00	0.15	1.00	1.07	3.66	0.23
8-C8	1.00	0.82	0.00	0.22	1.00	1.10	3.66	0.18
8-C9	1.00	0.87	0.00	0.15	1.00	1.07	3.66	0.23
8-C10	1.00	0.93	0.00	0.08	1.00	1.03	3.66	0.29
8-C11	1.00	0.94	0.00	0.07	1.00	1.03	3.66	0.30
Mean	1.00	0.85	0.00	0.19	1.00	1.09	3.66	0.21

Exp=expected value; Obs=observed value.

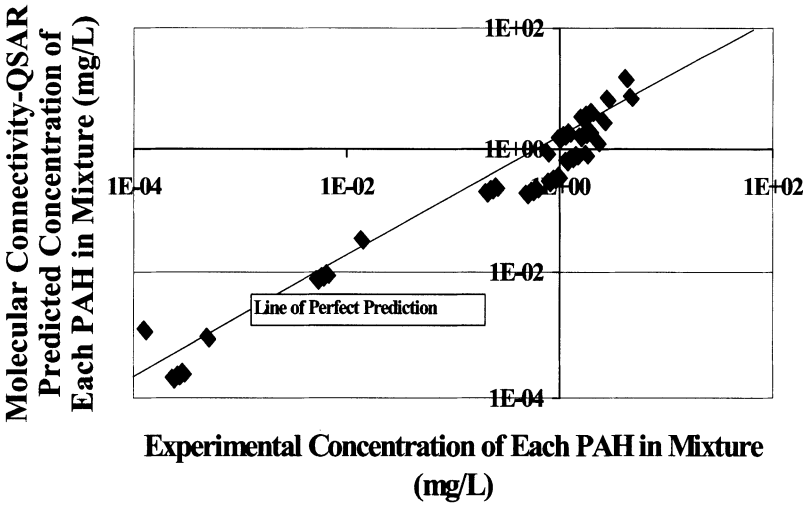


Fig. 13 Comparison between experimental and QSAR-predicted concentrations of each PAH compound in mixtures causing 50% inhibition

5.3 Predictive QSPR Model for Estimating Sorption Coefficients

Sorption/desorption is the key property for estimating the mobility of organic contaminant leachates from solid phases. There is a real need to predict such mobility at aqueous-solid phase interfaces. Solid phase sorption influences the extent of contaminant volatilization from the solid phase surface, its lateral or vertical transport and biotic or abiotic processes (biodegradation, bioavailability, hydrolysis and photolysis). The transport rate of an organic contaminant depends mainly on the partitioning between the vapor, liquid and solid phase of an aqueous-solid phase system.

In order to understand the complex interactions of organic contaminants at aqueous-solid phase interfaces and to predict their mobility, which can be determined from their sorption coefficients, it is necessary to consider: (1) the variation of molecular and structural properties of the contaminants concerned, and (2) the heterogeneous solid phase chemistry and physics. In the present section, sorption coefficients of various PAH compounds determined with five different sorbents are shown to be accurately predicted using a quantitative structure-property relationship (QSPR) model.

5.3.1 Model Development

The following shows the development of the predictive QSPR model. The descriptors considered for the model include geometric and topological descriptors, electronic properties, charge-dependent properties, physico-chemical properties, and accumulation factors. The solid phases studied include three soil types (mollisol, ultisol and aridisol) and two aquatic sediments.

5.3.1.1 Determination of Sorption Coefficients

The sorption behavior of 11 PAH compounds (a training set, Table 14) on various solid phases (three soils and two sediments) with different properties relevant to sorption (organic carbon content, clay content, pH, cation exchange capacity "CEC"; Table 15), was determined by batch equilibrium studies [1]. Batch equilibrium tests were designed to determine rates of equilibrium sorption under conditions of high mixing and high surface areas of the solid particles.

