

Sustainable Practices in Geoenvironmental Engineering

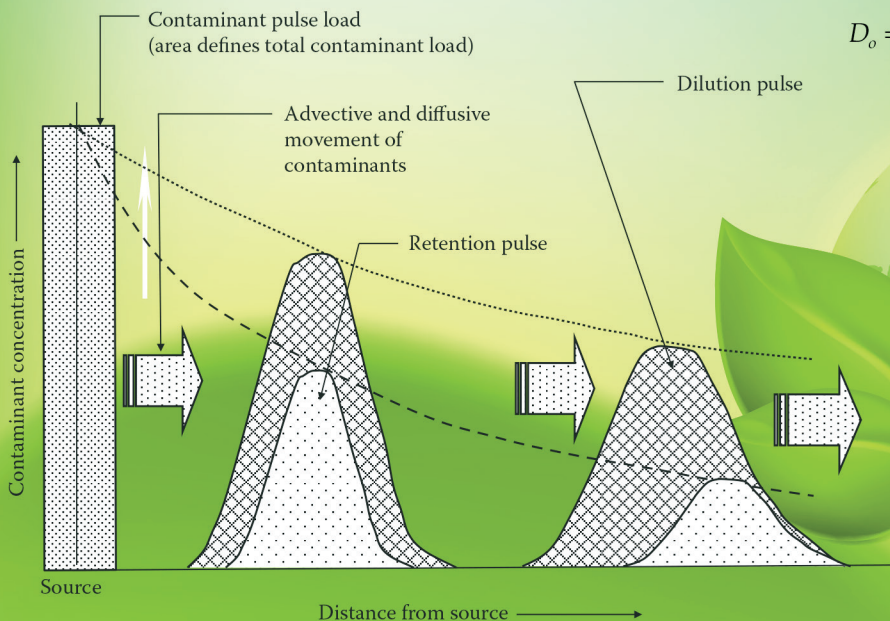
Second Edition

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$$D_o = \frac{RT\lambda^o}{F^2|z|} = 8.928 \times 10^{-10} \frac{T\lambda^o}{|z|}$$



Raymond N. Yong
Catherine N. Mulligan
Masaharu Fukue

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Preface to the First Edition

There are many who would argue that sustainability is a fashionable word that has lost its meaning when used in the context of society and the environment. They would further say that the word has been overused and that it never had any cachet because of one's inability to properly define what sustainability means. There are also those who will maintain that it is indeed foolhardy to attempt to write on the subject chosen for this book, simply because of the very amorphous nature of the subject.

The above notwithstanding, we have chosen to focus our attention on the geoenvironment and the need to protect the health and quality of the natural capital items that comprise the geoenvironment. We fully recognize that so long as continued depletion of the nonrenewable natural resources contained within the geoenvironment occurs, sustainability of the geoenvironment cannot be attained. We also recognize that the physical, chemical, and biological impacts to the geoenvironment from the various stress generators (humans, industry, agriculture, forestry, mining, cities, etc.) create situations that do not allow for sustainability goals to be achieved. If one combines all of the preceding impacts and their outcome with the recent spate of natural catastrophic disasters such as the earthquakes, floods, hurricanes, slides, famine, etc., it will become all the more evident that geoenvironmental sustainability is an impossible dream. Faced with all of these, one has two simple choices: (a) to admit defeat and prepare to face the inevitable or (b) to correct, ameliorate, mitigate, and even prevent those detrimental elements that can be corrected, mitigated, and eliminated, and to find substitutes and alternatives that will replace the depleting nonrenewable resources. The material in this book is a first step in adoption of the second choice.

The subject addressed in this book is both an ambitious one and also a very difficult one, not only from the viewpoint of the basic science–engineering relationships involved in dealing with the various kinds of impacts on the geoenvironment, but as much or more so from the fact that many crucial elements contributing to the generation of these same impacts cannot be properly addressed. One part of the problem is that many of these elements are either not within the purview of this book (especially the critical subject of biological diversity). The other part of the problem is that there are many elements that are dictated by prominent forces. Among these are (a) social–economic factors and business–industrial relationships, (b) public attitudes, awareness, sensitivity and commitment, and (c) political awareness and will.

The terrestrial environment, which is a major part of the geoenvironment is the engine that provides the base or platform for human sustenance—food, shelter, and clothing. By all accounts, there is universal consensus that the stresses and demands imposed by society on the ecosphere have far surpassed the capability of the world's natural resources to regenerate and replenish themselves to meet sustainability requirements. It is contended that there are insufficient resources to meet the continued demands of the present world population, and that collapse of society will inevitably occur. Some of the major factors involved include (a) loss of biological diversity, (b) increasing discharge of greenhouse gases to the atmosphere, (c) loss of soil quality, (d) increasing generation of wastes and pollutants, (e) depletion of nonrenewable natural resources such as fossil fuels, and (f) depletion of natural living resources such as fisheries and forests. Considerable attention is being paid to many of these issues by researchers, policy makers, and other professionals well

versed in engineering, scientific, and socioeconomic disciplines to alleviate the stresses to the geosphere and to seek sustainability and ways for society to live in harmony with the environment.

The primary focus of this book is on the geoenvironment and its importance as a resource base for life-support systems. Mankind depends on the ecosphere and in particular on the geoenvironment, to provide the raw materials to support life. Because of the many threats and negative impacts on the various life-support systems within the geoenvironment, there is a pressing need for one to (a) develop a better appreciation of the stresses imposed on the geoenvironment by mankind and (b) determine the requirements for sensible and proper management of our environmental resources to achieve a sustainable society.

The basic elements that define the geoenvironment will be developed in systematic detail and fashion, particularly in respect to their relationship to the five thematic areas: (a) water and sanitation, (b) energy, (c) health, (d) agriculture, and (e) biodiversity known as WEHAB. These were identified as key areas of concern by the Johannesburg World Summit on Sustainable Development (WSSD) in 2002. Industrialization, urbanization, agriculture (food production), and resource exploitation (including energy) are basic activities associated with a living and vibrant society. We consider these basic elemental activities to be necessary to sustain life and also to be integral to *development*. In general terms, we consider *development* to (a) embody the many sets of activities associated with the production of goods and services, (b) reflect the economic growth of a nation, state, city, or society in general, and (c) serve as an indication of the output or result of activities associated with these four main elemental activities. Questions often arise as to how these activities accord with the aims of sustainability (of a society), and how one structures and manages programs and activities that would provide for a sustainable society.

The first two chapters provide the basic background needed to address the assimilative capacity of soils, particularly in the light of management of pollutants in the ground, and also in the light of sustainable development and land use. The intent of Chapter 1 is to provide an introduction to many of the basic issues that arise in respect to impacts and assaults on the geoenvironment as a result of anthropogenic activities associated with the production of goods and services. In Chapter 2, we will focus on contamination of the land environment as one of the key issues in the need to protect the natural capital and assets of the land environment. We will be paying particular attention to the various aspects of ground contamination and land management requirements to meet sustainability goals in this chapter.

In Chapter 3, the importance of water is also highlighted. The quality of the water can be and is significantly impacted by all four components within "Sustenance and Development," "Industrialization," "Urbanization," "Resource Exploitation and Agriculture." Adequate quantities of good quality water are also essential for health, agriculture, energy, and biodiversity. We will examine the sources and impacts so that they can be controlled to maintain the water quality and supply for future generations.

Chapter 4 examines the built environment. Populations within cities require clean water, sewage, and waste management systems, housing, and transportation. They consume significant resources while polluting the air, land, and water. The increasing urban population will increase pressures on the geoenvironment in the years to come. The discussion in Chapter 5 will be confined to industrial activities associated with the extraction of nonrenewable mineral, nonmineral, and energy mineral natural resources (uranium and tar sands). Activities associated with the mining, extraction, and on-site processing of the extracted natural resource material (mineral and nonmineral) contribute significantly to the inventory of potential impacts to the terrestrial ecosystem.

In Chapter 6, we are concerned with the land environment and sustainability of the land ecosystem in relation to food production. We do not focus on food production from an agriculture engineering or soils science point of view since all the subjects and aspects of food production are well covered by soil science and agriculture engineering. Instead, the focus is from a geoenvironmental perspective on the results of activities in food production and in agroindustry on the geoenvironment itself. Chapter 7 directs its attention to the impacts on the geoenvironment in relation to industrial ecology. We consider the interactions on the geoenvironment by activities associated with manufacturing and service industries. Insofar as geoenvironmental resources are concerned, and in respect to sustainability goals, the primary concerns are (a) use of natural resources both as raw materials and energy supply and (b) emissions and waste discharges. Since the purview of this book addresses resource use from the geoenvironment framework and not from the industry perspective, we acknowledge the fundamental fact that the consequences of depletion of nonrenewable natural resources to society is a problem that must be confronted, and that the solution is not within the scope of this book. Accordingly, from the geoenvironmental protection point of view, we concentrate our attention on the impacts resulting from the discharge of liquid and solid wastes and waste products into the environment.

In Chapter 8, we discuss (a) the threats to the health of the coastal sediments realized from discharge of pollutants and other hazardous substances from anthropogenic activities, (b) the impacts already observed, and (c) the necessary remediation techniques developed to restore the health of the coastal sediments. A healthy coastal marine ecosystem ensures that aquatic plants and animals are healthy and that these do not pose risks to human health when they form part of the food chain.

Chapter 9 addresses the subject of land environment sustainability as it pertains to its interaction with the various waste discharges originating from industrial and urban activities. We focus our attention on developing concepts that involve the natural capital of the land environment. Chapter 10 discusses the magnitude of the problem of urbanization and industries. Particular attention is paid to the example of sites contaminated with hazardous wastes and other material discards. The discussion in this chapter recognizes that the impact from the presence of pollutants in the ground need to be mitigated and managed—as a beginning step toward protection of the resources in the environment and also as a first step toward achievement of a sustainable geoenvironment. The emphasis will be on using the properties and characteristics of the natural soil–water system as the primary agent for such purposes. Finally in Chapter 11, we (a) discuss the case of nonrenewable nonliving renewable natural resources, (b) look at some typical case histories and examples of sustainability actions, and (c) present the geoenvironmental perspective of the present status of “where we are in the geoenvironmental sustainability framework,” with a view that points toward “where we need to go.”

Given the nature and scope of the multidisciplinary material covered in this book, the limitations, and given the need to present the information to highlight the importance of the land environment and sustainability of the land ecosystem in relation to food production etc., we have had to make some difficult decisions as to the amount and level of “basic theory” needed to support the discussions presented. It was not our intent to develop or present extensive basic theories in any one discipline area of this multidisciplinary problem—except as is necessary to support the discussion from the sustainability viewpoint. There are basic textbooks that will provide the background theories for the various parts of the multidisciplinary problem treated in this book.

In the preparation of this book, the authors have benefited from the many interactions and discussions with their colleagues and research students, and most certainly with the

professionals in the field who face the very daunting task of educating the public, industry, and the political bodies on the need for conservation and protection of our natural resources. We have identified the sources of various kinds of noxious emissions in our discussions in the various chapters and have discussed the serious impact and consequences of such discharges. We have made mention in many chapters on the excess consumption of renewable resources and the significant problems of depleting nonrenewable resources—especially the energy resources. We have not embarked on detailed discussions on the kinds of alternate and/or substitute energy sources and the very pressing need for such sources to be found (researched and developed). That the need exists is eminently obvious. It was felt that this subject of depleting energy resources, together with the subject of climate change deserve full attention from books dedicated specifically to these very important subjects.

It is well understood that there is considerable effort directed toward alleviating many of the impacts described by industry, consumers, legislative bodies, the general public, and the professionals responsible for developing and implementing solutions. We wish to acknowledge these efforts and to remind all that much greater effort is needed. Finally, the first author wishes to acknowledge the very significant support and encouragement given by his wife Florence in this endeavor.

**Raymond N. Yong
Catherine N. Mulligan
Masaharu Fukue**

Preface to the Second Edition

Much has happened in the past 7 years since publication of the first edition of this book (*Geoenvironmental Sustainability*). Since that time, the combination of population growth and increased exploitation of both renewable and nonrenewable natural resources have added increased stresses on the quality and health of the geoenvironment. This is especially true when viewed in the context of the growing demand for food and shelter, and particularly for energy and mineral resources and their resultant effects on the natural capital of the geoenvironment. There is considerable need for governments, stakeholders, and geoenvironmental scientists and engineers to develop and implement measures needed to manage the natural capital and resources of the geoenvironment to ensure that future generations of humankind are not compromised because of the lack of availability of geoenvironmental resources.

As we have pointed out in the preface for the first edition of this book, continued harvesting or exploitation of the nonrenewable geoenvironmental natural resources means that we will never be able to achieve geoenvironment sustainability. We recognize this and acknowledge that the means and measures to diminish the depletion rate of the nonrenewable resources (conservation?) lie with *industry*. That being said, it is the renewable natural resources and the natural capital of the geoenvironment that need to be managed to ensure their sustainability. This means the development and implementation of technology and practices that seek to protect the quality and health of the natural resources and capital in the face of chemical, mechanical, hydraulic, thermal, and biogeochemical stressors originating from natural and anthropogenic sources.

The material in this new edition focuses on the application of geoenvironmental engineering procedures and practice to mitigate and ameliorate the adverse impacts generated by stressors imposed on and in the geoenvironment from anthropogenic sources. Although *industry* and *society* have made considerable efforts in recent years to adopt practices and procedures to “protect the environment” (i.e., to go “green”), there are still many activities that generate geoenvironment stressors, the impacts of which are seen to be adverse to the quality and health of the geoenvironment. What is needed is a set of tools and/or procedures and concrete examples that can be used by competent professionals to minimize and perhaps even eliminate the adverse consequences of the stressor impacts. For this to happen, it is necessary to identify the sources of the geoenvironment stressors and also the nature of the stressors (Chapters 3 through 9). With this knowledge, it then becomes possible to structure and/or develop technological and engineering tools and procedures to eliminate, where possible, or alleviate the adverse impacts to the geoenvironment (Chapters 10 through 13). We have chosen to call these engineering procedures and practices *sustainable practices in geoenvironmental engineering*.

In short, *sustainable practices in geoenvironmental engineering* is the application of geoenvironmental engineering practice to manage (control, alleviate, mitigate, etc.) stressor impacts on the geoenvironment from natural and anthropogenic sources in a manner that protects the quality and health of the natural resources and capital of the geoenvironment and ensures that these geoenvironmental natural resources and capital remain available for future generations (i.e., sustainability of the natural resources and capital). Geoenvironmental engineers and scientists have the knowledge and the various sets of tools to provide regulators, stakeholders and other interested parties with the capability to

protect the geoenvironment from stressor impacts. What is needed now is a deeper integration of the various disciplines such as soil physics and chemistry, microbiology, hydrogeology, and geochemistry, into the encompassing field of geoenvironmental engineering. As we have indicated before, to provide the kinds of technology and solutions needed to safeguard the quality and health of the geoenvironment, it is necessary for one to utilize all the pertinent science from the other disciplines.

The new concepts brought into the discussions on sustainability requirements include (a) the nature of indicators and how one specifies the different types of indicators, (b) site functionality and restoration and the choice and use of attributes, (c) remediation and management of contaminated soil, (d) techniques for remediation that include chemical, biological, chemical–thermal, and biological, (e) sustainable ground improvement using carbonate and artificial diagenetic processes, (f) exploitation and state of renewable resources, and (g) sustainable assessment tools. We are grateful to our many colleagues from the different disciplines for their invaluable input throughout our many discussions on the problem of *geoenvironmental sustainability*.

Raymond N. Yong
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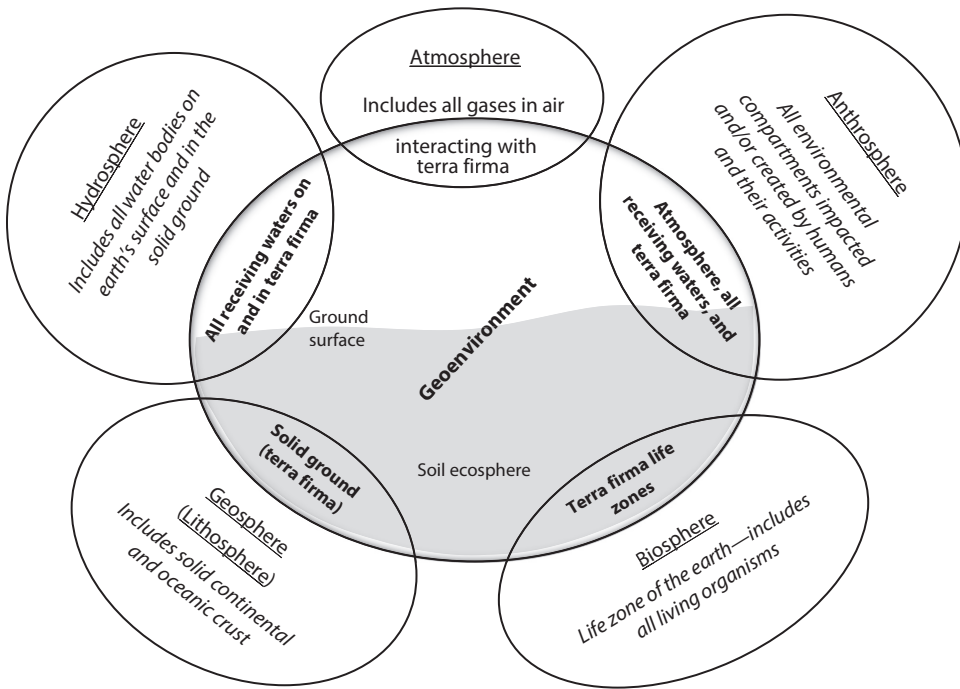
Geoenvironment Management and Sustainability

1.1 Introduction

There is growing concern and alarm that the demands on the ecosphere to provide for “food, shelter, and clothing” for the well-being of humankind are fast coming to the point where (a) continued exploitation of the nonrenewable natural resources such as fossil fuels and minerals will be highly prohibitive and (b) renewable resources will not be able to regenerate and replenish themselves to meet sustainability criteria. The stresses generated by these demands create, in most cases, adverse impacts on the geoenvironment such as (a) loss of biological diversity, (b) increasing discharge of noxious gases and particulates that find their way back to the land surface, (c) loss of soil quality and soil functionality, (d) increasing generation and discharge of wastes and pollutants to the land and aquatic environments, and (e) most importantly, decreased geoenvironment carrying capacity. Considerable attention is being paid to many of these issues by researchers, policy makers, and other professionals well-versed in engineering, scientific, and socioeconomic disciplines to alleviate the stresses to the geosphere and to seek sustainable ways for society to live in harmony with the environment.

The above sustainability concerns have been studied, documented, and published by researchers and government bodies dealing with *sustainable development* issues. The reader is well advised to consult these sources for discussions on these subjects. The primary focus of this book is on the *geoenvironment* and its importance as a resource base for life-support systems—with particular attention on issues relating to its carry capacity and capability for regeneration of the geoenvironment natural resources. We define the *carrying capacity of the geoenvironment* as the ability of the geoenvironment to indefinitely sustain the population at hand (or a growing population) with its naturally derived resources. Although some degree of human intervention is required to capitalize on these natural resources, e.g., agriculture, forest management, breeding, hydro-power generation, it must be understood that the basic natural resource being exploited is the factor that enters into the calculation of the carrying capacity of the geoenvironment. Humans depend on the ecosphere, and in particular on the geoenvironment, to provide the basic materials to support life. Because of the many threats and adverse impacts on the various life-support systems within the geoenvironment, there is pressing need for one to (a) develop a better appreciation of the stresses imposed on the geoenvironment by humankind and (b) determine and implement the requirements for sensible and proper management of our geoenvironmental resources to meet the goals of a sustainable society.

Many of the terms used in this book will have slightly different meanings depending on one's background, perspective, and scientific-engineering discipline. It would be useful, at the outset, to establish what we mean by the term *geoenvironment*. The geoenvironment

**FIGURE 1.1**

Venn diagram showing the various elements in the five ecosphere components (atmosphere, hydrosphere, geosphere, biosphere, and anthrosphere) that make up the geoenvironment.

is a significant part of the ecosphere. Figure 1.1 shows the various components of the ecosphere and their relationship to the geoenvironment. The ecosphere shown in the Venn diagram in Figure 1.1 consists of the (a) atmosphere, (b) geosphere, which is also known as the lithosphere, (c) hydrosphere, (d) biosphere, and (e) anthrosphere. The various elements contributing to the attributes and features of the geoenvironment will be discussed in Section 1.2.

Industrialization, urbanization, agriculture (food production), and natural resource exploitation (including energy) are basic activities associated with a living and vibrant society. We consider these basic elemental activities to be necessary to sustain life and also to be integral to development. In general terms, we consider development to (1) embody the many sets of activities associated with the production of goods and services; (2) reflect the economic growth of a nation, state, city, or society in general; and (3) serve as an indication of the output or result of activities associated with these four main elemental activities. Questions often arise as to how these activities are compatible with, or are in conflict with the carrying capacity of the geoenvironment.

1.1.1 Impacts on the Geoenvironment

Almost any physical or chemical action or event that happens in the ecosphere will impact on the geoenvironment. The question of whether these impacts will add value to or detract from the functionality of the geoenvironment and its ecosystems highlights some of the issues at hand. It is difficult to catalogue or list all of the impacts resulting from all the various kinds of stresses imposed on the geoenvironment. It is not only because this cannot

be done, but also because we need to arrive at some sets of criteria that will tell us “what constitutes an impact.” In many instances, we may not readily recognize or be aware of the impacts from many sets of activities or events—natural or man-made. To some extent, this is because (a) the effects of the impacts will not be immediately evident, for example, in the case of long-term health effects, and (b) the effects or results of the impacts cannot be recognized, i.e., we have yet to learn or recognize the results or effects of the impacts on the various biotic receptors and the environment itself. The important lesson to bear in mind is that any kind of geoenvironment impact, i.e., impact on and in the geoenvironment, may, sooner or later, produce reactions and/or conditions in the geoenvironment that may be benign, beneficial, or adverse to the geoenvironment.

1.1.2 Geoenvironment Impacts from Natural Events and Disasters

The impacts on the geoenvironment from “natural” events (disasters), for example, earthquakes, tsunamis, hurricanes, typhoons, floods, and landslides, to name a few, are obvious, inasmuch as they are well reported in the daily newspapers. Recent events such as (a) the late December 2004 tsunami in South East Asia, (b) the various hurricanes in late summer 2005 that battered the gulf region of North America, (c) the typhoons and floods in East Asia and floods in Central America in the same period, (d) the earthquake in October of 2005 in the Pakistan–Afghanistan–India region, and (e) the March 11, 2011, East Japan Great earthquake and the accompanying devastating tsunami are reminders that natural events can have considerable impact not only on the geoenvironment and its landscape, but also on human life and other life forms (domestic animals and other wildlife).

Some of the dramatic impacts on the geoenvironmental landscape due to these natural catastrophic events include (a) collapse of man-made and natural structures and other infrastructure facilities such as roads, pipelines, transmission towers, etc.; (b) floods; (c) deposition of airborne toxic substances released from damaged structures such as the radioactive nuclides released from the tsunami-associated damaged nuclear power reactors in the East Japan earthquake; (d) landslides; and (e) fires. Displacement of thousands and even millions of people due to loss of dwellings and loss of life due to collapsing structures, floods, and landslides, ground contamination from deposited airborne toxic substances, restriction or prohibition of agricultural and food-production activities in lands contaminated by deposition of airborne toxic substances, and ingestion of polluted waters are some of the impacts to humans. All of these events and their impacts on human life and other life forms and local and global societal response to such events merit serious and proper consideration and attention in books and treatises devoted to the various aspects of these catastrophic events. They are not within the purview of this book. What is of direct concern in this book is the impact of anthropogenic activities on the health and carrying capacity of the geoenvironment.

1.1.3 Anthropogenic Forces and Impacts on Geoenvironment

The intent of this chapter is to provide an introduction (a) to the many basic issues that arise from impacts and assaults on the geoenvironment resulting primarily from anthropogenic activities and (b) to the kinds of geoenvironmental engineering practices oriented toward restoring and/or preserving site (or region) functionality and carrying capacity of the geoenvironment, i.e., sustainable practices. We consider the geoenvironment to consist of the terrestrial (land surface) ecosystem. As seen in Figure 1.1, this includes the aquatic ecosystems contained within and contiguous to the land mass. Many of the driving forces responsible for these impacts and assaults can be attributed to actions of *production* and

implementation technology. A large proportion of these actions are not willful. The adverse impacts on the environment and the geoenvironment in particular, resulting from many of these actions are the result of a lack of understanding of the fragility of the geoenvironmental systems. A pertinent example of this is the presence of historic and orphan toxic and nontoxic waste-polluted sites populating the land surface in many parts of the world. These are the legacy of our historic lack of appreciation of the damage done to the land environment by the many activities in support of production of goods and services. These kinds of goods and activities are necessary items in support of industrial development and a vibrant society. Not all of the kinds or types of natural and man-made impacts on the geoenvironment resulting from these activities can be considered. The geoenvironmental impacts that are health-threatening constitute the major focus of this book. By and large, these (impacts) result from discharges from industrial operations and urban activities. A more detailed description and discussion of the anthropogenic impacts on the geoenvironment will be considered in the next chapter.

1.2 Geoenvironment, Ecosystems, and Resources

The *geoenvironment* is a specific compartment of the environment, and as such, concerns itself with the various elements and interactions occurring in the domain defined by the dry solid land mass identified as *terra firma*. These include a significant portion of the geosphere and portions of the atmosphere, hydrosphere, biosphere, and anthrosphere.