Solutions with a defined solid/solution ratio and containing one of five initial concentrations of the PAH of interest in the training set (Table 14) were tumbled for 24 h until equilibrium was reached. After centrifugation of the samples, the PAH concentration was determined in the liquid phase. The determined PAH concentrations in the liquid and solid phases (by difference) were used to calculate distribution coefficients (k_d) and to obtain k_f values using the Freundlich equation as shown in Table 1 (Eq. 5). In order to reduce

Table 14 Difference between predicted and observed logK_{OC} values for the training and validation data sets for soils and sediments

Data set	Compound name	Difference between predicted and observed logK_{OC} values	
		Soils	Sediments
Training data set	Naphthalene	4.39	−3.86
	1-Methylnaphthalene	1.05	−0.84
	2-Methylnaphthalene	1.05	−0.82
	2,6-Dimethylnaphthalene	−0.89	1.47
	Acenaphthylene	−1.81	0.55
	Phenanthrene	−3.09	3.23
	Anthracene	−3.59	3.69
	Fluoranthene	−0.21	−1.00
	Benzo[*a*]pyrene	0.30	−0.05
	Benzo[*e*]pyrene	0.30	−0.05
	Perylene	2.50	−2.35
Validation data set	Indane	11.25	−6.5
	1,2-Dimethylnaphthalene	0.41	1.04
	1,3-Dimethylnaphthalene	0.31	0.62
	1,4-Dimethylnaphthalene	−0.39	1.05
	1,5-Dimethylnaphthalene	−0.69	1.14
	2,3-Dimethylnaphthalene	−0.49	1.00
	1-Ethylnaphthalene	−0.29	0.92
	2-Ethylnaphthalene	−0.69	1.02
	1,4,5-Trimethylnaphthalene	1.20	−0.18
	Biphenyl	12.80	2.08
	4-Methylbiphenyl	11.76	2.43
	4,4′-Dimethylbiphenyl	12.81	0.46
	Diphenylmethane	13.46	3.32
	Bibenzyl	−2.69	4.85
	trans-Stilbene	−1.89	3.46
	Acenaphthene	−3.00	1.86
	Fluorene	−4.35	3.81
	1-Methylfluorene	0.51	−1.27
	1-Methylphenanthrene	1.85	−2.14
	9-Methylanthracene	1.85	−2.24
	2-Methylanthracene	1.85	−2.24
	9,10-Dimethylanthracene	5.41	−4.79
	Pyrene	−1.11	−0.20
	Benzo[*a*]fluorene	−0.85	−0.06
	Benzo[*b*]fluorene	0.85	−2.26
	Chrysene	7.80	21.69
	Triphenylene	−4.70	4.08
	p-Terphenyl	7.05	−7.97
	Naphthacene	−0.10	−0.82
	Benz[*a*]anthracene	7.30	−8.12
	Benzo[*b*]fluoranthene	2.50	−2.35

Table 14 (continued)

Data set	Compound name	Difference between predicted and observed logK_{OC} values	
		Soils	Sediments
Validation data set	Benzo[*j*]fluoranthene	-3.90	4.25
	Benzo[*k*]fluoranthene	-0.60	0.85
	7,12-Dimethylbenz[*a*]anthracene	-1.59	2.07
	9,10-Dimethylbenz[*a*]anthracene	-1.59	2.07
	3-Methylcholanthrene	0.86	0.11
	Benzo[*ghi*]perylene	5.16	-4.09
	Dibenz[*a,c*]anthracene	-0.59	2.14
	Dibenz[*a,h*]anthracene	0.71	0.74
	Dibenz[*a,j*]anthracene	0.51	0.94
	Pentacene	-0.49	2.04
	Coronene	-3.60	6.40

Table 15 Characteristics of the different solid phase particles

Solid phases		$\%C_{org}$	pH	CEC (mval 100 g)	$CaCO_3$ (%)	Grain size analysis		
Type	Name					Sand (%)	Silt (%)	Clay (%)
Soils	Olyic	6.18	6.8	25.3	14.2	64.2	21.3	14.5
	Woodburn	6.44	6.9	18.8	10.3	55.3	28.7	16.0
	Sagehill	1.91	6.7	11.7	8.7	66.2	12.3	21.5
Sediments	Willamette River, OR	1.81	7.1	14.7	12.6	26.9	49.5	23.6
	Yaquina Bay, OR	2.58	7.3	13.4	13.9	30.5	55.3	14.2

the variance in sorption coefficients (i.e., K_{OC}), the distribution coefficient (k_d or k_f) was frequently normalized to the organic carbon content (% OC) of the solid phase particles. For the training data set of 11 PAH compounds (Table 14), different sorption isotherm models were tested, namely: linear, Langmuir and Freundlich isotherms (see Table 1 for the corresponding equations). In general, the Freundlich isotherm model showed high correlation coefficients (Table 16).

5.3.1.2 Descriptor Calculations

The parameters used for regression analysis in the present case study were calculated based on the Quantum Chemical Programs Exchange program

Table 16 Summary of average values of the regression equation constants for the training data set (11 PAHs) on different solid phases (note: base 10 logs)

Solid phase type		Model isotherm	Y axis	Intercept	Slope	X axis	R^2
Soils	Olyic	Linear	C_s	0.0000	0.05422	C	0.7665
		Langmuir	C/C_s	36.1966	−7.6737	C	0.5437
		Freundlich	logC_s	0.8944	0.65068	log$C$	*0.8996*
	Woodburn	Linear	C_s	0.0000	0.0649	C	0.3536
		Langmuir	C/C_s	5.3679	4.0567	C	0.8862
		Freundlich	logC_s	2.6734	2.7456	log$C$	*0.9735*
	Sagehill	Linear	C_s	0.0000	0.0754	C	0.6777
		Langmuir	C/C_s	38.3664	3.2456	C	0.2867
		Freundlich	logC_s	2.6935	1.7546	log$C$	*0.8999*
Sediments	Willamette River	Linear	C_s	0.0000	0.0664	C	0.7696
		Langmuir	C/C_s	11.5671	3.7566	C	0.2699
		Freundlich	logC_s	3.6454	1.5765	log$C$	*0.8866*
	Yaquina Bay	Linear	C_s	0.0000	0.0764	C	0.5388
		Langmuir	C/C_s	4.8451	5.7472	C	0.8986
		Freundlich	logC_s	3.1467	2.7382	log$C$	*0.9895*

according to the AMI algorithm [5, 46–51, 58, 71]. The quantum mechanical parameters calculated were the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) and the difference between them, the ionization potential, electronegativity, dipole moment, and charge distribution. Depending on the charge distribution obtained, some further electronic descriptors, such as self-polarizability and the probability of a nucleophilic/electrophilic attack, were calculated. Geometrical descriptors calculated were the molar refraction, the molecular volume and the minimum and maximum diameter of the molecule [5, 102, 103]. The Randi indices used for analysis were calculated according to Kier and Hall [46–48, 51–52].

5.3.2 Model Testing and Validation

For the training data set (Table 14), few parameters of the 22 physical-chemical properties of the PAHs showed high significance versus logK_{OC}. These are the logK_{OW}, molecular weight and molecular connectivity indices (^3X_p, $^6X_v^p$, ^2X_v). Table 17 shows the correlation coefficients between logK_{OC} and various molecular descriptors, while Fig. 14 illustrates the regression equation models used for logK_{OC} prediction for both soil and sediment solids from their molecular connectivity indices.

The validation data set constitutes 42 PAHs (Table 14) comprising both unsubstituted and substituted compounds with a wide range of physical and chem-