We consider the *geosphere* to include the inorganic mantle and crust of the Earth, including the land mass and the oceanic crust. Also included in this category are the solid layers (soil and rock mass) stretching downward from the mantle and crust. One could say that one part of the geoenvironment is the *terra firma* component of the geosphere—as seen in Figure 1.1.

The *hydrosphere* refers to all the forms of water on Earth, i.e., oceans, rivers, lakes, ponds, wetlands, estuaries, inlets, aquifers, groundwater, coastal waters, snow, and ice. The geoenvironment includes all the receiving waters contained within the *terra firma* in the *hydrosphere*. This excludes oceans and seas, but is meant to include rivers, lakes, ponds, inlets, wetlands, estuaries, coastal marine waters, groundwater, and aquifers. The inclusion of coastal (marine) environment in the geoenvironment is predicated on the fact that these waters are impacted by the discharge of contaminants in the coastal regions via runoffs on land and discharge of polluted waters from rivers or streams. Chapter 8 examines sustainability issues of coastal marine environment in detail.

The *biosphere* is the zone that includes all living organisms, and the *environment* is the biophysical system wherein all the biotic and abiotic organisms in the geosphere, hydrosphere, and atmosphere interact. The geoenvironment includes the life zones in or on *terra firma* from the *biosphere*.

The *atmosphere* refers to all the gases in air that interact with the land environment (*terra firma*).

The *anthrosphere* refers to the various environmental compartments impacted by humans and their activities.

The term *ecosystem* refers to a system where the various individual elements and organisms interact singly or collectively to the advantage or detriment of the whole. The relationships formed between these elements and organisms can be symbiotic or antagonistic. For an ecosystem to be self-sustaining, the relationships between the communities in the ecosystem need to be symbiotic, and furthermore, the interactions must be mutually beneficial. The various ecosystems that exist in the geoenvironment have functions, uses, resources, and habitats that are crucial to the production of goods and the means for ensuring life support.

The biological component within the ecosystems that comprise the terrestrial ecosystem do not fall within the purview of this book except insofar as they contribute to the persistence, transformation and fate of pollutants in the ground. In particular, we will be concentrating on the land aspects of the terrestrial ecosystem, and more specifically with the land surface (landscape), the soil ecosystem, and subsurface systems. The term *pollutants* is used to denote *contaminants* that have been classified by regulatory agencies as toxic or noxious substances that are threats to the health of humans and the environment. *Contaminants* are substances that are not indigenous to the location under consideration. All pollutants are contaminants, but not all contaminants are pollutants.

1.2.1 Ecozones and Ecosystems

Ecology is generally defined as the study of the relationship between living and nonliving organisms and their environment. The study of these relationships is facilitated by establishing ecozones or ecosystems. Strictly speaking, *ecozones* are zones that are delineated according to some sets of established ecological characteristics. They are essentially basic units of the land or marine environment that are distinctly characterized by the living and nonliving organisms within that region. *Ecozones* are geographical units that are usually several hundreds of square kilometers in spatial extent. The *ecosystem* or ecosystems bounded or resident within an ecozone deals with the mutual interactions between the living and nonliving organisms in this zone. An *ecosystem* is defined herein as a discrete system that (a) contains all physical (i.e., material) entities and biological organisms and (b) includes all the results or products of the interactions and processes of all the entities and organisms in this system. With this classification scheme, one can distinguish between the two primary ecosystems constituting the ecosphere, namely the land and aquatic ecosystems. The delineation of ecozones and ecosystems is somewhat arbitrary and can be performed or undertaken according to several guidelines. The boundaries demarking the ecozones are not fixed.

Classification and characterization of these land ecosystems can be performed according to various standards or guidelines. Classification according to the physiographic nature of the land is one of the more popular schemes available. Under such a scheme, one has therefore such ecosystems as alpine, desert, plains, coastal, arctic, boreal, prairie, etc. Another popular scheme for classification is the resource-based method of classification. This approach is based on the identification of the sets of activities or the nature of the primary or significant resources constituting the specific land environment under consideration—such as agro ecosystem and forest ecosystem. Within each ecosystem, there exist numerous elements and activities that can be examined and documented in respect to *before* and *after* ecosystem impact. One of the primary reasons for classification of any of the ecosystems is to define, bound, or document the *sphere of influence or examination wherein all the elements of the ecosystem interact, and are dependent on the welfare of each individual element for the overall state, benefit, and function of the ecosystem*.

1.2.2 Natural Resources and Biodiversity in the Geoenvironment

Natural resources in the geoenvironment are defined as commodities that have intrinsic value in their natural state. They are the natural capital of the geoenvironment. In describing the natural resources in the geoenvironment, the most obvious ones are often cited immediately. These include water, forests, minerals, coal and hydrocarbon resources (oil, gas, and tar sands, for example), and soil. Other not so obvious resources are the developed resources such as agricultural products and alternative energy generation (resources) such as solar, geothermal, wind, tidal, and hydro.

One natural resource that is often overlooked is biological diversity (biodiversity). This is one of the most significant of the natural resources in the ecosystem. We use the term biodiversity to mean the diversity of living organisms such as plants, animals, and microbial species in a specific ecosystem. They play significant roles in the development of the many resources that we have identified above, through mediation of the flow of energy (photosynthesis) and materials such as carbon, nitrogen, and phosphorous. According to Naeem et al. (1999), ecosystems consist of plants, animals, and microbes, and their associated activities, the results of which impact on their immediate environment. They point out that a functioning ecosystem is one that exhibits biological and chemical activities characteristic for its type and give the example of a functioning forest ecosystem that exhibits rates of plant production, carbon storage, and nutrient cycling that are characteristic of most forests. It follows that if the trees in the forest are harvested or if the forest ecosystem is converted to another type of ecosystem, the specific characteristics of a functioning forest ecosystem will no longer exist.

For the purpose of this book, we define a *functioning ecosystem* to include not only the biological and chemical activities, but also the physicochemical activities and physical interactions characteristic of the type of ecosystem under consideration. Trevors (2003) has enumerated a noteworthy list for consideration in respect to the role of biodiversity as part of our life-support system. Included in the detailed Trevors (2003) list are such considerations as:

- Maintenance of atmospheric composition and especially the production of oxygen by photosynthesis and the fixation of carbon dioxide,
- Water cycle via evaporation and plant transpiration,
- Interconnected nutrient cycles (e.g., C, N, P, S) driven by microorganisms in soils, sediments, and aquatic environments,
- Carbon sources and sinks,
- Pollination of agricultural crops and wild plants,
- Natural biocontrol agents, for example, in microbial degradation of pollutants in soil, water, sediments, wastewater, and sewage treatment facilities.

1.3 Geoenvironment Sustainability

Since the natural resources of the geoenvironment provide the main elements and basis for production of “food, shelter, and clothing” for the global population, the question that begs itself is, “How sustainable is the geoenvironment?” There is no single answer to this seemingly simple question—primarily because one needs to include in the discussions

(1) the ingenuity of mankind to develop technologies, tools, and devices designed to alleviate stressful demands on the geoenvironment and (2) the effect and influence of governmental and societal regulations on practices designed to manage the natural resources of the geoenvironment. In recognition of these two fundamental factors, the discussions in the chapters of this book center around (1) the impacts on the geoenvironment due to the stresses generated by mankind (anthropogenic stressors and their impacts) and (2) the practical ways in which one could alleviate, ameliorate, mitigate, etc., these impacts. The remedial activities required to meet the goals ensuing from item (3) can be considered to form the basis for geoenvironment sustainable practices. The principal focus for these activities is on the land component of the geoenvironment and its included waters.

1.3.1 Geoenvironment as a Natural Resource Base

Figure 1.2 shows a schematic of the various elements and interactions that contribute to the well-being of society. The three basic components shown at the top of the schematic (energy, water and soil, and natural resources) are primary resource constituents of the geoenvironment. Figure 1.3 shows some of the primary natural resources in combination with various land and aquatic ecosystems. The health and accessibility of these are essential rudiments of life-support systems. The beneficial interaction between all the elements shown in Figure 1.3 is needed to produce the necessary ingredients required for production of goods and services to sustain the population in a society. The ultimate goal for all of humankind is to obtain a sustainable society, i.e., a society that can regenerate itself without compromising the various resources for future generations.

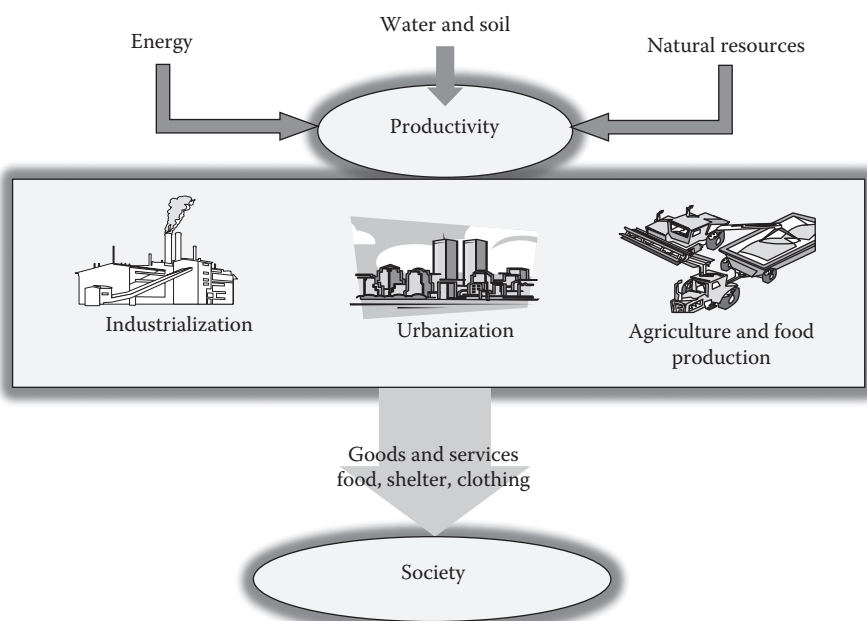


FIGURE 1.2

Exploitation and harvesting of basic elements such as hydrocarbons and hydro power (*energy*), minerals and metals (*natural resources*), and interactions contributing to the production of goods and services (*food, shelter, and clothing*) necessary to sustain society.

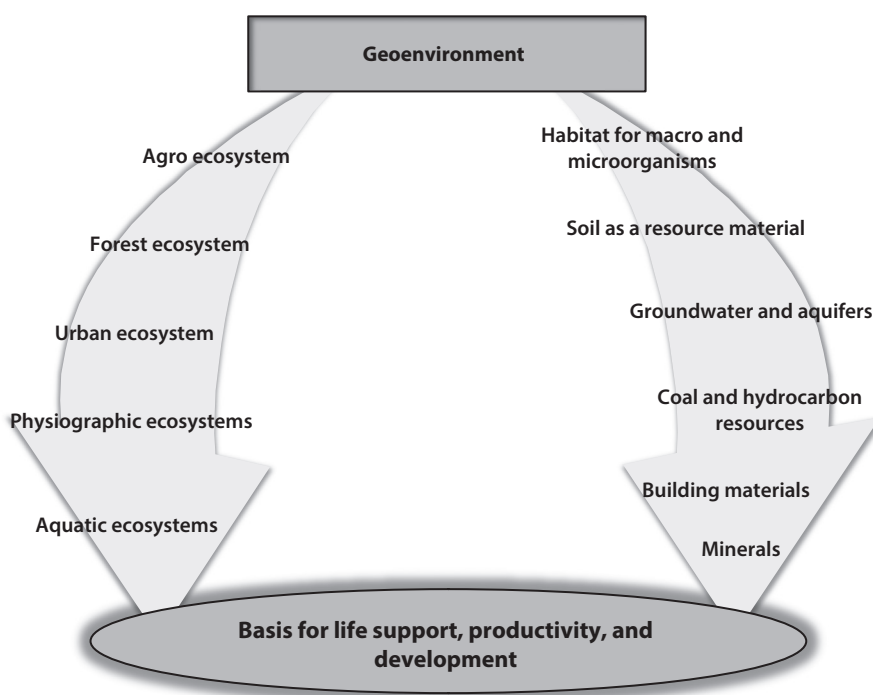


FIGURE 1.3

Some of the major ecosystems, resources, and features of the geoenvironment. Note that the physiographic ecosystems include, coastal, alpine, desert, arctic ecosystems.

It has been contended that since the beginning of the industrial revolution, “mankind’s occupation of this planet has been markedly unsustainable” (Glasby, 2002) and that the concept of sustainable development as defined by in the World Commission on Environment and Development 1987 Report is a chimera. At the present rate of exploitation of the renewable and nonrenewable resources, *sustainable development* is a goal that is not readily achieved so long as depletion of nonrenewable resources occurs and so long as excessive exploitation of renewable resources outstrips the replenishment rate of these resources. The term *sustainable development* is used herein to mean that *all the activities associated with development in support of human needs and aspirations, must not compromise or reduce the chances of future generations to exploit the same resource base to obtain similar or greater levels of yield*. Many of these issues will be addressed in the other chapters of this book from a geoenvironmental perspective.

Specifically, recognizing that the land environment houses the terrestrial and aquatic ecosystems, and that these are the fundamental components in the engine responsible for life support, one needs to determine:

- Whether the economic growth and prosperity obtained as a result of all these activities contribute to the production of beneficial or adverse impacts on the land environment.
- Whether such impacts improve, increase, reduce, or degrade the functional capability of the land (terrestrial) and aquatic ecosystems that comprise the land environment, i.e., the carrying capacity of the land environment.

Evidence of environmental mismanagement from past activities associated with development abounds. Commoner (1971) has suggested, for example, that the wealth gained by the modern technology-based society has been obtained by short-term exploitation of the environmental system. Although protection of the geoenvironment may lead to a preservation of many of the features and assets of the geoenvironment, it is clear from the various resource and habitat features shown in the right-hand compartment of Figure 1.3 that protection of the geoenvironment does not necessarily lead to sustainability of the geoenvironment. We recognize that techniques, procedures, and management programs should be structured to permit exploitation of the geoenvironment to occur with minimal adverse impact on the geoenvironment. To that end, the intent of this book is to provide an appreciation and understanding of (a) the geoenvironmental impacts that result from activities associated with mankind and (b) measures, requirements, and procedures needed to avoid, minimize, and/or mitigate these impacts.

We have previously defined the *geoenvironment* to include the land environment. This includes all the geophysical (geological and geomorphological) features, together with the aquatic elements classified as receiving waters. Figure 1.3 shows a simple schematic of the various major ecosystems, habitats, and resources that constitute the geoenvironment. The major ecosystems that constitute the land ecosystem, shown in the left compartment of Figure 1.3, consist of a mixture of physiographic and resource-type ecosystems. The mixed method of presentation of ecosystems shown in the diagram has been chosen deliberately because it does not require one to detail every single physiographic unit and every single resource-type unit.

The geoenvironment contains all the elements that are vital for the sustenance and well-being of the human population. Commoner (1971) states that the ecosphere, together with the Earth's mineral resources, is the source of all goods produced by human labor or wealth. It is obvious that any degradation of the ecosphere will impact negatively on the capability of the ecosphere to provide the various goods produced by human labor or wealth.

1.3.2 Impacts on the Geoenvironment

The posit that the geoenvironment is in itself a natural resource is founded on the fact that it provides the various elements necessary for life support such as food, energy, and resources. Degradation of any of the physical and biogeochemical features that permit life-support systems to function well will be a detriment to the requirements for a sustainable society.

1.3.2.1 Impacts due to Population Growth

The Malthusian model (Malthus, 1798), for example, links availability of food with population growth (or reduction). Postulating that food is necessary for human existence and that rate of food production increases linearly, the Malthusian model contends that since the rate of human population increase is geometric, there will come a time when food production will not be sufficient to meet population needs. Although no account was given to availability of resources and industrial output in the original model, one presumes that these were accounted for in the *ceteris paribus* condition.

The Meadows et al. (1972) systems dynamics model, which considered five specific quantities, industrialization, population, food production, pollution, and consumption of non-renewable natural resources, concluded (phase I study) "The Project on the Predicament of

Mankind”) that, “If present growth trends in world population, industrialization, pollution, food production, and resource depletion continue unchanged, the limits to growth on this planet will be reached sometime within the next hundred years,” although some have argued that the conclusions are perhaps too pessimistic, since the system dynamics model used in the Meadows et al. (1972) report, by their own admission, was, at the time of publication of the report, somewhat “imperfect, oversimplified, and unfinished.” However, it cannot be denied that the essence of the model and the analyses were fundamentally sound. The five specific quantities examined in the model were deemed significant in view of the global concern on “accelerating industrialization, rapid population growth, widespread malnutrition, depletion of non-renewable resources, and a deteriorating environment.”

The subsequent analyses by Meadows et al. (1992) using data gained from the 20-year period following their first publication showed that “in spite of the world’s improved technologies, the greater awareness, the stronger environment policies, many resource and pollution flows had grown beyond their sustainable limits.” They concluded that not only were the initial conclusions in Meadows et al. (1972) valid, these conclusions needed to be strengthened. In particular, their first conclusion reflects the growing concern we have regarding the capability of our geoenvironmental resources to provide the long-term necessities to sustain life at the pace we now enjoy. The Meadows et al. (1992) report suggest that, “Human use of many essential resources and generation of many kinds of pollutants have already surpassed rates that are physically sustainable. Without significant reductions in material and energy flows, there will be in the coming decades an uncontrolled decline in per capita food output, energy use, and industrial production.” Glasby (2002) has offered the suggestion that a marked decrease in world population (to 1.2 billion) is needed if sustainability is to be achieved.

It is well recognized that to meet the present and future needs of the ever increasing global population, there will be increased requirements for adequate supplies of goods and services to feed, shelter, and clothe the population. The 27 principles articulated in the 1992 Rio Declaration show the need for protection and maintenance of environmental quality while meeting the needs of the global population. These were reinforced in the 2002 World Summit on Sustainable Development (WSSD) held in Johannesburg. Principles 1, 3, and 4 of the Rio Declaration state that:

Human beings are at the center of concerns for sustainable development. They are entitled to a healthy and productive life in nature. (Principle 1)

The right to development must be fulfilled so as to equitably meet developmental and environmental needs of present and future generations. (Principle 3)

In order to achieve sustainable development, environmental protection shall constitute an integral part of the development process and cannot be considered in isolation from it. (Principle 4)

There are many who maintain that such declarative statements are designed to show a measure of political will and are not necessarily practical or supportable from a scientific point of view—given that development at the expense of depletion of scarce resources will never be sustainable. Although this book is not the forum for a debate on whether the goals identified by the declarative statements issued by world bodies can be successfully implemented or met, it is nevertheless necessary to take guidance from such statements. By highlighting the need for development in a sustainable manner, in both the WSSD

(2002) and the Rio Summit declarative statements of principles, it follows that development of the necessary knowledge and tools to address the goals of sustainability is required.

1.3.2.2 Impacts from Natural Resource Exploitation

Arguments against consideration of the environment, and specifically the geoenvironment, as a limited natural resource are generally based on a very limited appreciation of the totality of the geoenvironment as an ecosphere, and also on negligent attention to the many adverse impacts attributable to anthropogenic activities. Not all the geoenvironmental resources are nonrenewable (e.g., forest resource). However, for those resources that are renewable, overuse or overexploitation will surpass their recharge and replenishment rate, thus creating a negative imbalance. Is geoenvironmental deterioration a threat to human survival? Commoner (1971) has examined the overall environmental problem and has posed the question in terms of ecological stresses: “are present ecological stresses so strong that—if not relieved—they will sufficiently degrade the ecosystem to make the earth uninhabitable by man?” His judgment? “based on the evidence now on hand,...the present course of environmental degradation, at least in industrialized countries, represents a challenge to essential ecological systems that is so serious that, if continued, it will destroy the capability of the environment to support a reasonably civilized human society....”

The declaration issued at the beginning of U.S. National Environmental Policy Act (NEPA) of 1969 recognizes “the profound impact of man’s activity on the interrelations of all components of the natural environment, particularly the profound influences of population growth, high-density urbanization, industrial expansion, resource exploitation, and new and expanding technological advances” and further recognizes “the critical importance of restoring and maintaining environmental quality to the overall welfare and development of man.” The significance of this declaration cannot be overlooked. We can easily appreciate the need for environment protection and sustainability of the geoenvironment.

The geoenvironment is the resource base that serves as the engine that provides for the various elements necessary for human sustenance. Through resource exploitation and industrial activities, it is the source for everything that is necessary for the production of *food, shelter, and clothing*. It is also the habitat for various land and aquatic biota. Adverse impacts to the geoenvironment and its ecosystem need to be minimized and mitigated if one wishes to undertake the necessary steps toward *sustainable development*. Management of the geoenvironment is required if a sustainable geoenvironment is to be obtained.

The sets of forces needed to sustain a forceful economic climate, and provide for a dynamic population base or population growth, can be gathered into two main groups. These are defined by some very clear factors:

- Urban-industrial: This grouping includes those efforts and industries associated with the production of *food, shelter, clothing, and economic health*.
- Socio-economic-political: The grouping of factors that include the social, economic, and political dimensions of a society.

The subjects covered in this book will deal with stresses on the geoenvironment resulting from the various activities associated with society and its desire for development. The framework within which these will be examined will be confined to the one determined by the urban-industrial factors defined above. This by no means diminishes the

significance of the socioeconomic–political grouping of factors. These are important, but are not within the purview of this book. From the geoenvironmental point of view, this means dealing with the impacts to the geoenvironment from anthropogenic activities. Yong and Mulligan (2004) show that to properly address the problems and issues connected with degradation of the land environment, a knowledge of the linkages, interactions, and impacts between the human population and a healthy, robust, and sustainable land environment is required (Figure 1.4). The illustration in Figure 1.4 shows the linkages and identifies some of the major issues and land environment impacts. The observations made by Yong and Mulligan (2004) regarding the major land environment or geoenvironmental issues shown in Figure 1.4 are cited directly as follows:

- *Waste generation and pollution:* Wastes generated from the various activities associated with resource exploitation, energy production, and industry associated with the production of goods and services will ultimately find their way into one or all of three disposal media: (a) receiving waters, (b) atmosphere, and (c) land. Land disposal of waste products and waste streams appears to be the most popular method for waste containment and management. The various impacts arising from this mode of disposal and containment include degradation of land surface environment and ground contamination by pollutants.

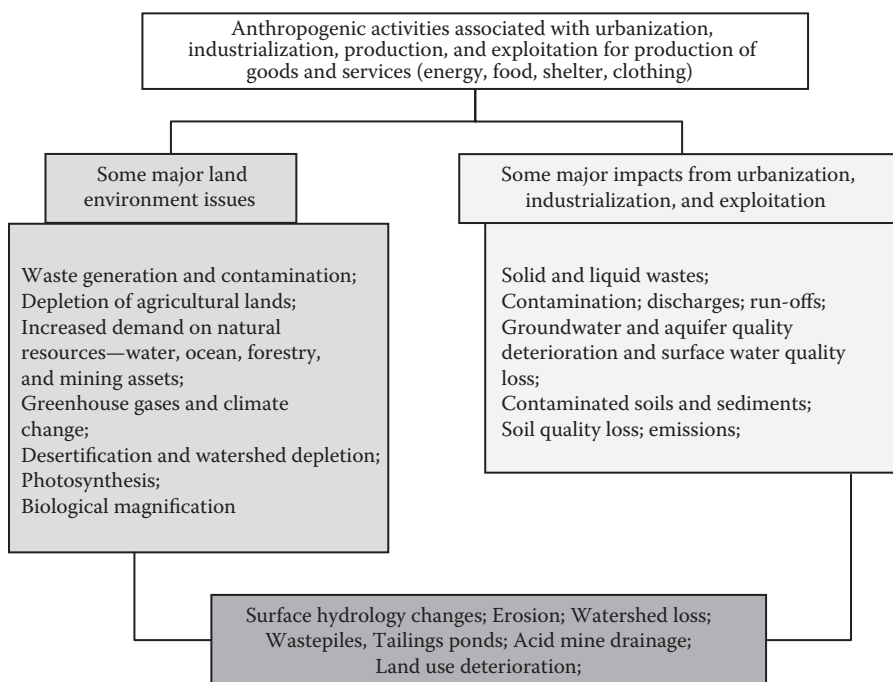


FIGURE 1.4

Some major land environment issues and impacts resulting from activities associated with urbanization, industrialization, production, and exploitation for production of goods and services. (Adapted from Yong, R.N. and Mulligan, C.N., 2004, *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp.)

- *Depletion of agricultural lands and loss of soil quality:* This will arise because of increased urbanization and industrialization pressures, infrastructure development, exploitation of natural resources, and use of intensive agricultural practices. The loss of agricultural lands places greater emphasis and requirement on higher productivity per unit of agricultural land. The end result of this is the development of high-yield agricultural practices. One of the notable effects is soil quality loss. To combat this, there is an inclination to use pesticides, insecticides, fertilizers, more soil amendments and other means to enhance productivity and yield. A resultant land environment impact from such practices is contamination of the ground, groundwater and receiving waters from runoffs and transport of contaminants.
- *Increased demand on natural resources and depletion of natural capital:* The various issues related with all the generated exploitation activities fall into the categories of: (a) land and surface degradation associated with energy production, mining and forestry activities, and (b) water supply, delivery, and utilization. Surface hydrology changes, erosion, watershed loss, tailings and sludge ponds, acid mine drainage, etc., are some of the many land environment impacts.
- *Greenhouse gases, climate change, desertification:* To a very large extent, these are consequences of industrialization, urbanization, and production. Their impact on the land environment can be felt, for example, in acid rain (and snow) interaction with soil and undesirable changes in photosynthesis processes and erosion of coastal areas due to increasing water levels.
- *Photosynthesis:* The processes associated with photosynthesis are important since they in essence constitute about 20% of the available oxygen in the atmosphere. Desertification, deforestation, and many of the activities associated with mineral and other natural resource exploitations will degrade the capability of the various participants (land and aquatic plants) to engage in these processes.
- *Biological magnification:* This concerns itself with the concentration of various toxic elements or pollutants by plants and such biotic receptors as aquatic organisms and animals, is a problem that needs to be addressed in the containment and management of pollutants.

1.3.3 Stressors and Sources

Stresses imposed on the geoenvironment originate from various agents and sources. In respect to the land element of the geoenvironment, these stresses arise from physical, thermal, hydraulic, and mechanical actions and forces and from physicochemical, chemical, and biologically mediated reactions and processes. Their actions, reactions, or processes are the result of (a) natural environmental events, such as volcanic eruption, earthquakes, tsunamis, forest fires, landslides, drought, tornados, and hurricanes, and (b) from human-related activities such as deforestation and habitat destruction, containment of hazardous and radioactive wastes, soil contamination from high-intensity agroindustry practices and from waste leachates, exploitation of mineral and hydrocarbon resources, constructed facilities, etc. The actions that result in imposition of stresses on the land compartment of the geoenvironment are called *stressors*. Since the terms *stressors* and *stresses* are used in many different disciplines and also used to describe particular situations, we should not

confuse their concept when they are applied to the land compartment of the geoenvironment. Yong et al. (2012) have provided some examples of stressor sources and stressors in the soil environment, as shown in Table 1.1.

The types of stressors acting on a piece of land mass can be mechanical, hydraulic, thermal, chemical, physicochemical, electrical, gaseous, radioactive, etc., with sources that are either natural or human-related. The Venn diagram in Figure 1.1 shows that the natural

TABLE 1.1

Examples of Stressors and Effects on Land Mass (Soil Properties)

Stressor Sources	Stressors for Soils	Kinetics Induced in Soils	Affected Soil Properties and Behavior
<i>Natural Sources</i>			
Volcanic eruption	Ejecta, heat	Alteration of soil Heat transfer	Soil elements, water retention Thermal and hydraulic properties
Forest fire, deforestation	Heat	Heat and water transfer Alteration of soil elements	Soil structure, water retention Thermal and hydraulic properties
Landslides, floods, and avalanches	Soil elements, water	Mass runoff	Soil elements, soil structure
Cyclical temperature and drying	Heat, water	Heat and water transfer	Soil structure, thermal and hydraulic properties
<i>Anthropogenic Sources</i>			
Industrial effluents	Leachates	Adsorption, chemical reaction	Chemical composition, soil structure, and hydraulic properties
Mining and metal processing	Contaminants	Water and solute transfer	
Constructed facilities			
Buried waste barrier	Water, solutes, heat	Water, solute, and heat transfer	Hydraulic, chemical, and thermal properties
Structural loads	Pressure	Shear stress consolidation	Mechanical properties and behavior
<i>Agricultural Land Use</i>			
Fertilizing	Chemical compounds	Adsorption, chemical reaction	Chemical composition, soil structure
Irrigation and drainage	Water	Water and solute transfer	Salt accumulation, water retention
River embankments	Overburden pressure	Mass runoff, shear stress, consolidation	Hydraulic properties, mechanical behavior
Underground water use	Water, solutes	Adsorption and desorption	Chemical composition, salt accumulation
<i>Abnormal Climate</i>			
Gas component in air	CO ₂ , CH ₄ , N ₂ O, etc.	Adsorption, gas transfer	Chemical composition, soil structure
Air temperature	Heat	Heat transfer	Water retention
Acid rain	Acid precipitation	Chemical reaction, solute transfer	Hydraulic properties

Source: Yong, R.N., Nakano, M., and Pusch, R., *Environmental Soil Properties and Behaviour*, CRC Press, Boca Raton, FL, 435 pp., 2012.

stressor sources delivering stressors can be elements from the atmosphere, anthrosphere, biosphere and hydrosphere, and stressors generated in the individual ecospheres by actions originating in the anthroposphere.

1.3.3.1 Natural Stressor Sources and Stressors

The two categories of stressor sources are *natural* and *anthropogenic*, as illustrated in Table 1.1. It is not often easy to distinguish between natural geoenvironment stressor sources and those associated with or related to human activities and products. Well-defined natural events that readily classify as natural geoenvironment stressor sources generally fall under the category of *natural disasters* or *geo-disasters*. (The subject of geo-disasters is covered in Chapter 12.) These include such events as hurricanes, earthquakes, tsunamis, tornadoes, volcanic eruptions, rainstorms, and blizzards—generating various types of stressors and stresses in a land or soil mass. For example, earthquakes generate dynamic forces, e.g., seismic force, to a soil mass through two types of body waves—primary or *P* waves and secondary or *S* waves.

Volcanic eruption and forest fires are also classified as typical natural disasters that will generate various types of stressors. They cover land surface with ejecta and ashes, apply extreme high temperature or heat, and chemical components constituting ejecta and ashes to land surfaces that will migrate into soil and underground water through percolating rainwater. Since such heat and chemical compounds are defined as stressors, volcanic eruption, and forest fires can be classed as stressor sources.

Landslides and floods, which are often classified as natural disasters, can be classified as geoenvironment stressor sources. They are disasters that result from situational vulnerability to provocative events such as earthquakes and rainstorms. Landslides and floods can also occur in instances where human activities have created vulnerable circumstances. Deforestation of slopes could make them more susceptible to landslides, and harvesting of groundwater in low-lying coastal regions can lower ground surfaces to levels that invite flooding. Since landslides and floods transport various matter, such as soil components and relevant chemicals to downstream areas, these can be classified as sources responsible for generating such stressors as chemical elements, in the geoenvironment.

Cyclical events such as regular temperature (cold-hot) cycles and nonregular wetting-drying cycles that fall under the category as natural events do not normally classify as natural disasters. Regular cyclical events are events such as winter-summer cycles, and nonregular events are wetting-drying events where repeat cycles do not adhere to any time-calendar schedule. In the case of subzero temperatures that accompany winter seasons, for example, under the right conditions, ground uplift due to frost heaving can occur, thus resulting in considerable damage to overlying structures. The stressor source is sub-zero freezing temperatures (winter), and the geoenvironment stressors associated with this stressor source are thermal in nature. In the case of wetting-drying events involving extreme cases of deluge and drought, the deluge could result in severe flooding whereas the drought event could lead to parched-earth conditions. The types of stressors generated in the affected include thermal, hydraulic, chemical, and mechanical.

1.3.3.2 Anthropogenic Stressor Sources and Stressors

Anthropogenic geoenvironment stressor sources include (a) various industries such as mining, agro, manufacturing and processing, and industries associated with all facets

of resource exploration and exploitation and (b) human activities such as construction of facilities, disposal and land management of waste, as well as agricultural land use, underground water use, and abnormal climate, as shown in Table 1.1. How the various industries (life-supporting and manufacturing–production) and their associated activities interact with the geoenvironment can be viewed as follows:

1. *Resource extraction and processing*: The various industries included in this group use the geoenvironment as a resource pool containing materials and substances that can be extracted and processed as value-added products. The common characteristic of the industries in this group is *processing of material extracted from the ground*. Included in this group are (a) the metalliferous mining industries, (b) those industries involved in extraction and processing of other resources from the ground such as nonmetallic minerals (potash, refractory, and clay minerals, phosphates), (c) the industries devoted to extraction of aggregates, sand, and rock for production of building materials, and (d) the raw energy industries such as those involved in the extraction of hydrocarbon-associated materials and other fossil fuels (natural gas, oil, tar sands, and coal). Included in this list is the extraction and recovery of uranium for the nuclear power industry.
2. *Utilization of land and soil as a resource material in aid of production*: Essentially, this group includes the agro and forest industries and also the previously mentioned nonmetallic minerals industries.
3. *Water, groundwater, and aquifer harvesting*: We include the hydroelectric facilities and industries associated with extraction and utilization of groundwater and aquifers.
4. *Use of land as a facility*: This category considers land as a facility for use, for example, in the land disposal of waste products. Broadly speaking, we can consider the land surface environment here as a resource for treatment and containment of waste products generated by all the industries populating the previous three categories.

Some of the major negative or degradative geoenvironmental impacts resulting from the various activities associated with production technology, e.g., agriculture, forestry, mining, energy, and general production, are shown in Figure 1.5. The nature of the threats to the land environment and the waste streams are shown in Figure 1.6. These affect both soil and water quality. We will discuss the nature of some of the impacts in detail in the next few chapters. The diagrams show the nature of the threats originating from the source-activities and their immediate physical impact in the land environment. The bottom-most element in Figure 1.6 shows some of the required sets of action for reduction of threats such as pollution management and toxicity and concentration reduction. Note that problems such as habitat protection and impacts and air quality are not considered since the attention in this book is focused on the physical land environment itself. In that sense, for the problems and activities shown in Figure 1.5, pollution management and control will have to be exercised to minimize damage to the geoenvironment, which in most cases refer to the surface environment and the receiving surface water and groundwater. Since many of the sources of the impacts cannot be completely reduced to zero, impact management will have to be practiced. Many of the discussions in succeeding chapters of this book relate to the effects of anthropogenic stressors on the

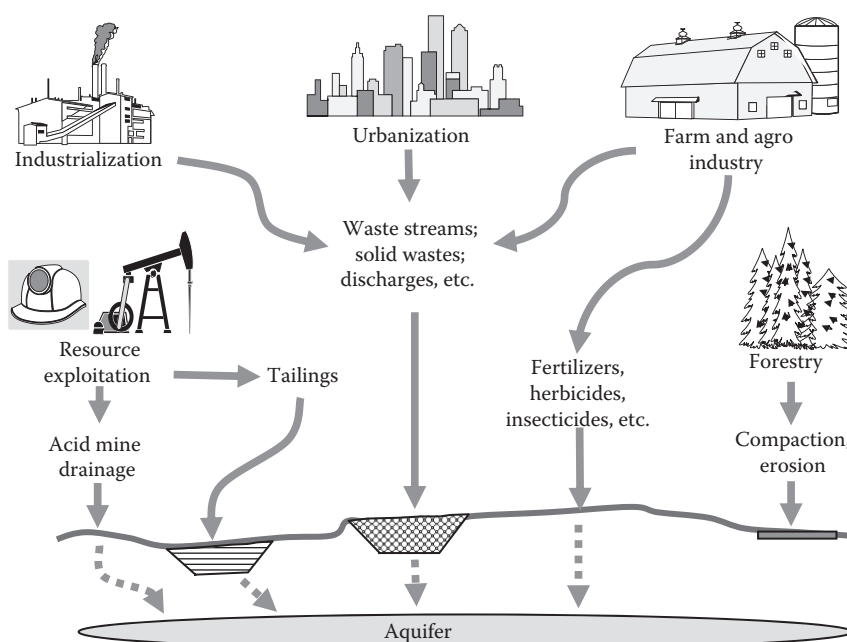


FIGURE 1.5

Nature of geoenvironmental impacts resulting from activities associated with industrialization, urbanization, resource exploitation, farm and agro industries, and timber harvesting.

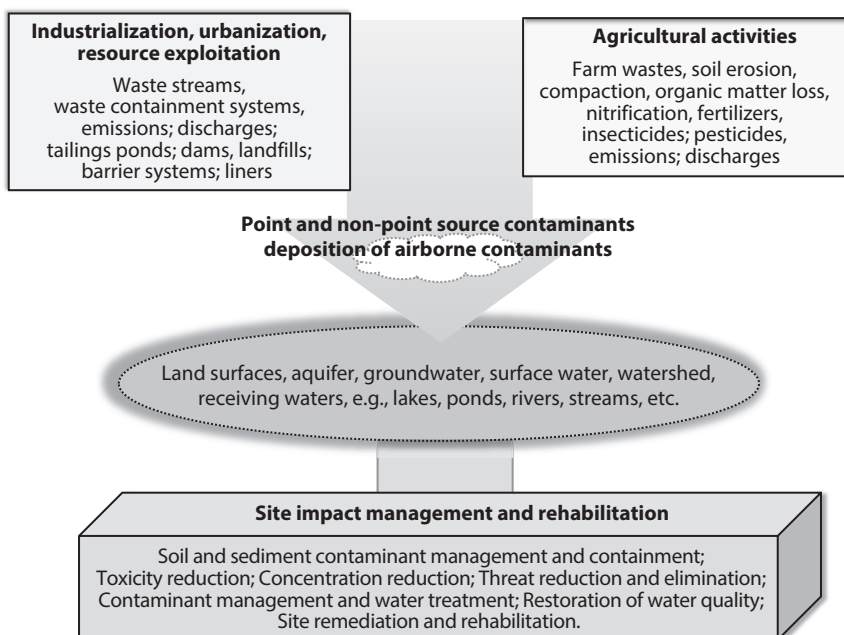


FIGURE 1.6

Threats and waste streams from anthropogenic activities in support of industrialization, urbanization, and resource exploitation, impacting on soil and water components of the physical land environment, and examples of requirements for restoration of impacted lands to pre-impact states.

geoenvironment, with particular emphasis on the soil environment, and the measures needed to counter the adverse impacts, i.e., measures that can be viewed as *sustainable geoenvironmental engineering practice*.

1.4 Geoenvironment Impacts on Soil and Water Resources

The sets of forces that, by their interactions, pose potential threats to the geoenvironment, are those resulting from activities mounted in pursuit of *industrialization, urbanization, energy and resource exploitation, and food production*. The net effect or impact of these activities and their stresses on the geoenvironment can, by their very nature, be disastrous if measures for protection of the geoenvironment are not put into practice. A reduction or degradation of geoenvironmental resources and the various ecosystems will diminish the capability of the geoenvironment to provide the elements necessary to sustain life. To avoid or to minimize the degradation, there needs to be (a) a proper audit of the geoenvironmental impacts on the prominent features that constitute the geoenvironment, and also on the ecosystem and (b) available sensible and logical sets of tools that can be used to mitigate and ameliorate the adverse effects of the impacts.

Good land management practice (a) minimizes and mitigates deleterious impacts to the land environment, (b) seeks optimal land use and benefit from the land, and (c) preserves and minimizes depletion of natural capital. The obvious threat to human health linked to detrimental geoenvironment impacts comes from waste discharge and impoundment, as shown in Figures 1.5 and 1.6. Most of the activities associated with manufacturing and production of goods will generate waste in one form or another. Table 1.2 shows some typical waste streams from a representative group of industries. Impacts on the geoenvironment from these activities and discharges take the form of (a) wastewater and solid waste discharge, and spills, leaks, and other forms of discharges to the land environment (including the receiving waters in the land environment) and (b) use of chemical aids in pest control and other intensive agricultural practices resulting in pollution of the receiving waters and excessive nitrogen and phosphate loading of the soil—leading to a consequent decrease in soil quality. Many of these issues will be discussed in detail in the chapters to follow.

TABLE 1.2

Typical Composition of Waste Streams from Some Representative Industries

Industry	Waste Streams
Laboratories	Acids, bases, heavy metals, inorganics, ignitable wastes, solvents
Printing, etc.	Acids, bases, heavy metals, inorganic wastes, solvents, ink sludges, spent plating
Pesticide user and services	Metals, inorganics, pesticides, solvents
Construction	Acids, bases, ignitable wastes, solvents
Metal manufacture	Acids, bases, cyanide wastes, reactives, heavy metals, ignitable wastes, solvents, spent plating wastes
Formulators	Acids, bases, ignitable wastes, heavy metals, inorganics, pesticides, reactives, solvents
Chemical manufacture	Same as metal manufacture, except no plating wastes
Laundry/dry cleaning	Dry clean filtration residue, solvents

1.4.1 Impacts on Land Mass and Soil

The impacts resulting from the various activities of humans take several forms depending on the types of stressors involved. As noted in Section 1.3.3, the stressors could be mechanical in nature or hydraulic, thermal, chemical, physicochemical, electrical, gaseous, and/or radioactive. Mechanical stressors generate physical stresses resulting in movement of land masses or pieces of a particular mass—leading to a degradation of its functionality and perhaps to an ultimate consequence of instability of the land mass, or failure of that particular unit of mass, i.e., a particular unit of soil mass. We pay particular attention to a unit of soil mass since this constitutes the basic building block of a land mass. Since the collective status of individual soil mass units defines the overall status of a particular land mass, it would be useful to pay attention to the “health” of a soil. In engineering terms, we can evaluate or categorize soil health in terms of its functionality.

1.4.1.1 Soil Functionality and Indicators

We define the *functionality* of a soil (i.e., *soil functionality*) as its capability to perform the various functions demanded of it, in accord with the status of the soil. For example, a major role of soil is its capability as a *plant growth medium*. Loss of functionality is evident when the soil fails to yield the kinds of crops harvested in previous years. In the case of soils required to support overlying loads, loss of support capability means diminished functionality. The key to an understanding of how stressors impact on a piece of land mass is to determine the functional state of a unit of soil mass in the land mass. The use of soil functionality indices (*SFI*) proposed by Yong et al. (2012) is a means not only to quantify the functionality of a soil but also is a means to determine if the soil is no longer capable of meeting its planned/designed function.

The concept of using soil functionality—i.e., soil functional capability—to denote the ability of a soil or a site to function according to design or service requirements is a novel concept, in that it addresses the performance aspects of a specific piece of soil or a soil mass. In most cases, the soil attributes used in assessment of soil functionality include (a) properties and characteristics of the particular soil under consideration and (b) performance requirements of the soil to meet design or service specifications over the short and long-term (periods). To determine soil functional capability—i.e., soil functionality—one needs to use *soil functionality index (SFI)* as an assessment tool. To appreciate how the *SFI* can be usefully utilized as a tool in assessment of soil functional capability (a) over the long term or (b) in relation to stresses generated by soil environment stressors, one needs to specify soil functionality indicators. These indicators constitute the parameters for computing soil functionality—using, for example, single-parameter analysis, dimensional analysis, multivariate analytical techniques, risk-based analysis, fuzzy logic, or lumped-parameter analysis. Figure 1.7 shows a graphic representation of how *SFI* might change with time under stressor impacts.

Indicators that are used or encountered in everyday events and situations include such common sensory ones as aural, visual, scent, and sensation. In vehicular traffic situations, for example, green lights at cross-roads indicate that one has the right of way, and red lights indicate that one should stop at the intersection. Indicators can (a) inform one of the status or nature of the situation at hand and (b) provide guidance or insight into the performance of a system or even a particular piece of equipment. In soil science, agriculture, and the earth environment, indicators are often used in soil quality and soil functionality assessments, with particular interest to soil health in relation to agricultural productivity,

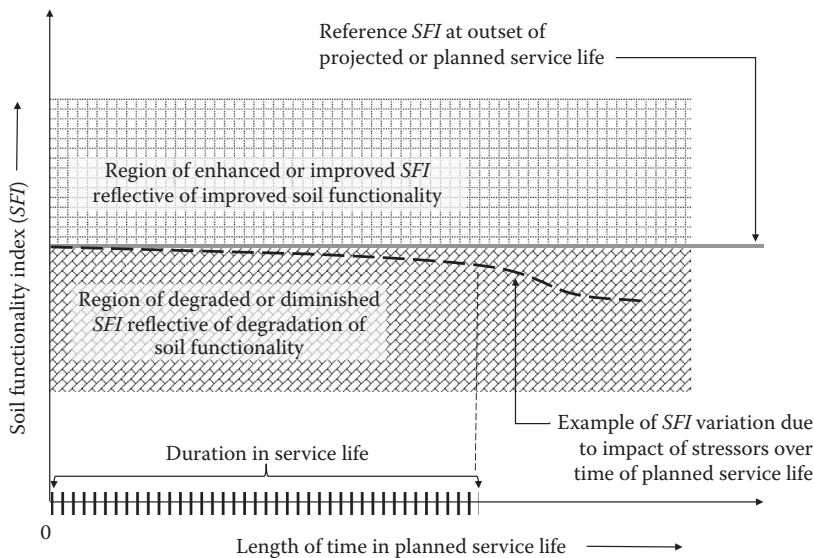


FIGURE 1.7

Example of time–SFI variation for an imaginary planned service project. Over the course of the *planned service life* shown on the abscissa, the SFI shows some level of degradation. (Adapted from Yong, R.N. et al., *Environmental Soil Properties and Behaviour*, CRC Press, Boca Raton, FL, 435 pp., 2012.)

human health, and preservation or improvement of habitats and biodiversity. Soil quality indicators can range from complex and involved techniques using microorganisms as indicators of soil health, to more simple ones such as the use of soil color to determine the soil constituents or components, the water content and water logging status of soil.

In the case of geoenvironmental engineering, soil contamination by pollutants and toxicants and land settlement and subsidence by overburden pressure from constructed facilities and excess withdrawal of groundwater are of significant concern. Indicators are used to monitor the status of soils threatened by pollutants and toxicants and by ground subsidence. These indicators are used as signals to inform the stakeholder that the system is functioning well or to alert the stakeholder to potential problems. An example of the use of certain soil attributes as indicators is shown in Figure 1.8.

1.4.2 Impacts on Water and Water Resources

It has been suggested by many that, in the future, conflicts among various groups, factions, and jurisdictions will arise over drinking water and its availability. We need only consider the availability and distribution of drinking water in the world to see that this suggestion has substance, as shown in Figure 1.9. Less than 5% of the global water is nonsaline water. Of this less than 5% nonsaline water, it is estimated that about 0.2% of the nonsaline water is contained in lakes and rivers, with the remaining proportion existing as snow, ice, wetlands, and groundwater (adapted from Yong, 2001). Values reported much earlier by Leopold (1974) give numbers such as 2.7% of total volume of water (i.e., global water) as freshwater, and of that freshwater, it was estimated by Leopold that about 0.36% was “easily accessible.” Figure 3.1 in Chapter 3 provides a more descriptive illustration of the distribution of readily accessible freshwater.

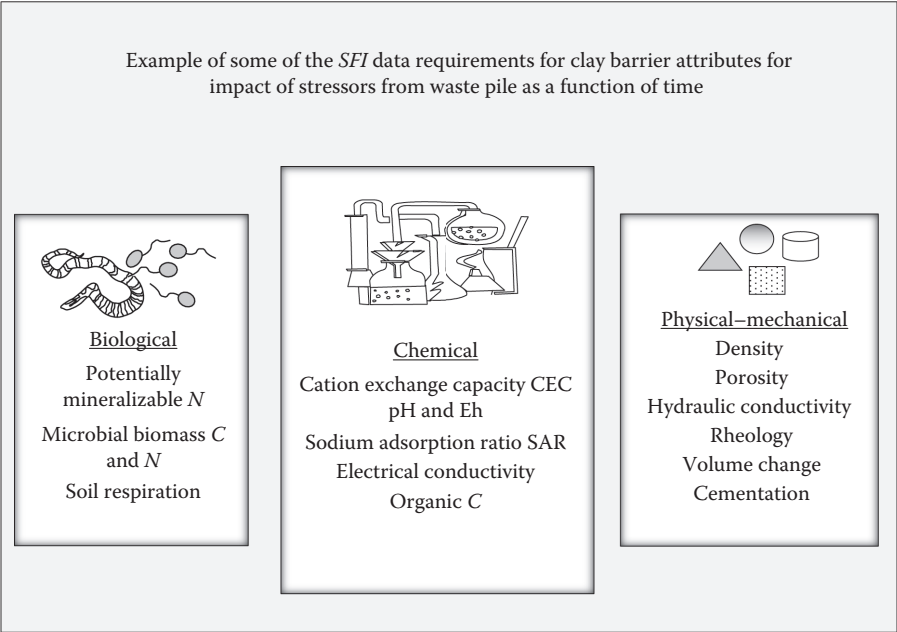


FIGURE 1.8
Some of the major soil attributes used as indicators for *SFI* data for a clay barrier component of multi-barrier system used for containment of waste pile in a landfill. (Adapted from Yong, R.N. et al., *Environmental Soil Properties and Behaviour*, CRC Press, Boca Raton, FL, 435 pp., 2012.)

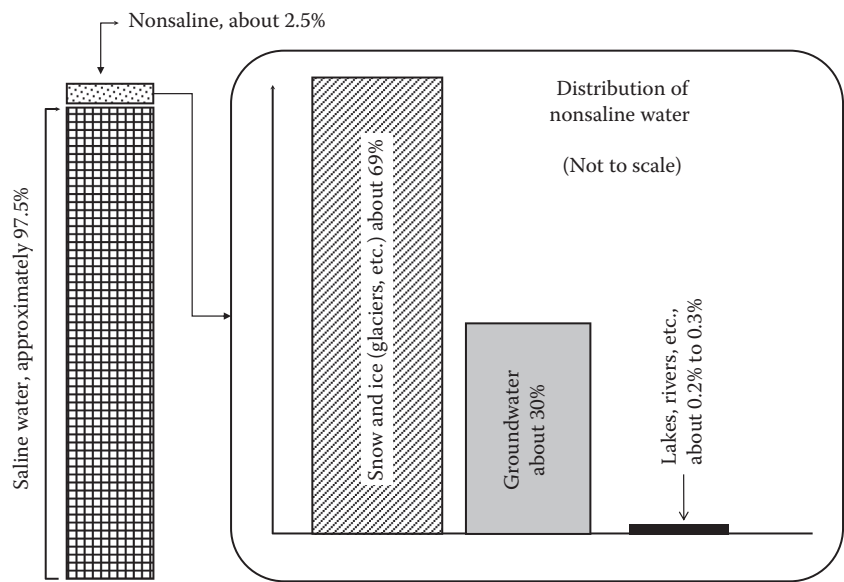


FIGURE 1.9
Distribution of global water. Note that of the approximately 2.5% nonsaline water, about 30% exists in the ground as groundwater. (Information from UNEP, *Vital Water Graphics: An Overview of the World's Fresh and Marine Waters*, 2nd ed., UNEP, Nairobi, Kenya, 2008.)