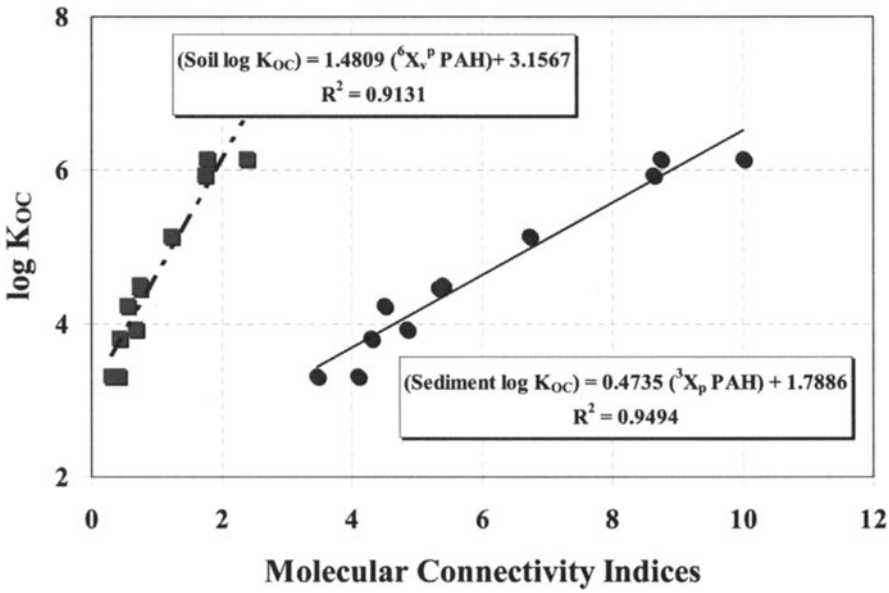
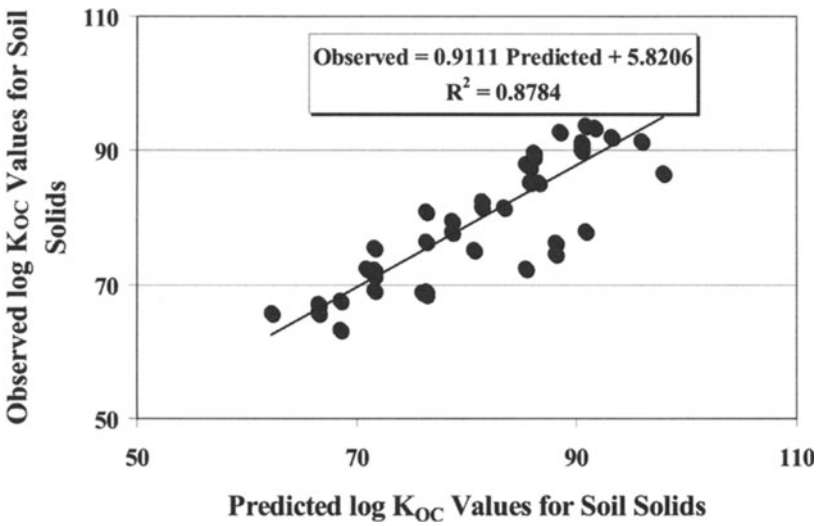


Fig. 14 Sorption coefficient (logK_{OC}) values vs molecular connectivity indices of the PAH training set for both soil and sediment solids

Table 17 Correlation coefficients between logK_{OC} and molecular descriptors of PAHs

Molecular descriptors		logK_{OC}	
		Soils	Sediments
logK_{OW}	0.8392	0.8563	
Molecular weight	0.8637	0.7837	
Geometric and topological parameters	Molar refraction	0.5796	0.5736
	Molar volume	0.6886	0.5716
Molecular connectivity indices	^3X_p	0.8950	*0.9494*
	$^6X_v^p$	*0.9131*	0.9010
	^2X_v	0.8634	0.8914
Electronic descriptors	Self polarizability	0.6495	0.7174
	D_N[a]	0.5895	0.4673
	Q_{tot}[b]	0.6568	0.6811
	Q_{ave}[c]	0.4862	0.5636

[a] Probability of nucleophilic attack; [b] total charge of molecule; [c] average charge of molecule.