Some of the more common and significant impacts to the quality of groundwater and receiving waters have been shown in Figures 1.5 and 1.6. Deterioration of the quality of these waters will not only limit their usefulness but will also cause distress to the animal and plant species that live in these waters. Considering that at least one half or more of the world's plant and animal species live in water, it is clear that any deterioration and/or decrease of water quality and water availability will have severe consequences on these species. Protection of both surface water and groundwater must be a priority. Chapter 3 discusses these and other issues in greater detail. Water usage by industry, for example, can produce liquid waste streams that are highly toxic by virtue of the chemicals contained in the waste streams, or by virtue of concentration of noxious substances. Before the liquid phase of any waste stream can be returned to the environment, it has to be treated and rendered harmless as a health threat to biotic receptors. As indicated previously, the source of these pollutants can be traced to waste streams and discharges from industrial plants, households, resource exploitation facilities, and from farms. Table 1.3 shows some chronic effects on human health from some of these waste products.

Farming and agricultural activities contribute agro-additives to the receiving waters and groundwater through surface runoff and through transport in the ground (Figures 1.5 and 1.6). All the other discharges and waste streams shown in Figures 1.5 and 1.6 are most likely contained in storage dumps, landfills, holding ponds, tailings ponds, or other similar systems. All of these containment systems have the potential to deliver pollutants to the receiving waters (ground and surface waters) because of eventual and inevitable leaks, discharges, and failures. Many of these phenomena will be discussed in greater detail in the later chapters of this book.

We highlight the importance of groundwater resources because, it is a major water resource (Figure 1.9), and as a rule, groundwater is more accessible than surface water. Furthermore, it is not uncommon for many rural communities to rely heavily on these

TABLE 1.3

Chronic Effect of Some Hazardous Wastes on Human Health

Waste Type	Carcinogenic	Mutagenic	Teratogenic	Reproductive System Damage
Halogenated organic pesticide	A	A	A	H
Methyl bromide			H	
Halogenated organic phenoxy herbicide	A	A	A	A
2-4-D ^a				
Organophosphorous pesticide	A	A	A	
Organonitrogen herbicide	A	A	A	
Polychlorinated byphenyls	A		A	
Cyanide wastes ^a				
Halogenated organics	H	H		
Non-halogenated volatile organics	A	A		
Zn, Cu, Se, Cr, Ni	H			
Hg		H	H	
Cd	H			

Source: Adapted from Governor's Office of Appropriate Technology, Toxic Waste Assessment Group, California, 1981.

Note: H and A, statistically verifiable effects on humans and animals, respectively.

^a No reportable information available.

groundwater resources as a source without proper treatment prior to use. We should note that contamination of receiving waters such as ponds, lakes, and rivers occurs also through leachate transport through the soil and, quite obviously, from surface runoff from point and non-point pollutant sources. From the perspective of the geoenvironment, protection of both surface water and groundwater quality requires one to practice impact mitigation and management, as shown, for example, in Figure 1.10 for management of liquid waste discharge into the environment to avoid impacting the receiving waters. The decision points shown in the protocol diagram include criteria, procedures, tests, etc., that need to be conducted to satisfy regulatory requirements.

To provide proper protection of the health of biotic receptors in the geoenvironment, treatment of the liquid waste streams requires detoxification and removal of all toxic and hazardous constituents and suspended solids before discharge. Reuse of the treated waste streams is encouraged. Typical reuse schemes include irrigation (in farming and agriculture activities), process streams (such as resource extraction) and cooling towers. Waste streams that cannot be treated effectively and economically to reach acceptable discharge standards will require impoundment in secure ponds. Procedures have been developed that will reduce the liquid content of these noxious liquid waste streams. To protect the resources in the geoenvironment, the product(s) will most likely need to be incinerated or contained in secure impoundment facilities. Typical containment and impoundment facilities would be landfills. Co-disposal of these kinds of waste products with other types of waste products has been proposed as a means to accommodate these waste products. Figure 1.11 shows two typical barrier systems used to line landfill facilities. The details for these kinds of containment and waste management systems will be discussed in the next chapter.

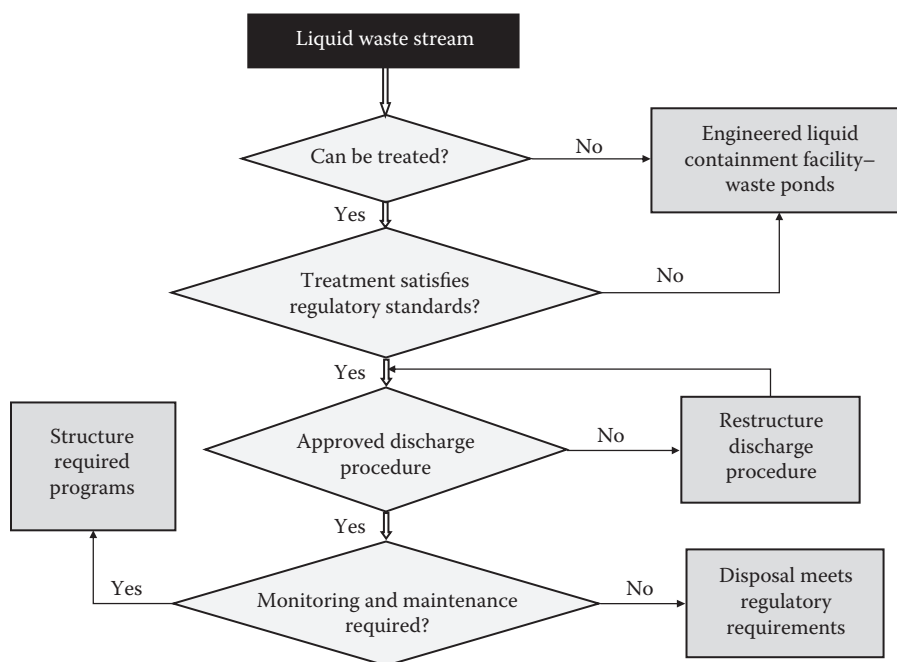
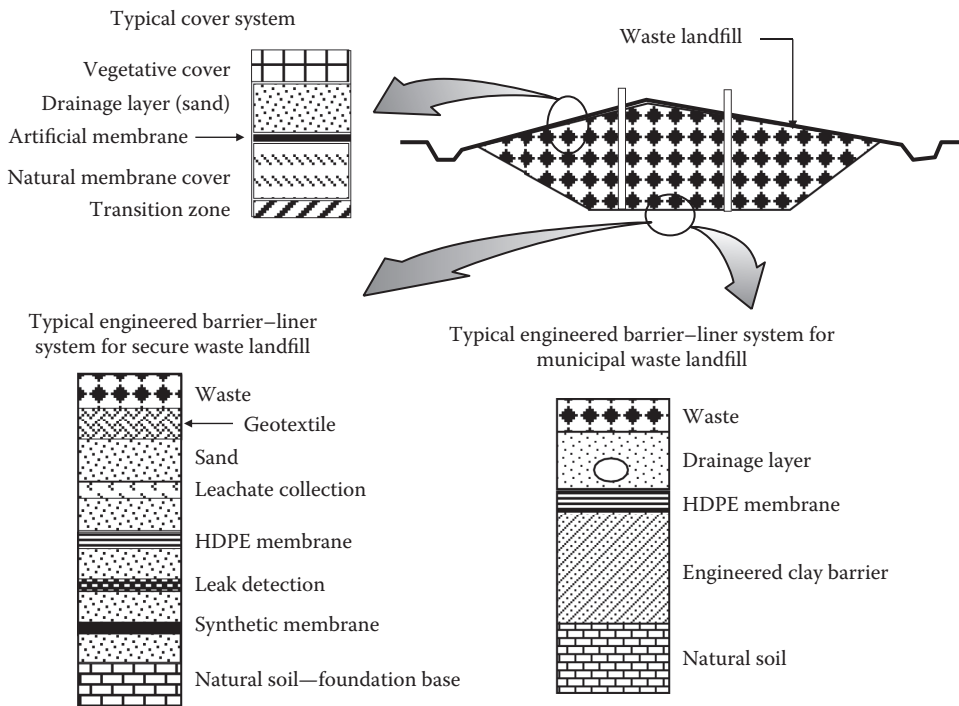


FIGURE 1.10

Program for management of liquid waste stream discharge into receiving waters and land surface areas.

**FIGURE 1.11**

Waste landfill system showing typical top cover and bottom barrier-liner systems. Two liner systems are shown: the maximum security barrier system (left) and the bottom barrier system generally used for landfills containing MSWs. (From Yong, R.N. and Mulligan, C.N., 2004, *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp.)

1.5 Sustainability

In a Gaean world, the earth is a living being where all the living organisms and nonliving entities function and interact independently but contribute to collectively define and regulate the material conditions necessary for life. When stresses and resultant negative impacts associated with the activities of mankind in the production of *goods and services* arise, the Gaean hypothesis becomes somewhat untenable. This is because living matter in the geoenvironment will be constrained from regulating the material conditions necessary for life. Loss of species diversity is one of the major factors. The paramount terrestrial ecosystem imperatives are (a) protection and conservation of the various land environment resources and (b) ensuring that the capability to provide life support is not degraded or diminished. From the viewpoint of the geoenvironment and ecosphere, the pressures from *development stresses* and *WEHAB* (*water and sanitation, energy, health, agriculture, biodiversity*) combined with the processes necessary to satisfy sustainable development objectives are summed up by the schematic shown in Figure 1.12.

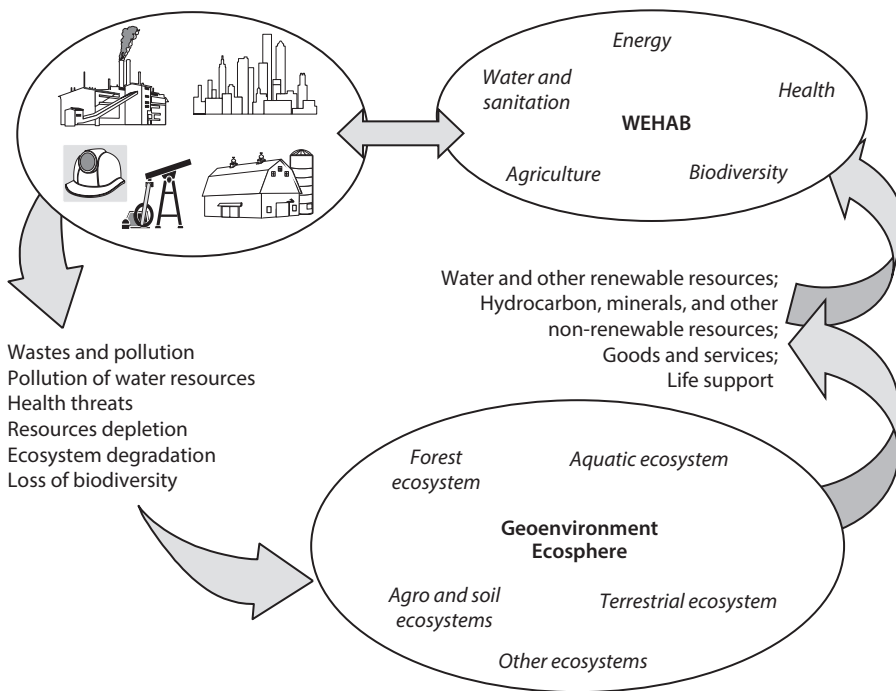


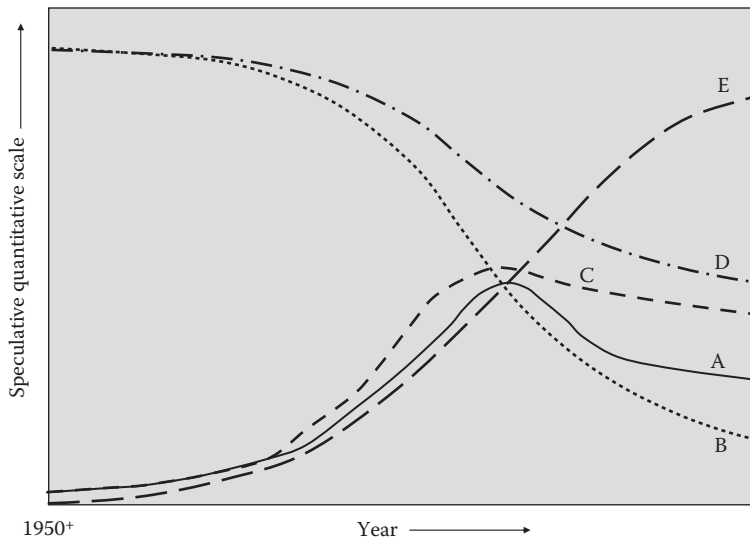
FIGURE 1.12

The continuous cycle of interaction among industry-production, WEHAB, and the geoenvironment, from a geoenvironmental perspective.

1.5.1 Renewable and Nonrenewable Geoenvironment Natural Resources

Sustainable development in itself may in all probability be a chimera—a non-attainable goal and an illusion. However, this should not deny the fact that proper environmental management and conservation measures are needed if we are to strive to meet the goals and objectives of sustainability. This includes resource conservation and management and preservation of diversity. Failure to do so will result in the diminution of the capability of the geoenvironment to provide the basis for life support. The case of renewable and nonrenewable geoenvironmental natural resources is a good demonstration of this point.

Following the spirit of the systems dynamics model predictions of Meadows et al. (1972), the chart shown in Figure 1.13 speculates on the status of the global population at some future time under conditions identified in Figure 1.13's caption. The curve identified as A shows the status of population based on current depletion rate of nonrenewable geoenvironmental natural resources in relation to some future time. The abscissa on the diagram shows "years at some future time," and the ordinate gives a qualitative appreciation of the growth or decline of the parameter under consideration. The curve identified as B is the speculative quantity of nonrenewable resources available assuming that the depletion rate of the nonrenewable geoenvironmental natural resources remains the same, i.e., constant in proportion to the population at hand. We consider the principal nonrenewable geoenvironmental natural resources to consist of fossil fuels, minerals, and geological building materials (stone, gravel, sand, and soil).

**FIGURE 1.13**

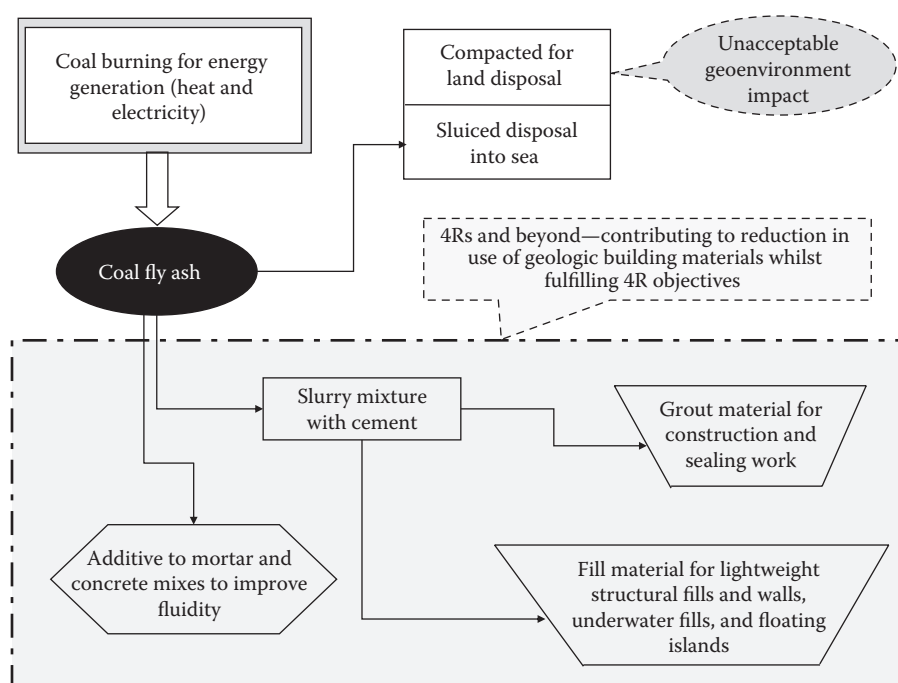
Speculative chart on status of global population relative to conservation of the nonrenewable natural resources. A is the status of population based on current usage of resources, B is the speculative quantity of nonrenewable resources remaining available, C is the status of population based on conservation of resources, use of 4Rs, and alternative materials and energy sources, D is the available nonrenewable natural resources using conservation management and 4Rs, E is the assumed availability of alternative materials and energy sources.

Assuming that conservation measures for nonrenewable geoenvironmental natural resources are in place and that these measures are bolstered by the use of the 4Rs (reduction, reuse, recycle, and recovery), we can further reduce the depletion rate of the nonrenewable resources using alternative energy sources such as geothermal, wind, solar, etc. The curve C shown in Figure 1.13 indicates the status of the global population based on conservation of the nonrenewable resources, use of 4Rs and use of alternative materials and energy sources, D is the available natural geoenvironmental resources using conservation management, 4Rs, and alternative energy sources. Finally, curve E shown in Figure 1.13 is an assumption of the resources that would be made available using alternative materials and various other alternative energy sources.

1.5.2 4Rs and Beyond

Although not strictly within the purview of geoenvironmental sustainability considerations, the implementation of 4Rs as a means to protect the geoenvironment and also to aid in reduction of nonrenewable resource depletion deserves special attention. Details of many aspects of these will be discussed in subsequent chapters.

By itself, the common understanding of the 4Rs is recovery, reuse, recycle, and reduction. Application of the 4Rs to waste products can reduce the depletion rate of many nonrenewable geoenvironmental resources. A good case in point is the use of coal fly ash as a backfill and liner material. Figure 1.14 shows some of the benefits—as they pertain to the geoenvironment and to the reduction in use of natural geo-materials (Horiuchi et al., 2000; Yamagihara et al., 2000). Traditional disposal of the coal fly ash on land or in the ocean is not an acceptable solution. Reuse of the material not only satisfies the aims of the 4Rs but


FIGURE 1.14

Example of application of principles of sustainability for waste product obtained in use of a nonrenewable resource for generation of heat and electricity.

also contributes to the reduction in use of the nonrenewable geoenvironmental natural resource, i.e., geological material. Other examples of 4Rs and beyond can be found, for example, in the use of paper sludge ash as backfill slurry (Horiuchi et al., 2002; Asada et al., 2003).

1.6 Concluding Remarks

The impacts of natural and catastrophic events such as earthquakes, tsunamis, hurricanes and typhoons, and associated floods and landslides are not discussed in this chapter (and not in this book). This does not mean that these are minor events or impacts—in comparison to the impacts on the geoenvironment generated by human activities. It is recognized that these natural catastrophic events can and do result in considerable loss of life and physical facilities. The problems and impacts generated by these natural disasters on the geoenvironment deserve proper recognition and discussion in a textbook or treatise specifically devoted to such subjects.

Proper management of the geoenvironment is essential if the platform for almost all the life-support systems is to be protected for future generations. The principles of *sustainability* require us to recognize a fundamental fact that geoenvironmental natural and cultivated resources are *renewable* and *nonrenewable*. Chapter 11 addresses this issue and the situations where renewable natural resources can become nonrenewable and hence

not sustainable. It is necessary to recognize that renewable geoenvironmental natural resources can be easily threatened and can become ineffective as a resource. A good case in point is *water*. Pollution of receiving waters will render such waters unacceptable for human consumption, therefore rendering this renewable geoenvironmental resource useless. The following items are some of the major issues facing us as we seek to maintain the life support base that provides us with the various goods and services:

- Depletion of nonrenewable resources or natural capital is a reality. Energy production relying on fossil fuels is an example of how nonrenewable resources are continuously depleted.
- Industrial wastes and wastes streams will need to be managed, and it is likely that some of the waste products will find their way into the land environment, resulting thereby in threats to the health and welfare of biotic receptors.
- Loss of soil quality due to various soil degradative forces such as erosion and salinization. In addition to reduction in capability of the soil for crop production, one faces a loss in the capability of the soil to act effectively as a carbon sink.
- Depletion of agricultural lands will occur because of urbanization pressures, thus requiring remaining agricultural lands to be more productive. Implementation of high-yield practices may exacerbate the problem of pollution of both land and water resources.
- Deforestation and inadequate replacement rates, thus contributing to the CO₂ imbalance.
- Contamination of groundwater and surface water resources can reach proportions that render such sources as health threats to biotic receptors.

In the context of the geoenvironmental perspective of environmental management, three particular points need to be stated in regard to the development-environment or sustainable society problematique:

- Soil is a natural resource. In combination with the other geophysical features of the land environment, they constitute at least 90% of the base for sustenance of the human population and production of energy and goods. The depletion rate of the natural capital, represented by all the natural resources, must be minimized.
- Technology and its contribution to environmental management. In addition to the various remediation and impact avoidance tools that technology can develop and contribute to environmental management, perhaps one of the more significant contributions that technology can make would be the development of renewable resources replacements for the nonrenewable resources that are being depleted.
- Protocols and procedures for management of changes in the environment: It is becoming very evident that changes to the geoenvironment that are presently occurring may reach proportions that require one to develop technology and new social attitudes to manage the change. A particular case in point might be, for example, global warming and the greenhouse effect.

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2

Stressors and Soil Contamination

2.1 Introduction

Two of the most important ecosystem components of the geoenvironment are soil and water. These two components, together with the atmospheric component provide almost all of the necessary elements needed to support life for all living species. This chapter focuses on the soil ecosystem component and the problem of stressor impacts on this component. The next chapter will pay similar attention to the *water* ecosystem component of the geoenvironment.

2.2 Stressors and Impacts

As pointed out in Chapter 1, almost any thing that happens (i.e., any input or any activity in the ecosphere) will result in the product of some kind of stressor-related impact on the geo-environmental landscape and its associated ecosystems. To protect the status and manage the geoenvironment, the nature of these impacts and whether these impacts will add value to the particular ecosystem—or subtract from the functionality of that particular ecosystem in the geoenvironment—needs to be determined and better understood. A complete listing of all the impacts on the ecosystems of the geoenvironment is not possible because we are not sure if we are fully aware of all the kinds of activities and interactions that are active in a functioning ecosystem. As previously defined, a *functioning ecosystem* includes not only the biological and chemical activities in the ecosystem, but also the physicochemical, mechanical, hydraulic, and thermal interactions that are characteristic of the type of ecosystem under consideration. With our present understanding of the geoenvironment and the associated functioning ecosystems, it is difficult (and virtually impossible) to fully catalogue all of these activities and interactions. What is possible at this stage is to examine and determine how the known activities and interactions are affected or changed because of the stresses, disturbances, alterations, etc., to the ecosystem of interest.

The major sources of impacts and the resultant nature of the impacts cannot be easily listed without specification of targets of the impacts. Some of these sources may not be immediately evident, and some of the impacts will not be readily perceived or understood—because the effects of the impacts may not be apparent and/or because the effects or results of the impacts cannot be readily recognized. A simple case in point is the effect of buried toxic substances in the ground on human health—particularly if the impact on the health of those that come in contact with the material is mutagenic or teratogenic.

As indicated in Chapter 1 that geoenvironmental impacts arising from natural causes such as earthquakes, tsunamis, tornadoes, floods, typhoons, and hurricanes do not fall within the purview of this book. The distress and damage to the geoenvironment can be readily perceived because the energy generated in these events in the form of forces and stresses can cause substantial physical damage to the geoenvironment and considerable loss of life. Although many of the sources or causes of the impacts are generally obvious, there are many that are not. This is because we do not have any hard and fast rule as to what constitutes an impact, and more importantly, when the particular impact under consideration causes irreversible damage. Damage to the geoenvironment of the same scale and magnitude as earthquakes and hurricanes can be obtained as a result of man-made activities, such as landslides and contamination of ground and receiving waters. However, more often than not, the impacts to the geoenvironment resulting from anthropogenic activities associated with the production of goods and services are less dramatic. That being said, they nevertheless endanger public safety and present health-threatening problems and issues.

2.2.1 Stressor Impacts on Soils

The categories of stressors include such groups as (a) hydraulic, (b) mechanical, (c) thermal, (d) chemical, (e) geochemical, and (f) biologically mediated. Some of the main impacts resulting from the actions of these types of stressor groups that have been discussed by Yong et al. (2012) are listed below.

2.2.1.1 Hydraulic

The stressors that classify under the *hydraulic* group are directly related to water and its actions in soils—with types of actions that result in application of pressures that act directly on and within a soil mass. The impacts from these stresses could:

- Initiate piping that could undermine the stability of overlying structures and facilities (adverse impact).
- Trigger erosion, landslides, debris flow, and *quick* soil conditions from excessive porewater pressures, self-detachment of soil particles (adverse impact).
- Restructure affected soils because of the pressures resulting in changes in soil properties and behaviour (could be adverse or beneficial impact).
- Dilute or decrease contaminant concentration in contaminated soils (generally considered to be beneficial).
- Initiate or increase advective transport of contaminants in the soil (adverse or beneficial impact, depending on initial conditions).
- Detach sorbed contaminants and contribute to the environmental mobility of the contaminants (probably more adverse than beneficial—again depending on initial conditions).
- Affect biological processes through changes in natural habitat and energy sources (mostly adverse impact).
- Influence natural soil-weathering processes leading to alteration and/or transformation of susceptible minerals (could be adverse or beneficial).

- Other actions classed under the hydraulic stressor grouping could include those associated with floods, droughts (lack of water as a hydraulic stressor), excessive rainfall and water availability detrimental to agricultural productivity, etc. (adverse impact).

2.2.1.2 Mechanical

The common types of stressors included in the *mechanical* group that act on soils are those that produce pressures and stresses in a soil mass. Natural stressor sources are earthquakes and avalanches, whereas anthropogenic sources include those activities associated with resource exploitation, agroindustry, primary and secondary industries, constructed facilities, and activities related to urbanization. The impacts generated by the stressors in the mechanical group include (Yong et al., 2012):

- Direct loading from a solid mass such as an overlying structure, e.g., a bridge abutment and foundation footings for a structure, or facility. Resultant effects in the affected soil include.
 - Collapse of overlying structure due to failure of the soil to support the applied load (adverse impact).
 - Settlement of the overlying structure due to consolidation, secondary compression, and/or creep of the supporting soil (adverse impact).
- Pressures on a soil mass as a result of actions related to water movement, e.g., swelling pressure in confined swelling soils, loss of bonding in collapsing soils, and pressures developed in the soil in unstable slopes.
 - For swelling soils under overlying structures, swelling pressure could undermine stable support of the structures, thereby causing collapse of the structure (adverse impact).
 - For collapsing soils, sudden or gradual loss of particle bonding mechanisms will result in collapse of soil structure.
 - For unstable slopes, instability of the slope will result in slope movement or slope failure (adverse impact).
- Soil freezing and frost heaving pressures resulting from formation of ice lenses. Although these impacts can be reckoned as the results of stressors classifying under the *thermal* group, their inclusion in this portion of the discussion shows that not all stressor sources reside solely in one single category. The consequent effects of soil freezing and developed frost heaving pressures are, in a manner of speaking, similar in principle to those experienced with swelling soils. In the case of ice lens formation, the consequent effects from subsequent thawing of the ice lens can be severe if ice lenses formed in the freezing stage have created significant frost heaving in the soil.

2.2.1.3 Thermal

The *thermal* group of stressors generate heat or cooling in soils. The *natural* stressor source is the summer–winter cycle. A significant anthropogenic source is canisters containing high-level radioactive wastes embedded in underground repositories generating heat over

long periods. The two sets of issues are (1) high temperatures and (2) freezing temperatures, and their impacts include:

- Water and vapor transfer in soils (e.g., evapotranspiration) resulting in changes in soil properties and behavior (could be adverse or beneficial impact).
- Types and rates of chemical reactions and biological processes resulting in changes in the nature and energy status of the affected soil—consistent with soil weathering processes (could be adverse or beneficial impact).
- Soil freezing and developed frost heaving pressures, as discussed under the *mechanical* group of stressors.
- Freeze–thaw phenomena and development of ice lenses in frost susceptible soils with water availability and thaw subsidence from disappearing ice lenses (adverse impact).

2.2.1.4 Chemical

Some of the *natural* stressors classifying under the grouping of *chemical* include acid rain, organic acids obtained from decomposing surficial organic matter, and the natural chemical constituents in soils. Waste landfills, discharge of contaminated wastewater, acidic leachates from mine heaps, acid rain, etc., are stressors attributable to human activities. Note that we include acid rain under both *natural* and *human activities* inasmuch as emissions into the atmosphere from production facilities are seen to be the principal contributors to the acid nature of rain and snow. The impact of actions and/or events in the chemical environment in soils will be felt, over time, in terms of changes in the nature and properties of the soil because of changes in (a) the nature of the soil fractions themselves, e.g., transformation of montmorillonite to illite or mixed layer clay mineral, (b) interactions between soil particles and between particles and water and soil–water energy characteristics, (c) biological processes in the soil, leading to changes in the nature and character of the soil, and (d) chemical reactions and processes, e.g., a decreasing pH (as would happen with acid rainfall onto and into the soil) could dissolve carbonates in the soil, thereby not only destroying carbonate cementation bonds between particles but also raising the possibility of releasing CO₂ from the affected soils.

2.2.1.5 Geochemical

In respect to soils, the stressors in the geochemical category are leachates or contaminants from mine heaps, constructed facilities, and excess fertilization in agriculture. The impacts from these stressors generated in a soil mass are (a) decomposition of soil minerals and chemical constituents in soils and (b) changes of soil particle surface functional groups. These decompositions and changes result in alteration of soil structure and chemical constituents in soil mass, thus affecting water, solute, and heat transfer phenomena in soils.

2.2.1.6 Biologically Mediated

The stressors in this category are microorganisms in the soil. The impacts of their interactions with soil constituents and other energy sources are decomposition of organic matter and alteration or decomposition of clay minerals and chemical constituents of soil. In turn, the outcome would be changes in nature of the soil—resulting in corresponding changes in not only hydraulic, mechanical, and thermal phenomena in soils but also the relevant soil properties.

2.2.2 Soil Contamination from Chemical Stressors

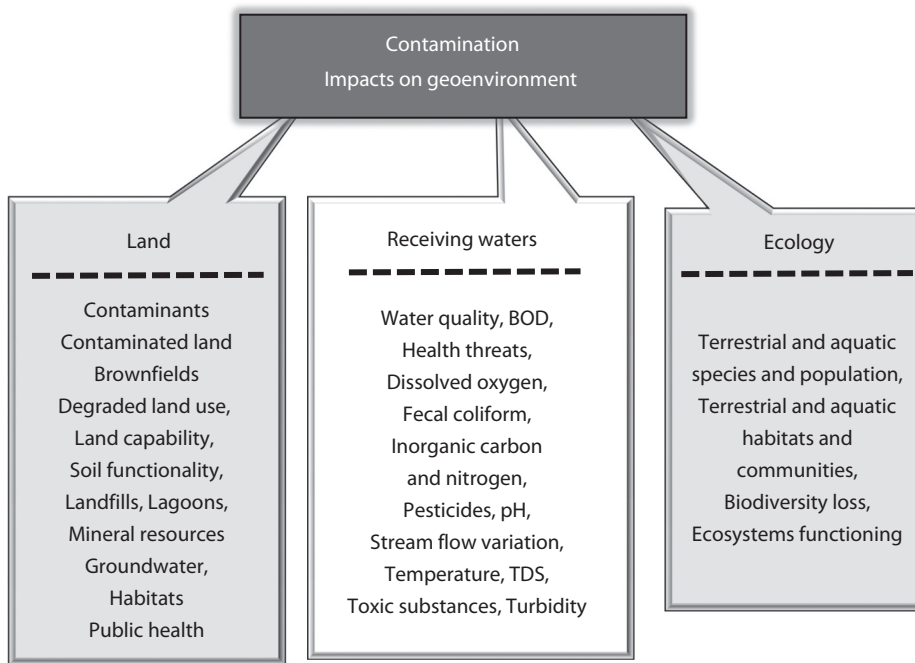
Chapter 1 points out that good land management practice (a) minimizes and mitigates deleterious impacts to the land environment, (b) seeks optimal land use and benefit from the land, and (c) preserves and minimizes depletion of geoenvironmental natural capital. Probably the most significant stressor responsible for degrading the quality of the land, its ecosystems, and especially the receiving waters (including groundwater) is the group of chemical stressors. The impact from these stressors is contamination of the land environment and its receiving waters by contaminants and hazardous substances, and as will be discussed in the latter part of this chapter and the next chapter, the importance of protection of the receiving waters cannot be overstated. Ground contamination—i.e., contamination of soil mass and receiving waters—by these same contaminants and hazardous substances poses threats to human health, other biotic receptors, and the environment. Our attention in this chapter will be focused on the various aspects of ground contamination and land management, together with remediation and restoration requirements needed to meet sustainability goals. The later chapters in this book will focus on actual technologies, procedures, and tools to implement sustainable geoenvironmental engineering land management practices. Once again, although it is recognized that depletion of nonrenewable resources and threats to renewable resources render absolute sustainability an impossible goal, it is nonetheless necessary and important to undertake measures for protection of the geoenvironment and its natural capital and resources—and where necessary, to restore the geoenvironment to its pre-impact state. Failure to do so will exacerbate the conditions that have already led to a compromised geoenvironment. As with all the chapters in this book, the actions discussed and proposed in these chapters recognize the need to strive for measures and actions that will relieve the adverse pressures and stresses on the geoenvironment.

Contamination of the land environment by hazardous substances, contaminants, and noncontaminants results primarily from man-made activities and events mounted to meet societal and industrial demands. Contamination from natural events can also occur. These include, for example, deposition of ash from volcanic discharge and seepage of sulfuric acid and iron hydroxide when pyrite (FeS_2) is exposed to air and water, according to the following relationship:



We can encounter more dramatic discharges of sulfuric acid in the phenomenon commonly referred to as acid mine drainage (AMD). In this instance, the contamination is considered to be associated with anthropogenic activities associated with metalliferous mining, as will be discussed in more detail in Chapter 5.

By and large, contamination due to anthropogenic activities is without doubt the greatest contributor to overall contamination of the environment and especially the geoenvironment. Accordingly, we will pay particular attention to this problem in this chapter. We use the term *contamination* to include contamination by contaminants, toxicants, hazardous substances, and all substances foreign to the natural state of the particular site and microenvironment. When necessary, the terms *contaminants*, *toxicants*, and *hazardous substances* will be used to highlight the substance under discussion or to lay emphasis to the problem. It (contamination) poses the most significant challenge in the maintenance and protection of the many land environment ecosystems and resources needed to support life on earth. Figure 2.1 shows a simple tabular sketch of some of the effects of impacts from contamination of the land environment—illustrated as concerns and issues, for *land*, *receiving waters*, and *ecological system*.

**FIGURE 2.1**

Simple schematic showing some of the impacts, articulated as concerns and issues, for *land*, *receiving waters*, and *ecological system* because of contamination of the land environment.

In view of the far-reaching primary and secondary effects of contamination of the land environment and because these (a) impact severely on our ability to implement sustainability practices for the geoenvironment, (b) directly affect our means to sensibly and responsibly exploit the natural resources in the geoenvironment, (c) diminish the quality of the land environment and the very resources needed for mankind to sustain life, (d) pose direct health threats to humans and other biotic receptors, and (e) degrade soil quality and reduce the ability of the soil to function as a resource material, the discussions in this chapter will pay particular attention to the problem of *soil contamination due to chemical stressors*. The requirements and measures needed to mitigate contamination impacts and the remedial actions required for recovery of soil functionality will be discussed in the later chapters of this book.

In addition to the very significant problem of contamination of the land environment, there are other stressor impacts to the geoenvironment that have considerable effect on the functioning of the land environment itself. The sources of these stressors originate from a group of man-made events that have substantial physical impacts on the geoenvironment landscape features, as discussed in Section 2.3. The projects and events included in this group, identified as the primary group, deal directly with the landscape features of the geoenvironment. As such, the effects or impacts arising from the stressors associated with this group of events or projects most often result in threats to public safety and loss or diminution of natural geoenvironment resources and natural capital. Examples of these are the physical sets of activities associated with mineral resources and hydrocarbon resources recovery (discussed in detail in Chapters 4 through 7).

2.3 Contamination and Geoenvironmental Impacts

Included in Title 1 of the U.S. National Environmental Policy Act (NEPA) of 1969 given in Chapter 1 are the three specific environmental requirements that we can consider as essential in management and control of the contamination–impacts to the geoenvironment. These include:

1. Environmental Inventory: This is essentially an environmental audit, i.e., a complete description of the environment as it exists in the area where a particular proposed (or ongoing) action is being considered. The physical, biological, and cultural environments are considered to be integral to the environment under consideration.
2. Environmental Assessment: The various components included in the assessment package are:
 - a. Prediction of anticipated change.
 - b. Determination of magnitude of change.
 - c. Application of importance or significant factor to the change.
3. Environmental Impact Statement (EIS): This is a very crucial document that needs to be written in a format specified by the specific regulatory agency responsible for oversight of the project or event. In respect to the geoenvironment, this document must contain the proper determination of the various impacts to the geoenvironment (i.e., geoenvironmental impacts) arising from implementation of the project under question or the event being investigated. In respect to the NEPA-type response, this document contains a summary of environmental inventory and findings of environmental assessment (referred to as 102 statements, i.e., a section of NEPA relating to requirements for preparation of EIS in NEPA).

To determine the nature of impacts to the geoenvironmental, it is necessary to:

- Develop a frame of reference. This is essentially a series of targets or receptors that are the recipients of the impacts. The reference frame will permit one to examine the effects of the geoenvironmental impacts in relation to the members constituting the reference frame. The following members constitute the essential elements of the reference frame:
 - The separate compartments (terra firma and aquatic) of the land environment. By and large, one determines the impacts of projects and events on the integrity of the landscape (including receiving waters and their boundaries).
 - Health of the human population and other biotic receptors in the geoenvironmental compartment (land and receiving waters). This requires examination of the impacts as threats to human health and the biotic receptors. Generally, this includes a study of waste and waste-contaminant streams and other catastrophic phenomena arising from man's activities.
 - Overall health of the environment. Terrestrial and aquatic habitat and community preservation are central to the health of the environment.

- Establish a general or broad impact-identification scheme. By doing so, this allows us to look for the source of the impact. Knowledge of the stressors and their source provides one with a better appreciation of the extent and details of the impact. In looking for the stressors responsible for the impacts, it is necessary to separate the *stressor source* from the *impact*, since it is not always easy to determine what constitutes the impact.

2.3.1 Reference Frame

The geoenvironmental impact reference frame provides or specifies the targets in the total land environment and the receiving waters contained therein. It provides a framework that requires questions to be raised as to whether the actions arising from projects or events will have adverse effects on the various physical and biological elements constituting the geoenvironmental compartment. The specific case of a contaminated ground shown in Figure 2.2 (from Yong and Mulligan, 2004) is a good example of the application of the reference frame for determination of geoenvironmental impacts. In this instance, one is concerned with the impacts resulting from the presence of contaminants in the ground. We define a *pollutant* to mean a contaminant that has been identified as a threat to human health and/or the environment. These are generally toxic elements, chemicals, and compounds and are most often found in priority pollutant lists of regulatory agencies. *Contaminants*, meanwhile, are defined as substances that are not natural to the site or material under consideration. These substances can include hazardous materials or elements, toxic substances, contaminants,

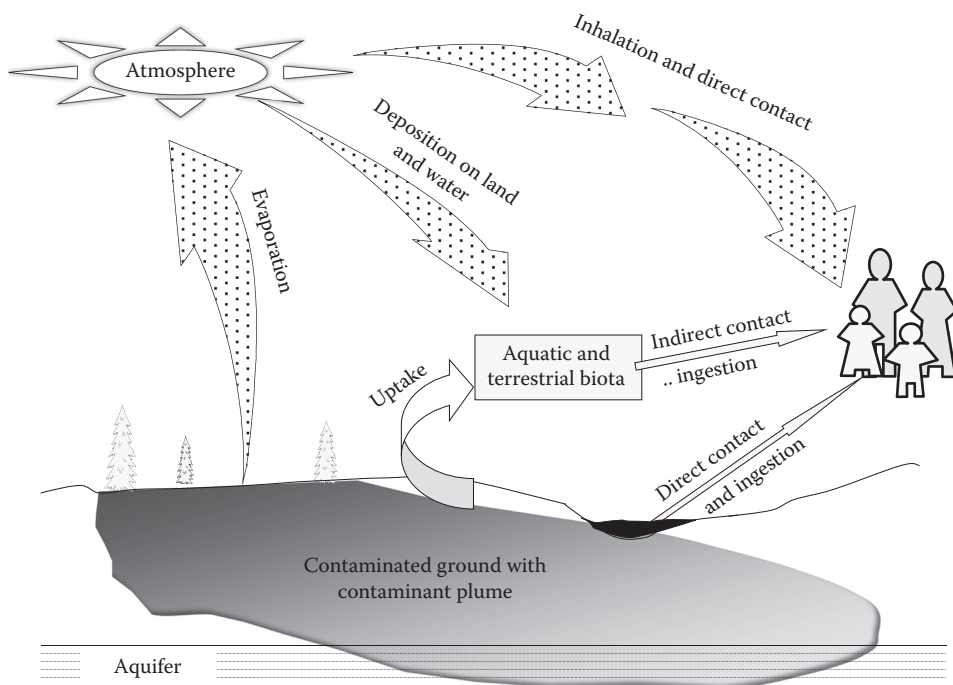


FIGURE 2.2

Schematic diagram showing contaminated ground with a contaminant plume as the source of health and environmental threats. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

and all other substances that are nonthreatening to human health and the environment. In other words, the term *contaminants* is used when we wish to refer to non-indigenous elements, substances, etc., found at a site or in a material under investigation.

In reference to Figure 2.2, the source of the contaminant plume at the site in question is at the ground surface, e.g., dump site, landfill, toxic dump. For this discussion, the reasons for locating the dump site, landfill, toxic dump, etc., are not addressed, even though they result in creating the contaminant source. Our interest is directed toward the impacts generated by the presence of these sources. The terms *stressor sources* and *impacts* need to be carefully differentiated. For the particular problem shown in Figure 2.2, the *event* or *action product* responsible for the contaminant plume is the landfill itself. The *stressor source* is the leachate plume containing fugitive contaminants—obtained as a result of dissolution of the waste material contained in the landfill. The *stressors*, which are the fugitive contaminants, are chemical stressors.

Some of the evident impacts to the geoenvironment resulting from the contaminants in the contaminated ground shown in Figure 2.2 include:

- Contaminants in the atmosphere carried into the atmosphere by evaporation and volatilization.
- Contaminants on the land surface within and outside the contaminated site, resulting from deposition of the airborne contaminants.
- Contaminants in the contaminated ground.
- Contaminated groundwater and surface water due to transport of the contaminant plume and also to deposition of contaminants in the atmosphere.
- Threats to habitats of terrestrial and aquatic biota.
- Threats to human health.

The impacts shown in the preceding list illustrate the targets (receptors) of the four members (land element, receiving waters, humans, and terrestrial and aquatic biota) of the reference frame. Using these as targets, one determines not only *what is being impacted*, but also the nature of the impact. There are obviously many more impacts that can be cited. We can, for example, discuss or speculate on the impact of the contaminants in the contaminated ground on the possible loss of biodiversity in the affected region, and the impact on the quality of the land and how this affects future land use. These impacts can be covered in the impact statements that need to be produced or developed in association with specific projects and events. These will be discussed in greater detail at various times throughout the book when specific projects and/or events are considered.

2.3.2 Characterization of Geoenvironmental Impacts

In addition to the geoenvironmental impact frame of reference, there needs to be a mechanism or means or criteria for one to determine *what constitutes an impact to the geoenvironment*. The group of questions that needs to be addressed include:

1. Whether reversibility (of damage) should be used as one of the decision mechanisms for determination of impacts.
2. How man-made improvements, amelioration, mitigation, and remediation procedures to the geoenvironment can be factored into the process of evaluation of geoenvironmental impacts and their effects.

There are many ways in which impacts to the geoenvironment can be categorized or classified. A useful and popular method is to categorize the geoenvironmental impacts in relation to natural or man-made causes leading to events that are determined to be responsible for the impact, as shown in Figure 2.3. Described within the two major categories shown in the figure are some typical causes for events leading to geoenvironmental impacts. *Floods* and *landslides* have been singled out as typical examples of both natural and man-made causes for events resulting in geoenvironmental impacts. For example, floods can arise naturally because of hurricanes or tsunamis generated by earthquakes, for example, shown by the massive floods caused in late summer of 2005 in the gulf region of Central and North America and in the U.S. Eastern seaboard in late 2012. Floods can also occur naturally because the natural waterways (rivers, brooks, and streams) do not have the capability to carry the excessive water load produced by an undue excessive rainfall occurring over a very short period. It is also possible for floods to occur because of man-made waterway constrictions and shoreline alterations that impair previously capable performance of the waterways.

Figure 2.3 shows that the anthropogenic events or stressor sources have been divided into two groups. The *primary* group refers to those anthropogenic sources of stressors acting on the physical landscape of the geoenvironment. The stressors generated are the result of various kinds of anthropogenic activities in support of physical projects such as excavations and mining, construction of infrastructure and buildings, resource recovery, drilling, tunneling, and waste landfills. The immediate evident geoenvironmental

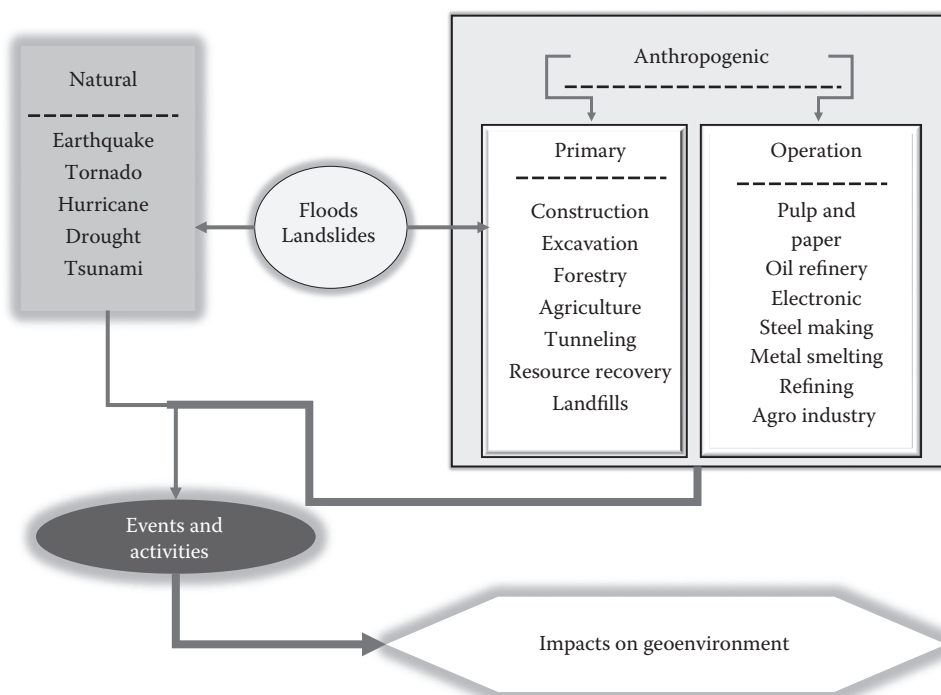


FIGURE 2.3

Categories of some typical stressor sources. Note that floods and landslides can be both natural and man-made causes for events resulting in geoenvironmental impacts.

impacts are mostly physical in nature. These generally involve alteration of the surficial and subsurface landscape features. Although these landscape alterations are evident as physical impacts of the land surface features, they also have the ability to serve as sources for stressors, as shown previously in respect to the example of AMD and the impact generated from physical extraction of metal ores from the ground. In this case, the AMD problem poses a very significant threat to the receiving waters and ultimately to the biotic receptors. Another less dramatic health threat example is the undercutting of a slope to facilitate the construction of a right-of-way for a highway system. Excessive undercutting without proper analysis of the stability of the slope could produce a situation where the undercut slope could subsequently trigger a slope failure. When such occurs, one needs to be concerned with the safety of the human and animal populations in the affected region.

The other grouping for anthropogenic stressor sources shown in Figure 2.3 is identified as *operations*. The impacts to the geoenvironment arising from this stressor-source group (*operations*) are the direct result of activities associated with midstream and upstream industries such as the agroindustry (outside of physical cultivation of the land), refining, mineral dressing, manufacturing, production and process industries, etc. The effects or results of the impacts on the geoenvironment can be physical, chemical, physicochemical, and biogeochemical in nature. One needs to factor into the analysis the resultant or potential threats to human health and other biotic receptors. Some examples of these are (a) application of pesticides and fungicides as pest controls in support of agricultural activities leading to non-point source contamination of ground and groundwater, (b) landfilling of hazardous wastes resulting in the production of contaminants in the fugitive leachate plumes, (c) discharge of waste streams from chemical and electronic industries resulting in contamination of the receiving waters, and (d) isolation–disposal of high level nuclear wastes in underground repositories.

2.3.3 Identifying and Assessing for Impact on the Geoenvironment

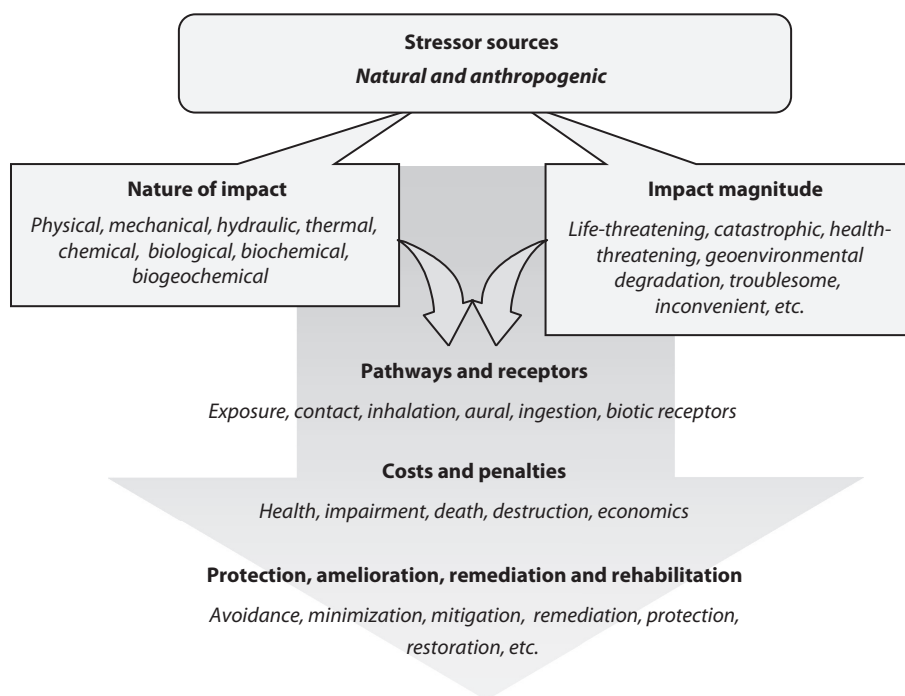
A useful procedure for performing a geoenvironmental impact scoping exercise is given in Figure 2.4. The various steps shown in the diagram are guidelines and are designed to provide one with specific objectives or targets.