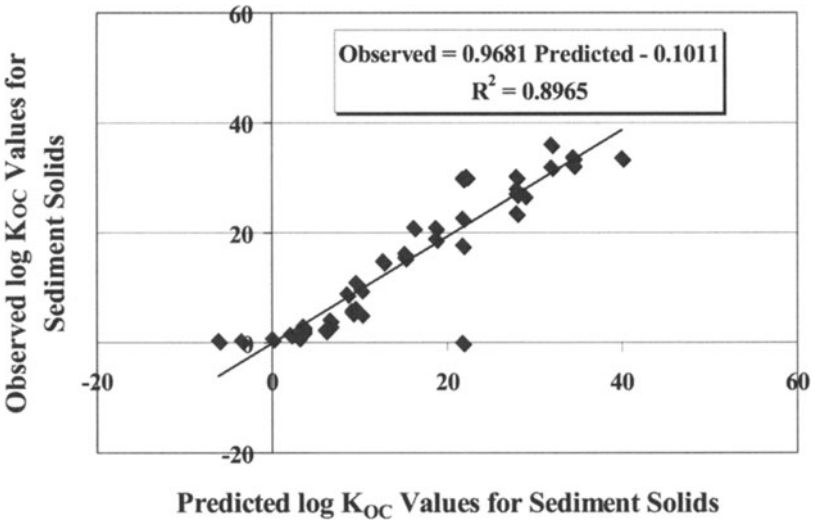


Fig. 15a–b Predicted vs observed values of sorption coefficients for (**a**) soil solids, and (**b**) sediment solids

ical properties. Predictive models developed for PAH compounds in the training data set (Fig. 14) were used to predict values of sorption coefficients. All predicted and observed values were regressed, and recorded significant R^2 values as shown in Fig. 15, while the difference between such values are presented in Table 14.

In summary, it can be stated that the characterization of sorption of hydrophobic compounds to the organic matter of solid phase particles by K_{OC} values

is a useful model for solids with a high organic carbon content and negligible clay content. For solids with a high clay content this is not applicable. Furthermore, this fact impedes the applicability to solids of other regions and composition.

6 Conclusions

Sorption and/or desorption (leaching) processes, an important chemodynamics behavior of contaminants leached from SWMs, constitute a consideration in the characterization of the nature of both solid wastes and contaminants. There is no simple and easy theoretical procedure that provides an exact quantitative prediction of what and how much will be sorbed by and/or leached from a certain solid phase over a period of time, and to predict the sorption/desorption-time relationship and the fate of contaminants once they are released into the environment.

It is important to differentiate between the two different types of sorption/desorption tests (batch and column-leaching), and the sorption characteristics determined from one should not be confused with the other. The purpose of laboratory testing to obtain contaminant-solid phase relationships is not only to obtain some insight into the accumulation and transmission characteristics of the solid materials with specific regard to the contaminant(s) of interest, but also to obtain physical input for transport modeling and chemodynamic purposes. It is also most important to conduct tests with the actual contaminant leachate or chemical species and with the solid particle samples representative of the field matrix.

There are a good number of sorption/desorption isotherm models which were developed in order to reflect the actual sorption/desorption processes occurring in the natural environment. Some models have a sound theoretical basis; however, they may have only limited experimental utility because the assumptions involved in the development of the relationship apply only to a limited number of sorption/desorption processes. Other models are more empirical in their derivation, but tend to be more generally applicable. In the present chapter, two main groups of models have been discussed, namely single component system (SCS) and multicomponent system models. SCS adsorption models actually deal with one contaminant component in an aqueous system or in a SWM leachate. To represent the equilibrium relation for SCS adsorption, a number of isotherm models reported in the literature were reviewed and comprise the following: double-reciprocal Langmuir, BET, Freundlich, Langmuir-Freundlich, Linear and Toth models. Multicomponent contaminants in an aqueous environment and/or leachate of SWMs, usually consist of more than one compound in the exposed environment. Multicomponent adsorption involves competition among contaminants to occupy the limited adsorbent surface available and the interactions between different adsorbates. A number of models have been developed to predict multi-

component adsorption equilibria using data from SCS adsorption isotherms. Multicomponent equilibria models include multicomponent Langmuir, modified multicomponent Langmuir, multicomponent Langmuir-Freundlich, Ideal Adsorbed Solution, and Simplified Competitive Equilibrium models.