2.3.3.1 Stressor Sources

Knowledge of the stressor sources (i.e., cause or events) can be helpful in narrowing the field of study or investigation. Take, for example, the case of a chemical plant producing various organic chemicals where inadvertent spills and fugitive discharges during storage are suspected to have occurred. If the spills and discharges are identified as the sources, the stressors associated with the sources would be the chemicals involved in the spills or discharges. The impacts to the geoenvironment can be readily identified.

2.3.3.2 Nature of Impacts

It is important to have a proper knowledge of the kind of impact. This allows determination or estimation of the extent of the *damage* or *improvement* of the geoenvironment resulting from the applied stressors. Using the previous chemical plant example, the damage inflicted on the geoenvironment is seen in terms of a contaminated site or ground.

**FIGURE 2.4**

Useful protocol for geoenvironmental impact scoping exercise. Scoping for impact assessment or determination can omit the last step (remedial actions) if a quick assessment is needed. The last step is needed if one has the ability to influence decision making concerning implementation of the project or event.

Guidelines are necessary to prevent one from rendering judgments on impacts without methodical and proper analyses just because the results of the impacts are dramatically visible—as opposed to impacts that do not show visible distress signs. It is not the magnitude of the distress caused by the impact that should determine what constitutes an impact. As we have pointed out in Chapter 1, the results of many impacts do not manifest themselves until many years hence. This is especially true for health-related issues. In the most general sense, the guidelines used to determine what constitutes an impact to the geoenvironment should be determined on the basis of whether the geoenvironmental impact will:

- Generate direct and/or indirect threats and problems relating to public health, natural habitats, and the environment. A good case in point is the contamination of receiving waters. These waters serve as habitats for aquatic species and, in many instances, will serve as sources for drinking water. Not only is such an impact a direct threat to the usable water supply for the human population, it is also a direct threat to the food supply for the same population because of the likely reduction in aquatic food supply for the population.
- Diminish the functioning of the ecosystems in the geoenvironment. An example of this can be found in the degradation of soil quality due to many of the activities associated with high-yield agriculture and mineral resources exploitation. This is particularly important since *soil quality* is a direct measure of the

capability of a soil to sustain plant and animal life and their productivity within their particular natural or man-managed ecosystem. The Soil Science Society of America (SSSA) defines soil quality as

The capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation. (Karlen et al., 1997)

- Any diminution of soil quality will impact on the capability of the soil to provide the various functions such as plant and animal life support, forestry, and woodland productivity and will also result in the loss of biodiversity and nutrients. Other prime examples of this can be found in the various activities associated with mineral extraction and energy resource development. To appreciate the impacts resulting from these activities, we can focus on the status of the biological, chemical, physicochemical activities, and physical interactions that define the functioning of the ecosystem of interest. In addition, we can also study the changes in land capabilities or land-use options.

2.3.4 Man-Made and Natural Combinations

It is not always easy or simple to distinguish between natural and anthropogenic stressor sources that impact directly or indirectly on the geoenvironment. This is because many geoenvironmental impacts are the result of a sequence combination of anthropogenic and natural sources. A very good example of this is the previously mentioned AMD problem—a problem that is triggered by the results of mining exposure of pyrite. The presence of pyrite (FeS_2) in rock formations where coal and metalliferous mining occurs will create problems for the environment if the pyrite is exposed to both oxygen and water. Given favorable geological and hydrological conditions, we have the situation where oxidation of the pyrite exposed during mining operations will produce ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}). For this first chemical reaction step, we can conclude that the trigger for the first sets of reactions is a man-made event or source, i.e., mining of the rock formation. Subsequent rate determining reactions, which may or may not be catalyzed by certain bacteria (e.g., *Thiobacillus ferrooxidans*), involve oxidation of the ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), to be followed later by hydrolysis of the ferric iron and its ensuing precipitation to ferric hydroxide [$\text{Fe}(\text{OH})_3$] if and when the surrounding pH goes above 3.5. Throughout these processes, hydrogen ions are released into the water, thereby reducing the pH of the surrounding medium. The sum total of the reaction products and the reducing pH condition is commonly known as the AMD problem. This problem is a significantly large problem because of the many sets of mining activities conducted all over the world, and particularly because of the presence of pyrite in many of these mines. Acid contamination of groundwater and other receiving waters creates conditions that are adverse to human health and other biotic species. Chapter 4 will discuss the problem and impact of AMD in detail—together with procedures for amelioration of AMD.

Another example of contamination of groundwater is the case of the arsenic-contaminated aquifers in West Bengal and Bangladesh. These aquifers serve a significant portion of the population of these two countries, and ingestion of water from these contaminated aquifers has led to the development of arsenicosis in thousands of unfortunate individuals. Tube wells sunk into the aquifers constitute a major drinking water supply source for the two countries. Investigations on tube-well water supply showed concentrations of arsenic

far in excess of allowable limits. Tests on these wells at time of installation showed arsenic concentrations, if any, well below threat levels. The present levels of arsenic concentration indicate arsenic poisoning developed several years after installation of the wells. By switching to groundwater resources to avoid waterborne diseases from ingestion of surface water supplies, the population now faces considerable risk of arsenic poisoning as a result of ingesting arsenic-contaminated water obtained from tube wells tapping into the groundwater.

If the aquifers were not contaminated by arsenic before extensive harvesting of the aquifer resource, how did the arsenic get there? Is the arsenic contamination due to natural causes? Or indirectly due to a man-made cause? Arsenic occurrence in the hard rock and sedimentary rock aquifers have been reported in Argentina, Nepal, Nigeria, Czech Republic, and many other countries. Although it is not uncommon to find vanishingly small concentrations of arsenic in the groundwater in many parts of the world, the arsenic concentrations in the samples obtained from the aquifers in Bangladesh and West Bengal for instance are too high to be attributable to natural processes for arsenic release from arsenopyrites. In fact, the arsenic concentrations in the Bangladesh and West Bengal aquifers are also too high to be accounted for by direct human activities such as those associated with metalliferous mining. There appears to be no doubt that the release of arsenic into the aquifers is from geological source materials. Why is arsenic being released from the source rocks? Is this a natural process or is the release of arsenic triggered by some man-made event?

In the Bangladesh case, two factors appear prominently: (1) presence of arsenopyrites and arseniferrous iron oxyhydroxides in the substrate material and (2) the use of tube

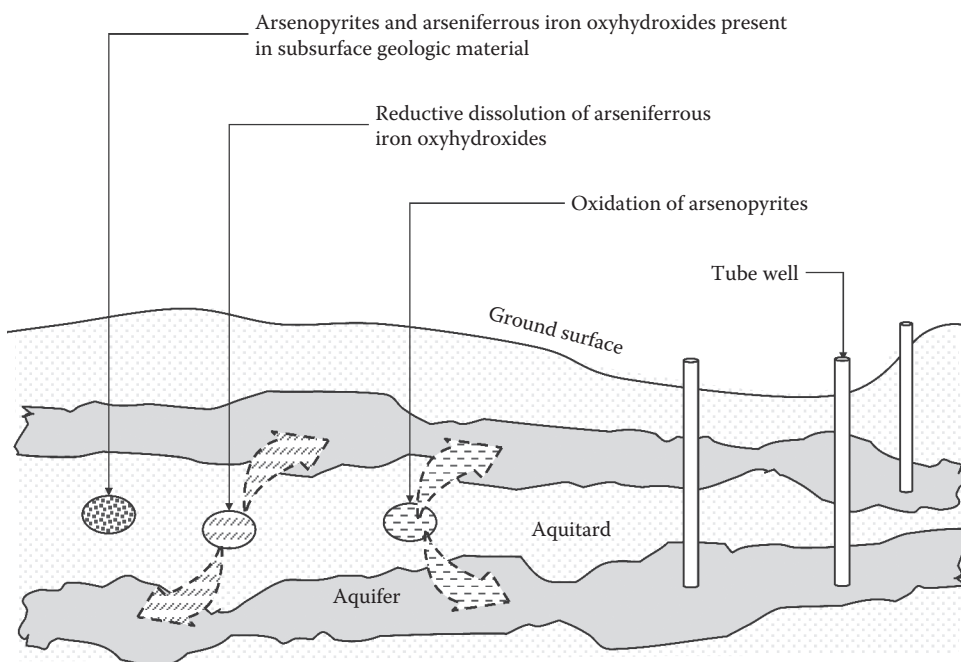


FIGURE 2.5

Schematic of speculative models for release of arsenic from arseniferrous iron oxyhydroxides and arsenopyrites into aquifers.

wells as a means for abstracting water. The two models proposed to explain the release of arsenic from the arsenic-bearing materials are shown in Figure 2.5. These include:

1. *Reduction mechanisms*: Reductive dissolution of arseniferrous iron oxyhydroxides releases the arsenic responsible for contamination of the groundwater.
2. *Oxidation processes*: Oxygen invades the groundwater because of the lowering of the groundwater from the abstracting tubewells resulting thereby in the oxidation of the arsenopyrite (FeAsS).

Based on these two possible mechanisms for arsenic release into the aquifer, and based on detailed field studies to determine the presence and distribution of As(III) and As(V) and other reaction products, there are some serious questions as to whether the arsenic releases processes are totally man-induced or a case of natural processes hastened and aggravated by man-made events, i.e., abstraction of water from the tube wells. The almost equal proportions of As(III) and As(V) in the aquifer testify to almost equal sets of activity from both arsenic-release mechanisms.

2.4 Wastes, Contaminants, and Threats

The discharge of liquid and solid wastes from industrial and energy-producing plants and facilities, together with extraction operations on site and inadvertent spills and deliberate dumping of waste materials, combines to introduce contaminants, toxicants, and other kinds of hazardous substances into the land environment—including the receiving waters contained therein. The term *contaminants* used in this section includes those contaminants that have are classified as pollutants (priority listing) by various regulatory agencies. The term *pollutant* will be used when necessary, to place emphasis on the hazardous nature of the contaminant in question. Pollutants pose significant threats not only to human health and other biotic receptors, but also to the health of the environment and the various ecosystems in the geoenvironment. In the treatment of threats to the environment and public health, there are several ways in which wastes and contaminants can be classified or categorized. One could categorize the wastes and contaminants in terms of source production, i.e., “where they come from.” Alternatively, one could categorize them in respect to:

- Level of toxicity, e.g., highly toxic, carcinogenic, priority listing.
- Inorganic or organic substances and chemicals, e.g., heavy metals, PAHs, PCE, styrene.
- Type of industry (source industry or source activity), e.g., pulp and paper, forest, electronic, pharmaceutical.
- Class of contaminants, e.g., pesticides, solvents.
- Nature of impact or threat, e.g., physical, chemical, biological.
- Type of receptor, e.g., land, water, human, other biota.

Experience has shown that although categorization of contaminants according to any single method as described above is not practical or feasible, it is always necessary to obtain

a proper identification of the types or species of contaminants. Considerable significance is placed on the potential health threat of contaminants. A popular approach that has gained the attention of many regulatory agencies is the SPR (source–pathway–receptor) method for determination of health threats and impacts created by the presence of contaminants in the geoenvironment and also by events or projects as source contaminants. There have been questions raised as to whether the SPR approach discriminates between levels of treatment or protection from health-threat events depending on the importance of the *receptors*. A school of thought suggests very strongly that risk management should be directly linked to receptor importance and also to certainty of pathways. It is not always clear that pathways to potential receptors are well defined. Nevertheless, one must include knowledge of the degree of certainty of pathways as an integral factor in the level of risk determination.

2.4.1 Inorganic Contaminants

Evidence of the presence of inorganic contaminants classifying as pollutants in the geoenvironment (land and water) show that these are mainly heavy metals such as Pb, Cr, Cu, etc. Yong (2001) has indicated that although those elements with atomic numbers higher than Sr (atomic number 38) are classified as heavy metals (HMs), it is not uncommon to include elements with atomic numbers greater than 20 as heavy metals. The 38 elements commonly considered as HMs fall into three groups of atomic numbers as follows:

1. From atomic numbers 22 to 34: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, and Se.
2. From 40 to 52: Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te.
3. From 72 to 83: Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, and Bi.

The more common heavy metals (HMs) found in the geoenvironment come as a result of anthropogenic activities such as management and disposal of wastes in landfills, generation and storage of chemical waste leachates and sludges, extraction of metals in metalliferous industries, metal plating works, and even in MSWs. The more notable HMs include lead (Pb), cadmium (Cd), copper (Cu), chromium, (Cr), nickel (Ni), iron (Fe), mercury (Hg), and zinc (Zn).

2.4.1.1 Arsenic (As)

Strictly speaking, arsenic is a nonmetal—although it is often classified as a metal. It is a metalloid (semi-metal) with atomic number 33 and is in group 5 of the periodic table. Arsenic is found naturally in rocks, most often in iron ores and in sulfide form as magmatic sulfide minerals. The more common ones are arsenopyrite (FeAsS), realgar (AsS), nicolite (NiAsS), and orpiment (As₂S₃). Arsenic is also found naturally in soils in association with hydrous oxides, and sometimes in elemental form in association with silver ores. Arsenic found in the geoenvironment can come directly from weathering of the arsenic-containing rocks and also from industrial sources such as manufacturing, processing, pharmaceutical, agriculture, and mining industries. Products such as paints, dyes, preservatives, herbicides, and semiconductors are some of the more common contributors to the arsenic found in the ground and in receiving waters. Extensive use of arsenic-containing (lead arsenate) pesticides, herbicides, and insecticides in agricultural and farm practices can contribute some considerable amounts of arsenic to the subsurface and the receiving waters.

Although the existent valence states for arsenic are -3 , 0 , $+3$ (arsenite), and $+5$ (arsenate), arsenite and arsenate are the more common forms of arsenic found in nature. Arsenic is a toxic element, and a regulatory limit of $50\text{ }\mu\text{g/L}$ in groundwater (aquifers) for drinking water has been adopted in many countries and regulatory agencies. In the United States, this limit was lowered to $10\text{ }\mu\text{g/L}$ for all water systems in 2006. Ingestion of arsenic for a period, for example, in the use of arsenic-contaminated waters in some regions of the world, can lead to serious health problems, e.g., mortality from hypertensive heart disease traceable to ingestion of arsenic-contaminated drinking water (Lewis et al., 1999) and arsenic-associated skin lesions of keratosis and hyperpigmentation (Mazumder et al., 1998). Similarly, inhalation of arsenic dust generated in ore refining processes can also lead to serious health problems, e.g., nasal septal perforation, and pulmonary insufficiency (USEPA, 1984).

2.4.1.2 Cadmium (Cd)

Cadmium can be found in nature as greenockite (cadmium sulfide, CdS) or otavite (cadmium carbonate, CdCO_3) and is usually associated with zinc, lead, or copper in sulfide form. The two major groups using cadmium include (1) cadmium as a filler, alloy, or active constituent for an industrial product, e.g., nickel–cadmium batteries, enamels, fungicides, phosphatic fertilizers, motor oil, solders, paints, plastics, and (2) cadmium as a coating or plating material, e.g., steel plating, metal coatings. The presence of Cd as a pollutant in the geoenvironment can be traced to:

- Non–point sources associated with the use of fungicides and fertilizers.
- Deposition of Cd particles in the atmosphere because of mining activities and burning of coal and other Cd-containing wastes.
- Specific sources such as industrial discharges and wastes and municipal wastes where the products manufactured and consumed include Cd as a filler, alloy, or active constituent.

From the viewpoint of human health effects and requirements, cadmium is considered to be a nonessential element. The USEPA Toxicity Characteristic Leaching Procedure (TCLP) regulatory level for Cd is 1.0 mg/L (roughly equivalent to 1 ppm). The EPA specifies a threshold limit of 5 ppb for drinking water and the Food and Drug Administration (FDA) specifies a limit of 15 ppm of Cd in food coloring (ATSDR, 1999). Accumulation of Cd in the liver and kidney from oral ingestion can lead to distress to these organs.

2.4.1.3 Chromium (Cr)

Chromium is found naturally as chromite (ferrous chromic oxide, FeCr_2O_4) and crocoisite (lead chromate, PbCrO_4) minerals. It is an essential element in human nutrition. The three common valence states for chromium are 0 , $+3$, and $+6$, i.e., chromium(0), chromium(III), chromium(VI). Chromium(III) is found naturally in the environment, whereas compounds of chromium are generally with chromium(VI). Trivalent chromium (chromium(III)) is stable and is considered to be relatively non toxic. Cr(III) can form various stable inert complexes: $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$, and $\text{Cr}(\text{H}_2\text{O})(\text{OH})_4^-$. Meanwhile, hexavalent chromium (chromium(VI)) is highly toxic and is considered to be a carcinogen. Oxidation of the trivalent chromium to the hexavalent chromium anions chromate (CrO_4)

and dichromate (Cr_2O_7) anions will not only render the previously nontoxic trivalent chromium toxic but will also make it more mobile. The major form of Cr(VI) is CrO_4^{2-} at pH greater than 6.5 and HCrO_4^- at pH less than 6.5. Both ions are very soluble.

Other than the natural sources, chromium found in the geoenvironment can be traced to waste discharges and tailing ponds associated with chromium mining. Principal uses for chromium (Cr) and its compounds include (a) use of chromium as alloys, with iron and nickel–stainless steel and super alloys as probably the best known alloys, (b) chromium compounds used in metal plating, tanning of hides, wood preservation, glass, and pottery products, and (c) production of chromic acid. Chromium in the land and aquatic compartments of the geoenvironment can be the result of production and waste discharges associated with the industries and from the tailing ponds associated with mining activities.

2.4.1.4 Copper (Cu)

Copper is found naturally in sandstones and in other copper-bearing oxidized and sulfide ores. These include such ores as malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$], tenorite (CuO), cuprite (Cu_2O), and chalcopyrite (CuFeS_2), with chalcopyrite being the most abundant. In addition to its natural occurrence in the land environment, contributions of Cu to the geoenvironment come from (a) deposition of airborne particles from mining of copper and combustion of fossil fuels and wastes, (b) discharges from industrial processes utilizing copper as a metal, and copper compounds (production of electrical products, piping, fixtures, and different alloys), and (c) industrial and domestic discharge of wastewater.

Copper deposited on the surface of the land environment from the various sources discussed in the preceding will initially be attached to organic matter and clay minerals, if such are present in the landscape. Degradation of the organic matter through anaerobic or aerobic means will release copper in its monovalent or divalent form, respectively. However, if the subsurface soils contain reactive soil particles, the released copper will be bound to these particles. Environmental mobility of copper in the substratum is not generally a big factor when the soil substratum is composed of fine soil fractions consisting of clay minerals and other soil fractions with reactive particles. Presence of copper in the receiving waters is most often confined to the sediments since the copper will attach itself to the fine particles in water.

In terms of health considerations, copper is considered to be an essential trace element in both human and animal nutrition. The amounts required, however, are extremely small. Threshold limits for human ingestion of copper vary between different countries and jurisdictions, with values of about 1.3 ppm for drinking water and 0.1 mg/m³ for airborne concentrations being reported.

2.4.1.5 Lead (Pb)

Lead in nature is found in sulfide, carbonate, and oxide forms. These are galena (lead sulfide, PbS), anglesite (lead sulfate, PbSO_4), cerrusite (lead carbonate, PbCO_3), and minium (lead oxide, Pb_3O_4). Although it has three valence states (0, +2, and +4), the most common state is +2. Compounds of Pb(II) have ionic bonds whereas the higher valence state, Pb(IV) compounds, have covalent bonds. Lead found in the land compartment of the geoenvironment will most often be bonded to reactive soil particles. It is a nonessential element.

Lead is used to a very large extent in the manufacture of lead-acid batteries and in the electronics and munitions industries. Other lesser uses for lead are in production of crystal glass, lead liner material, weights, insecticides, and in construction. Lead found in the

ground and in the receiving waters can be traced to deposition of airborne lead obtained from emissions such as burning of wastes and fuel and from transport of lead compounds in the soil. Lead is considered to be a nonessential toxic element, and ingestion or inhalation of lead will result in consequences to the central nervous system and damages to kidneys and reproductive system.

2.4.1.6 Nickel (Ni)

Nickel is quite widely found in nature in various soil deposits, e.g., laterite deposits, and generally in mineral form in combination with oxygen or sulfur as oxides or sulfides. These include nickel sulfide (NiS), nickel arsenide (NiAs), nickel diarsenide (NiAs₂), and nickel thioarsenide (NiAsS). Some debate exists concerning whether nickel is, or is not, an essential element. It is maintained that small amounts of nickel are essential for maintaining the good health of animals, and to a lesser extent, humans.

Nickel found in the geoenvironment, other than from natural sources, can be traced to fugitive atmospheric nickel and waste discharge associated with nickel mining activities, burning of waste, operation of oil- and coal-burning power plants, discharges from manufacturing industries using nickel alloys and compounds. Nickel does not precipitate but is sorbed onto clays, oxides of manganese and iron, and organic material occurs. Mobility increases with the formation of complexes with organic and inorganic ligands.

2.4.1.7 Zinc (Zn)

Similar to nickel, zinc is found in soil deposits and does not generally exist as a free element. Instead, it is found in mineral form in combination with oxides, sulfides, and carbonates to form zinc compounds. The sulfide form is perhaps the more common form for zinc found naturally in the environment. Some of the naturally occurring zinc compounds are zincite (zinc oxide, ZnO), hemimorphite (zinc silicate, 2ZnO·SiO₂·H₂O), smithsonite (zinc carbonate, ZnCO₃), and as sphalerite (zinc sulfide, ZnS). Natural levels of zinc in soils are 30 to 150 ppm.

Typical uses and products for zinc in element form as oxide and sulfide compounds include alloys, batteries, paints, dyes, galvanized metals, pharmaceuticals, cosmetics, plastics, electronics, and ointments. It follows that non-naturally occurring zinc found in the geoenvironment would be the zinc compounds associated with the production and use of industrial products. Deposition of airborne fugitive zinc from mining and extraction of zinc, together with discharges (spills, wastes, and waste streams) from the processing and production of products utilizing zinc compounds, account for the major sources of non-naturally occurring zinc found in the geoenvironment. Some of these sources are galvanizing plant effluents, coal and waste burning, leachates from galvanized structures, natural ores, and municipal waste treatment plant discharge.

Although not as toxic as cadmium, zinc is quite often associated with this metal. Under acidic conditions below its precipitation pH, zinc is usually divalent and quite mobile. In the divalent state, sorption onto the surfaces of reactive soil particles includes ionic bonding and sequestering by organic matter. At high pH, the solubility of its organic and mineral colloids can render zinc bioavailable. Zinc hydrolyzes at pH 7.0 to 7.5, forming Zn(OH)₂ at pH values higher than 8. Under anoxic conditions, ZnS can form upon precipitation, whereas the unprecipitated zinc can form ZnOH⁺, ZnCO₃, and ZnCl⁺.

2.4.2 Organic Chemical Contaminants

Organic chemical contaminants found in the geoenvironment classify as organic chemical pollutants. These have origins in (a) industries producing various chemicals and pharmaceuticals, e.g., refineries, production of specialty chemicals; (b) waste streams and disposal of chemical products, e.g., sludges, spills; and (c) utilization of various chemical products, e.g., use of petroleum products, pesticides, organic solvents, paints, oils, creosotes, and greases. There are at least a million organic chemical compounds registered in the various chemical abstracts services available, with many thousands of these in commercial use. By and large, organic chemicals found in the geoenvironment can be traced to sources and activities associated with humans. Figure 2.6 shows some of the main sources of contaminants (inorganic and organic) found in the land compartment of the geoenvironment.

The more common organic chemicals found in the physical landscape of the land environment can be grouped as follows:

- **Hydrocarbons:** including the PHCs (petroleum hydrocarbons), the various alkanes and alkenes, and aromatic hydrocarbons such as benzene, MAHs (multicyclic aromatic hydrocarbons), e.g., naphthalene, and PAHs (polycyclic aromatic hydrocarbons), e.g., benzo-pyrene.

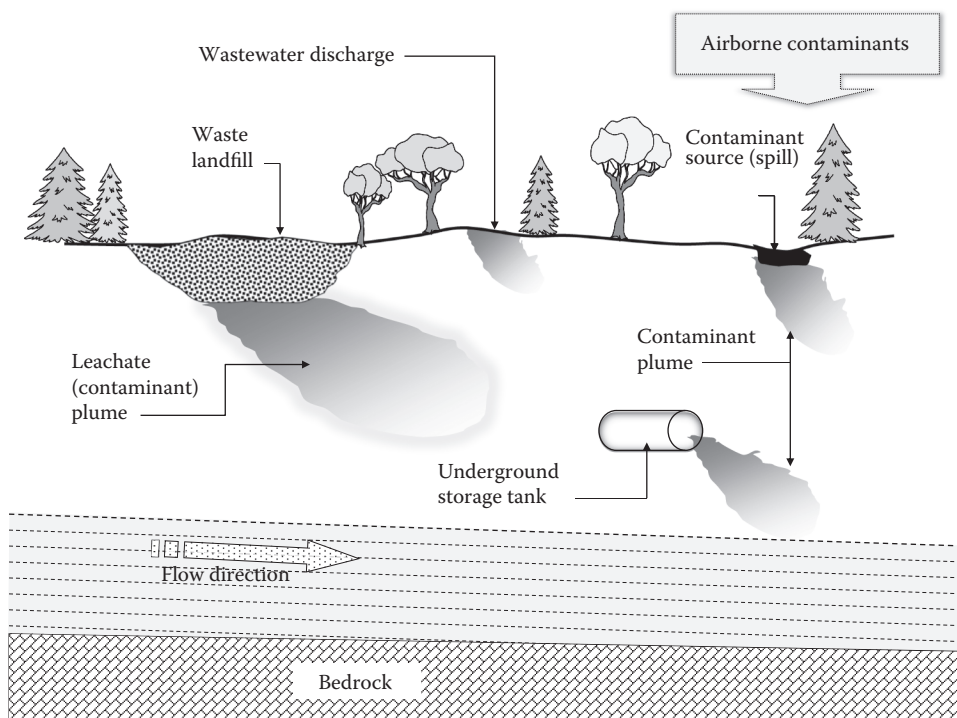


FIGURE 2.6

Schematic showing (a) leachate plume with contaminants emanating from a waste landfill, (b) contaminant plumes from a leaking underground storage tank and wastewater discharge, (c) deposition of airborne contaminants onto land surface, and (d) a surface contaminant source (spill). (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

- Organohalide compounds: of which the chlorinated hydrocarbons are perhaps the best known. These include TCE (trichloroethylene), carbon tetrachloride, vinyl chloride, hexachlorobutadiene, PCBs (polychlorinated biphenyls), and PBBs (polybrominated biphenyls).
- Oxygen- and nitrogen-containing organic compounds such as phenol, methanol, and TNT (trinitrotoluene).

Not all of the organic chemical contaminants are soluble in water. Those that are not, are identified as nonaqueous phase organics. Separation of the nonaqueous phase organic compounds into two classes, which distinguish between whether they are lighter or denser than water is useful because it tells one about the transport characteristics of the organic compound. These nonaqueous phase organics are called nonaqueous phase liquids (NAPL), and the distinction between the lighter than water and heavier than water is given as LNAPL and DNAPL, respectively (i.e., the LNAPLs are lighter than water and the DNAPLs are heavier than water). The schematic diagram in Figure 2.7 shows that because the LNAPL is lighter than water, it stays on the surface of or above the water table. Because the DNAPL is denser than water, it will sink through the water table and will come to rest at the impermeable bottom (bedrock). Some typical LNAPLs include gasoline, heating oil, kerosene, and aviation fuel. DNAPLs include the organohalide and oxygen-

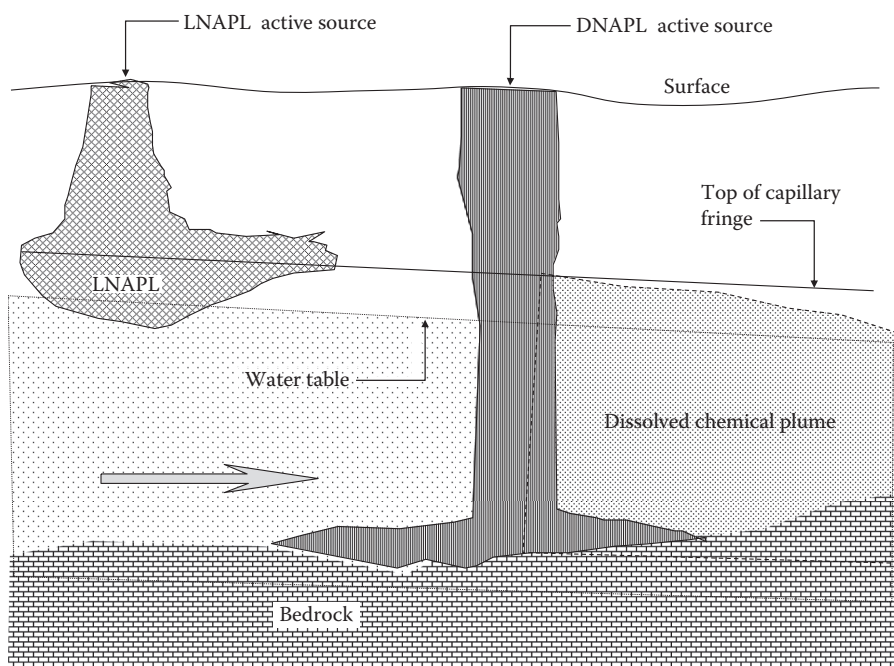


FIGURE 2.7

Schematic diagram showing LNAPL and DNAPL in the subsurface. Note that the LNAPL stays above the water table whereas the DNAPL penetrates into substratum and rests on the impermeable rock bottom. (From Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, FL, 307 pp., 2001.)

containing organic compounds such as 1,1,1-trichloroethane, creosote, carbon tetrachloride, pentachlorophenols, dichlorobenzenes, and tetrachloroethylene.

2.4.2.1 Persistent Organic Chemical Pollutants

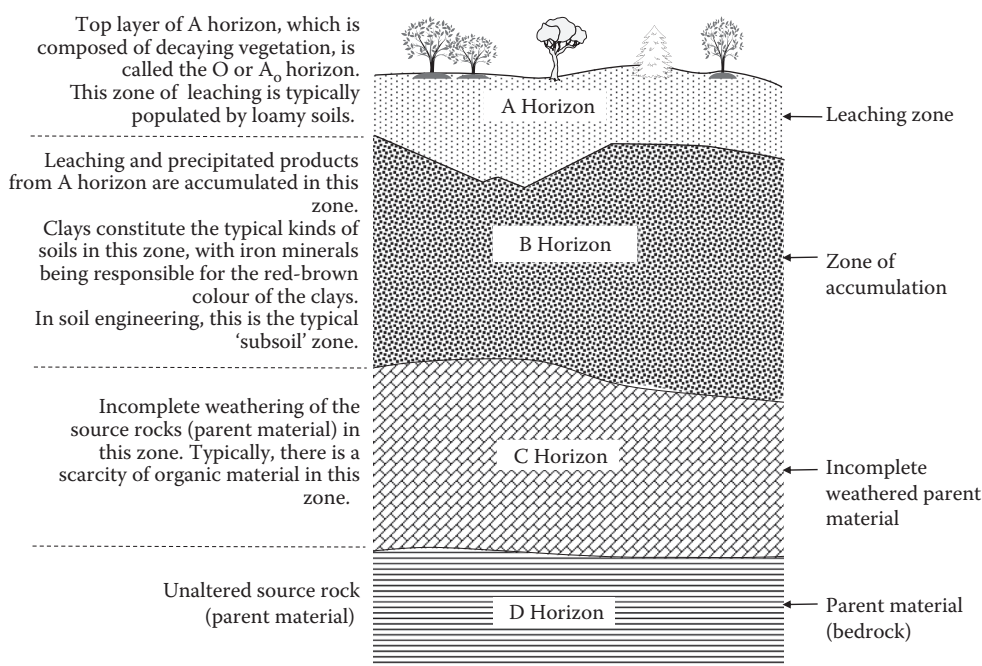
Not all the organic chemicals found in the geoenvironment will be biologically and chemically degraded. The characteristic term used to describe organic chemicals that persist in their original form or in altered forms that pose threats to human health is *persistence*. The acronym used to describe persistent organic chemical contaminants is POPs (persistent organic pollutants). These are generally defined as organic contaminants that are toxic, persistent, and bioaccumulative. Included in the POPs are dioxins, furans, the pesticides and insecticides (aldrin, chlordane, DDT, etc.), and a whole host of industrial chemicals grouped as polycyclic aromatic hydrocarbons (PAHs), and halogenated hydrocarbons (including the chlorinated organics). The top 12 POPs that have been identified by the United Nations Environmental Program as POPs for reduction and elimination are dioxins, furans, PCBs, hexachlorobenzene, aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, mirex, toxaphene. The majority of the top twelve POPs are pesticides. Because of their heavy use in agriculture, golf courses, and even at the household level for control of insects and other pests, it is not difficult to see how these find their way into the geoenvironment.

2.5 Surface and Subsurface Soils

Surface and subsurface soils constitute the uppermost portion of the mantle of the land environment, i.e., the unconsolidated material in the upper layer of the lithosphere. This upper layer is an integral part of the terrestrial ecosystem (Figure 2.8). When combined with the flora and fauna, this upper mantle constitutes the habitat for terrestrial living organisms. Soil, as a material, can be considered as a natural capital of the geoenvironment. There are many functions served by surface and subsurface soils. They provide the physical, chemical, and biological habitat for animals and soil microorganisms. In addition, they support growth of plants and trees, and are the vital medium for agricultural production—the virtual host for food production. Soil materials in the subsurface are very useful in the mitigation of hydraulic and chemical impacts of liquid wastes discharged on (and in) the land surface—because of their inherent chemical and physical buffering capabilities. Soil is a renewable resource that is in danger of becoming a nonrenewable renewable resource (see Chapter 10).

2.5.1 Soil as a Resource Material

Soils are considered as essential resource material. Food production, forestry, and extraction of minerals are some of the life-support activities that depend on soil. Surface and subsurface soils constitute the primary host or recipient of contaminants and contaminants. From the schematic shown in Figure 2.8, it is evident that the transport and fate of contaminants that find their way into this land compartment of the geoenvironment will be a function of (a) the properties of the soil, (b) the properties of the contaminants themselves, (c) the geological and hydrogeological settings, and (d) the microenvironment (regional controls). It is not the intent of this section or this book to deal in detail with the

**FIGURE 2.8**

Soil horizons typical of a mature soil. Immature soils (soils that have not had much exposure to weathering and leaching phenomena) will not show distinct layering for zone classification. (From Yong, R.N. et al., *Environmental Soil Properties and Behaviour*, CRC Press, Boca Raton, FL, 435 pp., 2012.)

properties and characteristics of soils. Nor is it intended to develop the basic fundamental principles of contaminant–soil interactions. These can be found in Yong and Warkentin (1975), Yong (2001), and Yong and Mulligan (2004). Instead, we will focus on the aspects of soils and their interactions that help us develop a better understanding of soils as they relate to the control of contaminant fate and transport.

2.5.2 Nature of Soils

Soils are three-phased systems—solids, aqueous, and gaseous. All three phases coexist to form a soil mass. The composition of the solids, the chemistry of the aqueous phase and the proportions of each phase at any location is a function of how the soil was formed, “how it got there,” and the governing regional controls and climatic factors. Soils are formed by natural processes associated with the weathering of rock and the decomposition of organic matter. Weathering or disintegration of the parent rock material can be either physical or chemical. In both cases, rock disintegration will produce smaller fragments, and ultimately, soil material is formed. Unless the soil material is transported to other regions after formation, for example, by wind forces, by water movement or even by glacial action, the in-place and resident soil material will reflect the primary compositional features of the parent rock. Further weathering of the soil material will produce the compositional features seen in the in-place soil. Weathering is at its highest intensity in the upper soil zone in temperate humid climate regions and deeper soil zones in humid tropics. The transformations occur principally in the regolith, the region between solid rock and the topsoil.

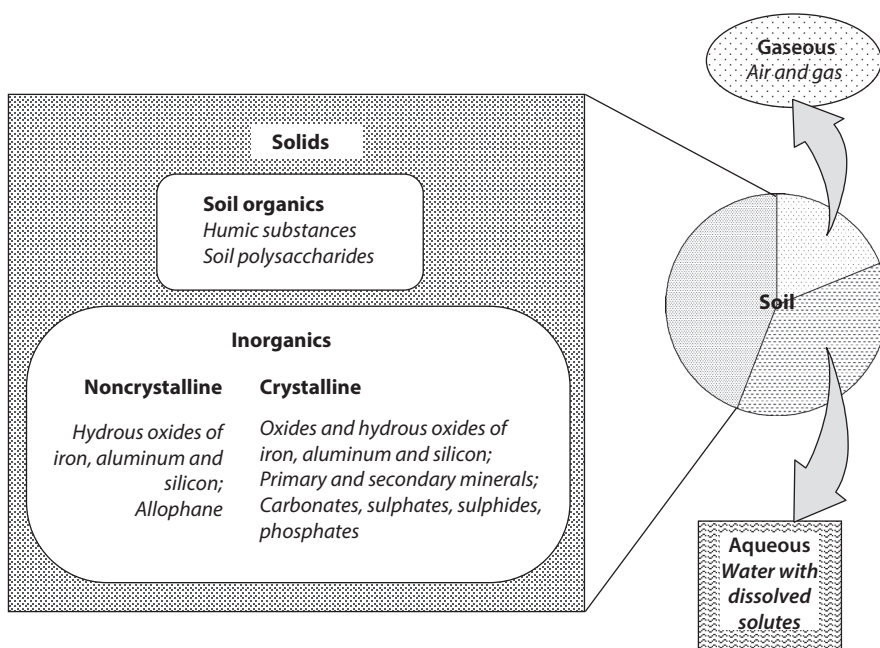
Figure 2.9 shows the three phases (gaseous, aqueous, and solids) of soils and the various kinds of constituents that make up a soil. The various constituents in the solid phases are generally identified as *soil fractions* since each type of constituent is a fraction of the soil solids that comprise the total soil itself. The various soil fractions combine to form the natural soils that one sees at any one site. The soils may have been transported and deposited as sedimentary deposits of alluvial, fluvial, or marine action. The soils derived from these actions are appropriately called fluvial soils, alluvium, and marine soils.

Figure 2.10 shows an idealized schematic of the various soil fractions grouped into a soil unit. Not all soils have all the various fractions shown in Figure 2.9. How the proportions and distributions of the different soil fractions occur will depend on not only the geological origin of the soil but also the regional controls and weathering processes existent at the soil location. At least five factors and four different processes are involved in the production of individual soil fractions. The five factors are:

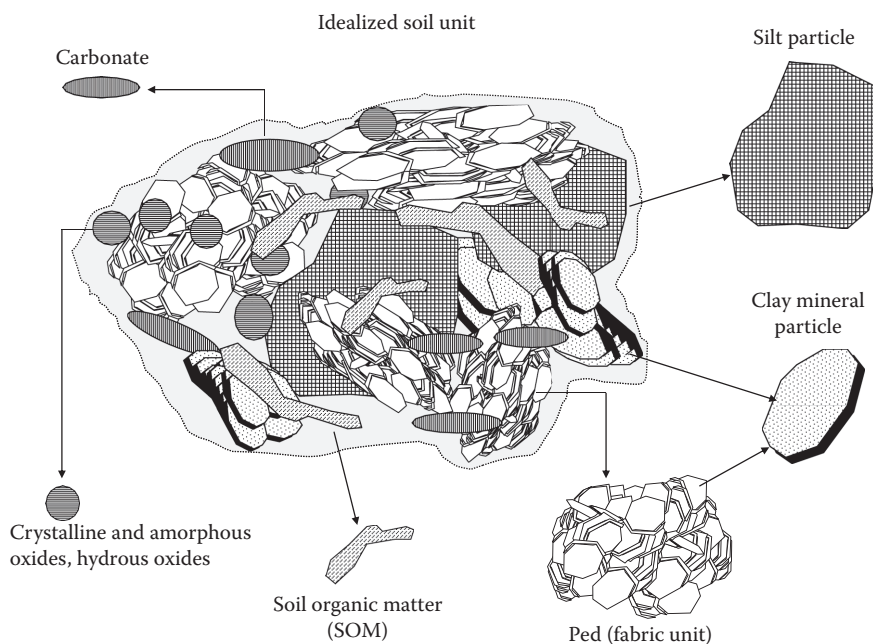
1. Parent rock material: Composition and texture are important. The influence of these features depends on where weathering occurs. In extreme humid conditions and temperatures, the influence of composition and texture are short lived. However, in arctic and arid regions, the influence of composition and texture of the parent rock material are long-lived and can even remain indefinitely. Alkali and alkaline earth cations are important factors in determining the weathering products. Thus, for example, rocks containing no alkali can only produce kaolinite or lateritic soils as weathering products. Meanwhile, weathering of igneous rocks, shales, slates, schists, and argillaceous carbonates will produce a large variety of weathering products because of the presence of alkalis, alkaline earth cations, alumina, silica, etc.
2. Climate: Temperature and rainfall are important climatic factors. Warm and humid climates encourage rapid weathering of the minerals of the parent rock material. Decaying vegetative products and organic acids contribute significantly to the weathering process.
3. Topography: This affects how water infiltrates into the ground. The greater the residence time of water, for example, found at low-lying areas that impound water, the greater are the reactions between the solutes in water and the soil material.
4. Vegetation: Decaying vegetation is a significant factor since this reacts with the parent silicate minerals.
5. Time: This is an important factor in situations where reaction rates are slow.

The four processes that are influential in the weathering sequences include:

1. Hydrolysis: This is the reaction between the H^+ and OH^- ions of water and other mineral ions, particularly for the rock-forming silicates.
2. Hydration: This is important for the formation of hydrous compounds with the minerals in the rocks such as the silicates, oxides of iron and aluminum, and the sulfates.
3. Oxidation: Since most rocks carry iron in the form of sulfides or oxides, oxidation of the Fe to FeS , FeS_2 could easily occur in the presence of moisture since this promotes the process of oxidation.
4. Carbonation: The interaction or reaction of carbonic acid with bases will yield carbonates. The process of carbonation in silicates is accompanied by the liberation of silica. The silica may remain as quartz or may be removed as colloidal silica.

**FIGURE 2.9**

Soil constituents. Proportioning of the three phases (gaseous, aqueous, and solids) is approximately representative of a partly saturated soil.

**FIGURE 2.10**

An idealized typical soil unit in a soil mass consisting of various soil fractions. The positions of the various fractions and the configuration define the structure of the soil. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

2.5.3 Soil Composition

Figures 2.9 and 2.10 show that the solid phase of soils contain both inorganic and organic constituents, and that the inorganic components can be minerals as well as other quasi-crystalline and noncrystalline materials.

2.5.3.1 Primary Minerals

We define *primary minerals* as those minerals derived in unaltered form from parent rock material, generally through physical weathering processes. The more common ones found in soils are quartz, feldspar, micas, amphiboles, and pyroxenes. By and large, primary minerals are generally found as sands and silts, with a small portion of clay-sized fractions qualifying as primary minerals. We classify particles less than 2 μm in effective diameter as clay-sized. This classification is made because it is necessary to distinguish between *clay-sized* particles and *clay minerals*.

2.5.3.2 Secondary Minerals

Secondary minerals are derived as altered products of physical, chemical, and/or biological weathering processes. These minerals are layer silicates, commonly identified as phyllosilicates, and they constitute the major portion of the clay-sized fraction of soil materials in clays. Because of the possibility for confusion in usage of terms and names, it is important to distinguish among the terms *clays*, *clay soils*, *clay-sized*, and *clay minerals*.

Clays and *clay soils* refer to soils that have particle sizes $<2 \mu\text{m}$ effective diameter. *Clay-sized* refers to soil particles with effective diameters less than 2 μm . No specific reference to the kind or species of particles is required, since attention is directed toward the size of the particles. *Clay minerals* refer specifically to the layer silicates. These are secondary minerals. They consist of oxides of aluminum and silicon with small amounts of metal ions substituted within the crystal structure of the minerals. Because of their size and their structure, secondary minerals have large specific surface areas (SSAs) and significant surface charges. The major groups of clay minerals include kaolinites, smectites (montmorillonites, beidellites, and nontronites), illites, chlorites, and vermiculites.

2.5.3.3 Soil Organic Matter

Soil organic matter (SOM) can exist in soils in proportions as low as 0.5% to 5%. Although their proportions may be small, their influence on the bonding of soil particles and aggregate groups, together with their ability to attenuate contaminants, cannot be overstated. SOM originates from vegetation and animal sources and is generally categorized in accord with its state of degradation into humic and non-humic material. Humic materials or substances are those organics that result from the chemical and biological degradation of non-humic material. Non-humic material or compounds, meanwhile, are organics that remain un-decomposed or are partly degraded. Humic substances are classified into humic acids, fulvic acids, and humins, with the distinction being made of the basis of their solubility to acid and base.

2.5.3.4 Oxides and Hydrous Oxides

The general list of oxide and hydrous oxide minerals includes the oxides, hydroxides, and oxyhydroxides of iron, aluminum, manganese, titanium, and silicon. The common

crystalline form of these minerals includes haematite, goethite, gibbsite, boehmite, anatase, and quartz. They differ from layer silicate minerals (secondary minerals) in that their surfaces essentially consist of broken bonds. In an aqueous environment, these broken bonds are satisfied by the OH^- groups of disassociated water molecules. The surfaces exhibit pH-dependent charges, i.e., the surfaces have variable charged properties.

2.5.3.5 Carbonates and Sulfates

The most common carbonate mineral found in soils is calcite (CaCO_3). Some of the other less common ones are magnesite (MgCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the most common of sulfate minerals found soils.

2.5.4 Soil Properties Pertinent to Contaminant Transport and Fate

The reactions between contaminants and soil during the time when the contaminant is in contact with a soil will determine its transport through the soil, and also its fate. Figure 2.11 shows a simplified schematic of an influent contaminant leachate entering a soil unit. Interaction between the various contaminants in the leachate stream with the exposed surfaces of the soil particles of the various soil fractions will ultimately determine the transport characteristics and fate of the contaminants in the leachate stream. The controlling factors involved, other than the properties and functional groups (chemically reactive groups) of the contaminants, are listed in the diagram.

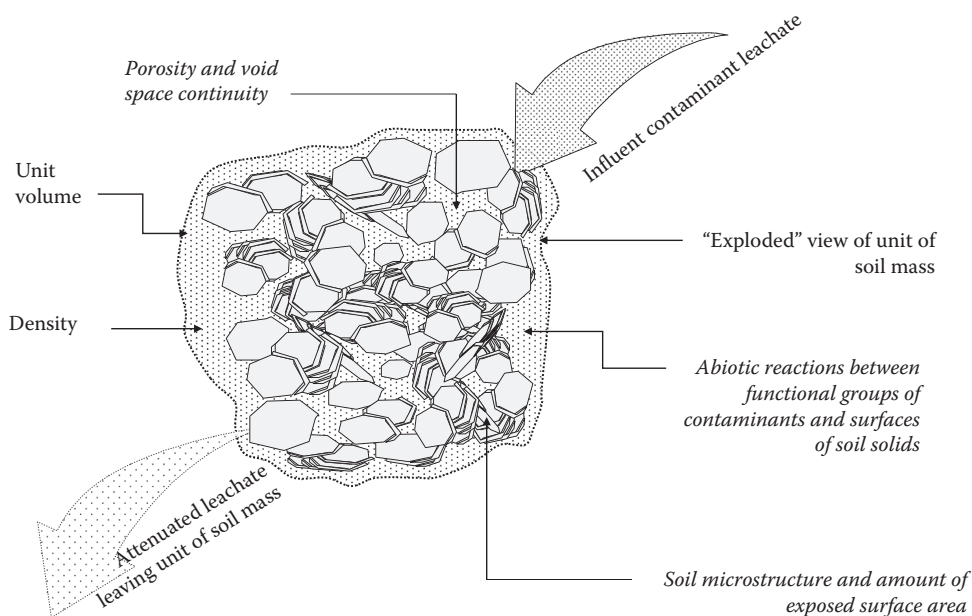


FIGURE 2.11

Schematic diagram showing the major physical soil factors (in italics) involved in controlling contaminant transport through the unit soil mass.

The two types of interactions involved in contaminant transport processes are:

1. Physical interactions: These interactions involve fluid and contaminant movement through the soil fabric and structure. As such, the nature of the void spaces and the amount of surface area presented by the soil particles to the liquid waste and leachate stream are important factors. The principal factors include:
 - a. Void spaces: The size distribution of voids and the continuity of voids are important factors in determining the rate of transport of the leachate stream through the soil. The nature of these voids, their continuity, and their distribution are all dependent on the density and structure of the soil. These in turn are functions of soil composition and manner in which the soil was formed in situ.
 - b. Surface area and microstructure: The interactions of the various contaminants in the leachate stream with the surfaces of the soil particles will be dictated by the amount of surfaces exposed to the contaminants. Because of the existence of soil microstructural units (i.e., packets of soil particles grouped together to form aggregate groups or pedes or clusters of particles), not every single particle will have its total surface area exposed to the leachate stream. The sizes and types of microstructural units that comprise the soil in question will determine the amount of surface areas exposed to the influent leachate. The detailed discussion on soil microstructure and hydraulic conductivity will be found in Section 10.5 in Chapter 10 in the discussion on mitigation of impacts from contaminant transport.
2. Chemical interactions: This grouping of interactions includes all the types of chemical reactions that occur when two chemically reactive participants interact with each other. The surface properties, and especially the surface chemistry of the soil solids, are very important factors. The surface chemically reactive groups for the soil solids and for the contaminants are identified as functional groups. These will be discussed in a later section in this chapter.

From the schematics shown in Figures 2.9 and 2.10, we obtain an appreciation of the constituents of a typical soil unit and have learned that the different soil solids are known as soil fractions. Although the types of soil fractions can range from sands to clay minerals to soil organics, it is the soil fractions with reactive surfaces that are of interest in the study of transport and fate of contaminants. *Reactive surfaces*, in the present soil unit context, are defined as those surfaces that can react chemically with dissolved solutes in the porewater of the soil. We should also note that contaminants in the ground will also have reactive surfaces, and in this case, these reactive surfaces can react chemically with other dissolved solutes in the porewater and also with the soil solids.