For simple systems, considerable success has been achieved but there is still no established method with universal proven applicability, and this problem remains as one of the more challenging obstacles to the development of improved methods of process design.

Kinetics plays an important role in understanding the reaction rate between contaminant and solid phases. In general, it is incorrect to conclude that a particular reaction order fits the data based simply on data conformity to an integrated equation. Multiple integrated equations should also be tested in order to show that the reaction rate is not affected by species whose concentrations do not change considerably during an experiment. A number of kinetic models reported in the literature could describe rate data very well, when based on correlation coefficients and standard errors of the estimates. Despite this, there often is no consistent relation between the equation that gives the best fit and the physico-chemical and mineralogical properties of the adsorbent(s) being studied. Another problem with some of the kinetic models is that they are empirical and no meaningful rate parameters can be obtained. In general, the overall kinetics of many contaminant-solid phase chemical interactions may often be better described by mass transfer and diffusion-based models than by simple models such as first-order kinetics.

Simulation and predictive modeling of contaminant transport in the environment are only as good as the data input used in those models. Field methods differ from laboratory methods in that an increase in the scale of measurement relative to most laboratory methods is involved. Determination of transport parameters (transmission coefficients) must also use actual contaminant chemical species and field solid phase samples if realistic values are to be specified for the transport models. The choice of type of test depends on personal preference and availability of material. No test is significantly better than another. Most of the tests for diffusion evaluation are flawed to a certain extent.

Understanding environmental partitioning mechanisms of organic contaminants requires the complete knowledge and analysis of most of the important physical and chemical properties of such contaminants. These properties can initially determine the chemodynamics of the contaminants once they are released to the environment. Even through the predicted values may be slightly more or less accurate than experimental values, they are considered to be better than no values at all. Comparisons between predicted and experimental values of various physical and chemical properties of contaminants can provide an insight into the accuracy and precision of the developed models.

The application of quantitative structure-activity and quantitative structure-property relationships (QSARs and QSPRs, respectively), as well as their various modeling techniques for environmental planning and engineering management, are important. Generally speaking, the molecular connectivity in-

dices (MCIs) are still a sensitive property for many organic contaminants. MCIs can be effectively used to predict the partitioning of contaminants at interfaces. The predictive ability of the QSAR and QSPR models generated for various chemical compounds depends strongly on the composition of the selected training sets themselves. Most often the standard way of selecting this training set is either to take all available data in a database, or to start with a lead compound and generate the training set by changing one substituent at a time. Usually these approaches lead to training sets with low information content and thereby to QSARs with low predictive power. Because of the complex mechanism of biological activity, the models used for QSAR/QSPR must necessarily be statistical in nature. Furthermore, due to the variation in biological mechanisms it is necessary to have separate models for different classes of compounds.

A mixture of toxic and/or carcinogenic compounds can exhibit a greater impact than the individual constituents themselves. Such an impact (the joint toxic effect of multiple chemicals) must be studied and modeled where it has an importance in environmental chemodynamics studies. An understanding and ability to predict joint effects of chemical mixtures is useful in order to assess, predict and manage the environmental hazards of synthetic compounds. This prediction of mixture toxicity/carcinogenicity can provide an insight about the bioavailable fraction of contaminants, and greatly enhance the decision-making processes in optimizing, limiting or preventing the disposal and/or recycling of solid wastes and synthetic chemicals until they meet certain environmental criteria.

Because of the possible wide differences among properties and characteristics of solid phases, and the varied chemical compositions of contaminants or a contaminant leachate, field measurement variables present average properties over a large volume/area. The problem that complicates this picture is that ideal models are applied to a material or space which is highly non-ideal, non-uniform, and does not permit easy specification or identification of both initial and boundary conditions. To avoid this discrepancy, field and laboratory methods should be developed or modified to complement one another. Therefore, ideal theory needs to be supported with physical evidence if rational applications to field studies and environmental simulation are desired.

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