2.5.4.1 Specific Surface Area and Cation Exchange Capacity

The soil fractions that have more particles with significant reactive surfaces are the clay minerals, oxides and hydrous oxides, soil organics, and carbonates. Table 2.1 gives the surface charge characteristics, SSA, and cation exchange capacity (CEC) for some clay minerals. We define the SSA as the total surface area of all the soil solids or particles per unit volume. Since theoretical calculations for SSA can become both complex and tedious, because of the irregular shapes and sizes of the soil particles, laboratory techniques are often used. A popular procedure is to determine the amount of gas or liquid (adsorbate)

TABLE 2.1
Charge Characteristics, SSA, and CEC for Some Clay Minerals

Soil Fraction	CEC (meq/100 g)	Surface Area (m ² /g)	Range of Charge (meq/100 g)	Reciprocal of Charge Density (nm ² /charge)	Isomorphous Substitution	Source of Charges
Kaolinite	5–15	10–15	5–15	0.25	Diectahedral; two thirds of positions filled with Al	Surface silanol and edge silanol and aluminol groups (ionization of hydroxyls and broken bonds)
Clay micas and chlorite	10–40	70–90	20–40	0.5	Diectahedral; Al for Si Triectahedral or mixed Al for Mg	Silanol groups, plus isomorphous substitution and some broken bonds at edges
Illite	20–30	80–120	20–40	0.5	Usually octahedral substitution Al for Si	Isomorphous substitution, silanol groups and some edge contribution
Montmorillonite ^a	80–100	800	80–100	1.0	Diectahedral; Mg for Al	Primarily from isomorphous substitution, with very little edge contribution
Vermiculite ^b	100–150	700	100–150	1.0	Usually triectahedral substitution Al for Si	Primarily from isomorphous substitution, with very little edge contribution

Source: Adapted from Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, FL, 307 pp., 2001.

Note: That ratios of the external to the internal surface areas are highly approximate since surface area measurements are operationally defined, i.e., they depend on the technique used to determine the measurement.

^a Surface area includes both external and intralayer surfaces. Ratio of external particle surface area to internal (intralayer) surface area is approximately 5:80.

^b Surface area includes both external and internal surfaces. Ratio of external to internal surface area is approximately 1:120.

that forms a monolayer coating on the surface of the particles. The choice of the adsorbate and the availability of soil particles in a totally dispersed state are important factors in production of the final sets of data. Because of the dependence on techniques used, we consider a laboratory measurement of the SSA of a soil sample to be an operationally defined property (i.e., dependent on technique, adsorbate used, and degree to which the soil has been properly dispersed).

To explain the *reciprocal of charge density* shown in Table 2.1, we need to explain what surface charge density means. The *surface charge density* is the total number of electrostatic charges on the clay particles' surfaces divided by the total surface area of the particles. The common procedure is to express this surface charge density in terms of its reciprocal, as shown in Table 2.1. We have omitted the values for the hydrous oxides such as goethite [FeOOH] and gibbsite [$\text{Al}(\text{OH})_3$] from Table 2.1 because the range of values for these types of soil fractions are dependent upon (a) their structure, (b) the specifically adsorbed potential-determining ions, and (c) the pH of the porewater.

The CEC is defined as the quantity of exchangeable ions held by a soil, and is generally equal to the amount of negative charge in the soil. This is usually expressed in terms of milliequivalents per 100 g of soil (meq/100 g soil). Exchangeable cations are associated with clay minerals, amorphous materials, and natural soil organics. Many of the surface functional groups of these soil fractions are direct participants in cation exchange, e.g., the oxygen-containing functional groups of SOM such as the carboxyl and phenolic functional groups. Although not reported in Table 2.1, we see measured values for CEC ranging from 15 to 24 meq/100 g soil for Fe-oxides, from 10 to 18 meq/100 g soil for Al-oxides, and from 20 to 30 meq/100 g soil for allophanes. CEC values of up to 100 meq/100 g soil for goethites and hematites, and from 150 to 400 meq/100 g soil for organic matter at a pH of 8 have been reported by Appelo and Postma (1993). Their empirical relationship for the CEC of a soil is given in terms of the percentage of clay less than $2\ \mu\text{m}$ and the organic carbon as follows:

$$\text{CEC (meq/100g soil)} = 0.7 \text{ Clay\%} + 3.5 \text{ OC\%}$$

where *Clay%* refers to the percentage of clay less than $2\ \mu\text{m}$ and *OC%* refers to the percentage of organic carbon in the soil.

By combining the density of charges with the amount of surface areas available and the CEC of the specific clay mineral, we will obtain some appreciation of the degree of reactivity of the clay mineral in question. This should not be construed as a quantitative estimate since actual field soils will not have all particles and their surfaces available for exposure to contaminants. Aggregate groups of particles such as flocs, domains, peds, and clusters will diminish the total calculated surface area obtained from single particle theory.

2.5.5 Surface Properties

The surface properties of soils are important because it is these properties, together with those surface properties of contaminants themselves and the geometry and continuity of the pore spaces that will control the transport processes of the contaminants. We have previously defined *reactive surfaces* to mean those surfaces which by virtue of their properties are capable of reacting physically and chemically with solutes and other dissolved matter in the porewater. The chemically reactive groups, which are molecular units, are found on the surfaces of the various soil fractions, are defined as *surface functional groups*. These surface functional groups give the surfaces their reactive properties.

The soil fractions that possess significant reactive surfaces include layer silicates (clay minerals), soil organics, hydrous oxides, carbonates, and sulfates. The surface hydroxyls (OH group) are the most common surface functional group in inorganic soil fractions (soil solids) such as clay minerals with disrupted layers (e.g., broken crystallites), hydrous oxides, and amorphous silicate minerals. The common functional groups for SOM include the hydroxyls, carboxyls, phenolic groups, and amines. More detailed explanations concerning the nature of these functional groups and their manner of interaction with the functional groups associated with contaminants can be found in soil science and geoenvironmental engineering textbooks (e.g., Sposito, 1984; Greenland and Hayes, 1981; Huang et al., 1995a,b; Knox et al., 1993; Yong, 2001; Yong and Mulligan, 2004; Yong et al., 2012).

2.6 Contaminant Transport and Land Contamination

The transport of contaminants in soils refers to the movement of contaminants through the pore spaces in soils. Liquid contaminants such as organic chemical compounds and inorganic/organic contaminants carried in waste streams and leachate streams that pass through the soil pore spaces will interact with the exposed surfaces of the soil fractions. The reactions arising from the interactions between contaminants and soil fractions will dictate the nature of the transport of contaminants, and indirectly or directly, the fate of the contaminants. It is useful to remember that except for liquid chemicals, water is the primary carrier or transport agent for contaminants. The liquid phase of a soil–water system—i.e., the porewater—consists of water and dissolved substances such as free salts, solutes, colloidal material, and/or organic solutes. All dissolved ions, and probably all dissolved molecules are to some extent, surrounded by water molecules.

The questions relating to *what happens to contaminants in the ground* are perhaps the most critical concerns at hand. Will they eventually disappear? How long will they likely stay in the ground? Will they move to other locations or be transported? Will they be harmful to human health and the environment? To address the questions, it is necessary to obtain an understanding of the partitioning mechanisms (i.e., the chemical mass transfer of contaminants from the porewater to the surfaces of the soil solids), and how these are related to the soil and contaminant properties. A detailed consideration of these will be found in Chapters 9 and 10. For this section, we will highlight some of the main elements of the interactions as they relate to the mass transfer of dissolved solutes in the porewater (i.e., partitioning of dissolved solutes).

2.6.1 Mechanisms of Interaction of Heavy Metal Contaminants in Soil

The processes of transfer of metal cations from the soil porewater can be grouped as follows:

- *Sorption*: This includes physical adsorption (physisorption), occurring principally as a result of ion-exchange reactions and van der Waals forces, and chemical adsorption (chemisorption), which involves short-range chemical valence bonds. The general term *sorption* is used to indicate the process in which the solutes (ions, molecules, and compounds) are partitioned between the liquid phase and the soil

particle interface. When it is difficult to fully distinguish among the mechanisms of physical adsorption, chemical adsorption, and precipitation, the term *sorption* is used to indicate the general transfer of material to the interfaces.

- *Physical adsorption*: This occurs when the contaminants in the soil solution (aqueous phase, porewater) are attracted to the surfaces of the soil solids because of the unsatisfied charges of the soil particles. In the case of the heavy metals (metal cations) for example, they are attracted to the negative charges exhibited by the surfaces of the soil solids (Figure 2.12). When the cations are held primarily by electrostatic forces, this is called *nonspecific* cation adsorption.
- *Specific cation adsorption*: This refers to the situation where the ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via O and OH groups to the structural cations. The valence forces are of the type that binds atoms to form chemical compounds of definite shapes and energies. This type of adsorption is also referred to as *chemisorption*.
- *Complexation with various ligands*: *Complexation* occurs when a metallic cation reacts with an anion that functions as an inorganic ligand. Metallic ions that can be complexed by inorganic ligands include the transitional metals and alkaline earth metals. The inorganic ligands that will complex with the metallic ions include most of the common anions, e.g., OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} . Complexes formed

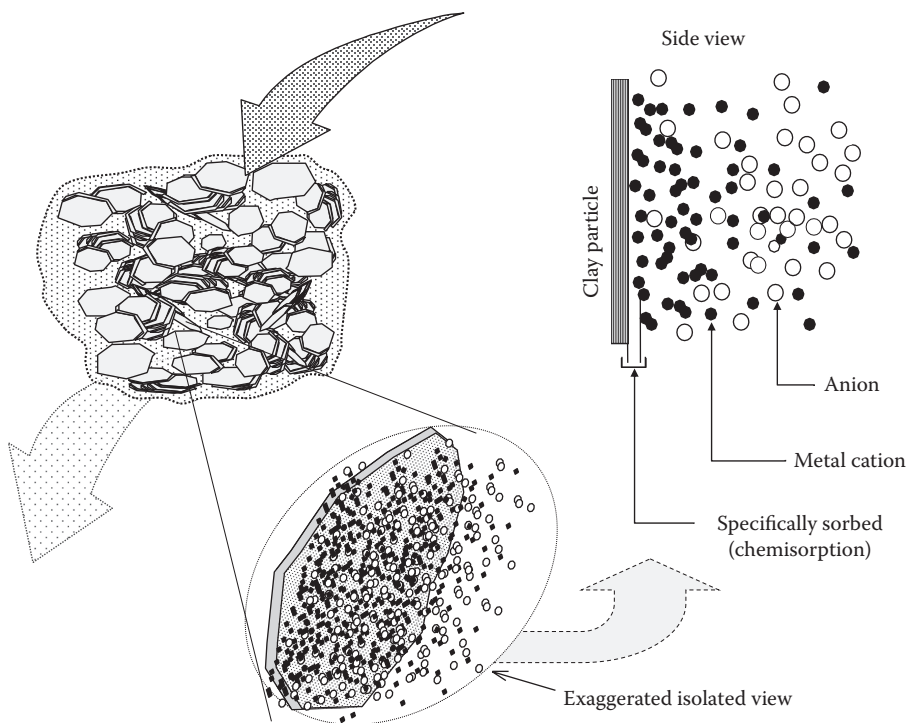


FIGURE 2.12

Exaggerated isolated view of interaction of metal cations (in the porewater) with soil particles. The soil particle shown is a clay mineral particle.

between metal ions and inorganic ligands are much weaker than those complexes formed with organic ligands.

- *Precipitation*: Accumulation of material (solutes, substances) on the interface of the soil solids to form new (insoluble) bulk solid phases. Precipitation occurs when the transfer of solutes from the aqueous phase to the interface results in accumulation of a new substance in the form a new soluble solid phase. Gibbs phase rule restricts the number of solid phases that can be formed. Precipitation can occur on the surfaces of the soil solids or in the porewater.

2.6.2 Chemically Reactive Groups of Organic Chemical Contaminants

When organic chemical compounds come in contact with soil, the nature of the chemically reactive groups in the organic molecules, their shape, size, configuration, polarity, polarizability, and water solubility are important factors in determining the adsorption of these chemicals by the soil solids. These chemically reactive groups, which are also known as functional groups populate the surfaces of both contaminants and soil solids. The chemical properties of the functional groups of the organic chemicals will influence the surface acidity of the soil particles. This is important in the adsorption of ionizable organic molecules by the soil solids (clays).

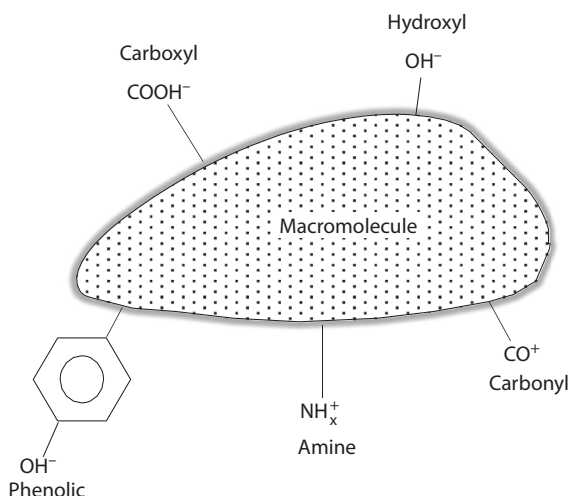
The mechanisms of interaction between organic chemicals and soil fractions include (a) London–van der Waals forces, (b) hydrophobic bonding, (c) charge transfer, (d) ligand and ion exchange, and (e) chemisorption. Sorption of organic chemicals is enhanced when there is no hydration layer (of water) on the surfaces of soil particles. Further sorption of other organic chemicals occurs through van der Waals type forces and hydrogen bond formation between functional groups such as the hydroxyl (OH^-) group on the soil particles and the carboxyl (COOH) group on the organic chemicals.

The *hydroxyl group* (OH^-) consists of a hydrogen atom and an oxygen atom bonded together. This group is by far the most common reactive surface functional group for soil fractions such as clay minerals, amorphous silicate minerals, metal oxides, and the other oxides (oxyhydroxides and hydroxides). The hydroxyl group is also present in two groups of organic chemicals:

1. Alcohols: Methyl, ethyl, isopropyl, and *n*-butyl. Alcohols can be considered as hydroxyl alkyl compounds (R-OH) and are neutral in reaction since the OH group does not ionize.
2. Phenols: Monohydric (aerosols) and polyhydric (obtained by oxidation of acclimated activated sludge (pyrocatechol, trihydroxybenzene).

The two other kinds of functional groups associated with organic chemical compounds (Figure 2.13), in addition to the hydroxyl (OH^-) group, are:

1. Functional groups having a C–O bond. These include the carboxyl, carbonyl, methoxyl, and ester groups. Compounds possessing the *carbonyl group*, called carbonyl compounds, include aldehydes, ketones, and carboxylic acids. The carboxyl group, which combines the carbonyl and hydroxyl groups into a single unit to form a new functional group, is the characteristic functional group of carboxylic acids, e.g., benzoic, acetic acids.

**FIGURE 2.13**

Some typical functional groups associated with organic chemicals. The macromolecule shown in the diagram is an organic chemical.

2. Nitrogen-bonding functional groups such as the amine and nitrile groups. The amino group NH_2 is found in primary amines. The amines may be aliphatic, aromatic, or mixed, depending on the nature of the functional groups, and are classified as:
 - a. Primary, e.g., methylamine (primary aliphatic); aniline (primary aromatic).
 - b. Secondary, e.g., dimethylamine (secondary aliphatic); diphenylamine (secondary aromatic).
 - c. Tertiary, e.g., trimethylamine.

Surface acidity is very important in the adsorption of ionizable organic molecules of clays. The chemical properties of the functional groups of the soil fractions contribute appreciably to the acidity of the soil particles. Surface acidity is an important factor in clay adsorption of amines, *s*-triazines, amides, and substituted urea. This is due to the protonation on the carbonyl group, as demonstrated by the hydroxyl groups in organic chemical compounds. As shown at the beginning of this section, there are two broad classes of these compounds: (1) alcohols (ethyl, methyl, isopropyl, etc.) and (2) phenols (monohydric and polyhydric). In addition, there are two types of compound functional groups: (1) a C–O bond (carboxyl, carbonyl, methoxyl, etc.) and nitrogen bonding (amine and nitrile). Amine, alcohol, and other organic chemicals that possess dominant carbonyl groups, which are positively charged by protonation can be readily sorbed by clays. In amines, for example, the NH_2 functional group of amines can protonate in soil, thereby replacing inorganic cations from the clay complex by ion exchange. The extent of sorption of these kinds of organic molecules depends on (a) the CEC of the clay minerals, (b) the composition of the clay soil (soil organics and amorphous materials present in the soil), (c) the amount of reactive surfaces, and (d) the molecular weight of the organic cations. Because they are longer and have higher molecular weights, large organic cations are adsorbed more strongly than inorganic cations. Polymeric hydroxyl cations are adsorbed in preference to monomeric

species because of the lower hydration energies and higher positive charges and stronger interactive electrostatic forces.

The unsymmetrically shared electrons in the double bond endow carbonyl compounds with dipole moments, thus allowing for hydrogen bonding between the OH⁻ group of the adsorbent (soil particles) and the carbonyl group of the ketone or through a water bridge. Sorption onto soil particles, especially clays, for the carbonyl group or organic acids (e.g., benzoic, acetic acids) occurs directly with the interlayer of cation or by the formation of hydrogen bonds with the water molecules (water bridging) coordinated to the exchangeable cation of the clay complex.

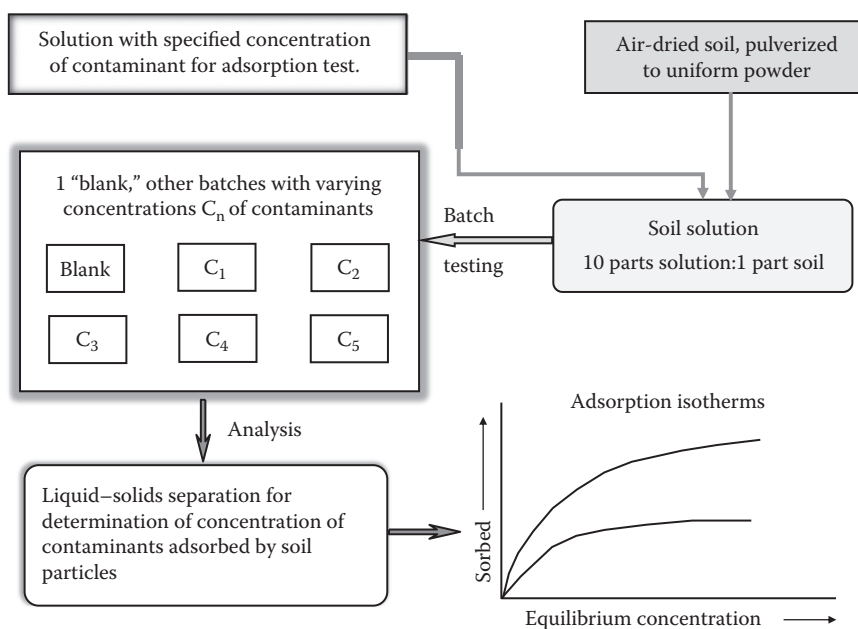
2.6.3 Partitioning of Contaminants and Partition Coefficients

Section 9.5 in Chapter 9 provides a more detailed discussion of contaminant partitioning in transport through a soil. The introduction to this subject in this section provides an overall appreciation of “what happens” when waste leachate streams enter the subsurface soil that constitutes the land environment. The *partitioning* of contaminants refers to the transfer of contaminants from the porewater in the soil to the soil solids by processes that include all of those described in Sections 2.6.1 and 2.6.2. It is important to determine the partitioning of target contaminants because this will tell us something about the distribution of contaminants, i.e., contaminants sorbed by the soil particles and contaminants remaining in the porewater. This can be interpreted in terms of the quantity or proportion of contaminants likely to move from one location to another. Determination of partitioning of inorganic contaminants is generally conducted using batch equilibrium tests. The conventional procedure shown in Figure 2.14 uses soil solutions. The candidate soil is used with an aqueous solution consisting of the contaminant of interest to form a soil solution. Figure 2.14 shows the various steps and analyses required. Results obtained from the tests and graphically plotted as shown in the diagram are called adsorption isotherms. Graphical representation of these results show sorbed concentration (of contaminants or contaminants) on the ordinate and equilibrium concentration of contaminants (contaminants) on the abscissa, as seen at the bottom right-hand part of Figure 2.14. The three common types of adsorption isotherms (Freundlich, Langmuir, and Constant) found in reported literature on sorption characteristics of inorganic contaminants are shown in Figure 2.15. The parameter k_n in the equations shown with the various curves denotes the slope of the curves.

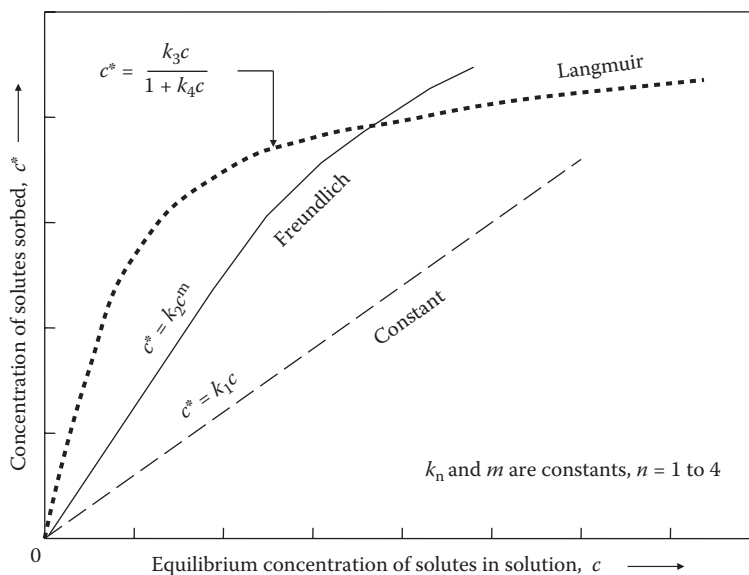
In the case of organic chemicals, partitioning is denoted by an *equilibrium partition coefficient* k_{ow} (i.e., coefficient describing the ratio of the concentration of a specific organic contaminant in other solvents to that in water). This coefficient k_{ow} , which relates the water solubility of an organic chemical with its *n*-octanol solubility is more correctly referred to as the *n*-octanol–water partition coefficient. It has also been found to be sufficiently correlated to soil sorption coefficients. The relationship for the *n*-octanol–water partition coefficient k_{ow} has been given in terms of the solubility S by Chiou et al. (1982) as

$$\log k_{ow} = 4.5 - 0.75 \log S \text{ (ppm)}.$$

Organic chemicals with $k_{ow} < 10$ are generally considered to be relatively hydrophilic. They tend to have high water solubilities and small soil adsorption coefficients. Organic chemicals with $k_{ow} > 10^4$ have low water solubilities and are considered to be very hydrophobic. The greater the hydrophobicity, the greater is its bioaccumulation potential (Section 9.5 in Chapter 9).

**FIGURE 2.14**

Batch equilibrium procedure for determination of adsorption isotherms. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

**FIGURE 2.15**

Freundlich, Langmuir, and Constant types of adsorption isotherms obtained from batch equilibrium tests. c , Concentration of solutes or contaminants; c^* , concentration of solutes or contaminants sorbed by soil fractions.

2.6.4 Predicting Contaminant Transport

There are many models that purport to describe the movement of contaminants, solutes, etc., in soil. For convenience in discussion, we will use the term *solutes* to mean contaminants and all other kinds of solutes found in the porewater. Most of the models deal with movement of solutes in saturated soils and is best applied to inorganic contaminants such as heavy metals. Application of the models for determination of transport of organic chemicals has been attempted by some researchers—with varying degrees of success. So long as the movement of the contaminants is governed by Fick's law, and instantaneous equilibrium sorption processes occur, some success in prediction of transport can be obtained. The ability to properly model partitioning of the contaminants remains as one of the central issue in determination of success or failure of predictions. The problem is complicated by the fact that a reasonably complete knowledge of the initial and boundary conditions is not always available. Additionally, the presence of multicomponent contaminants and their individual and collective reactions with the soil fractions will make partitioning determinations difficult. Detailed discussions of the modeling problems and the physicochemical interactions and partitioning of contaminants in soils can be found in textbooks dedicated to the study of contaminant fate and transport in soils, e.g., Knox et al. (1993), Fetter (1993), Huang et al. (1995a,b), Yong (2001), Yong and Mulligan (2004). The most common and widely used transport model has the relationship shown as:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\rho}{n\rho_w} \frac{\partial c^*}{\partial t} \quad (2.2)$$

where c is the concentration of solutes or contaminants, t is the time, D_L is the longitudinal dispersion coefficient, v is the advective velocity, x is the spatial coordinate, ρ is the bulk density of soil, ρ_w is the density of water, n is the porosity of soil, and c^* is the concentration of solutes or contaminants adsorbed by soil fractions (see Figure 2.15). If we assume a slope constant $k_d = k_1$ (as shown in Figure 2.15) for the constant adsorption isotherm, the concentration of solutes sorbed by the soil fractions c^* can be written as $c^* = k_d c$. The slope constant k_d is defined as the distribution coefficient and is meant to indicate the manner of distribution of the solutes being transported in the porewater of a soil–water system. Equation 2.2 can be written in a more compact form to take into account the distribution coefficient as follows:

$$R \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (2.3)$$

where R is the retardation factor, $\left[1 + \frac{\rho}{n\rho_w} k_d \right]$.

See Chapter 9 for a detailed discussion of the transport and fate of contaminants.

2.7 Geoenvironmental Land Management

The major geosphere and hydrosphere features that constitute the geoenvironment components for land management attention are shown in Figure 2.16. Land management, as

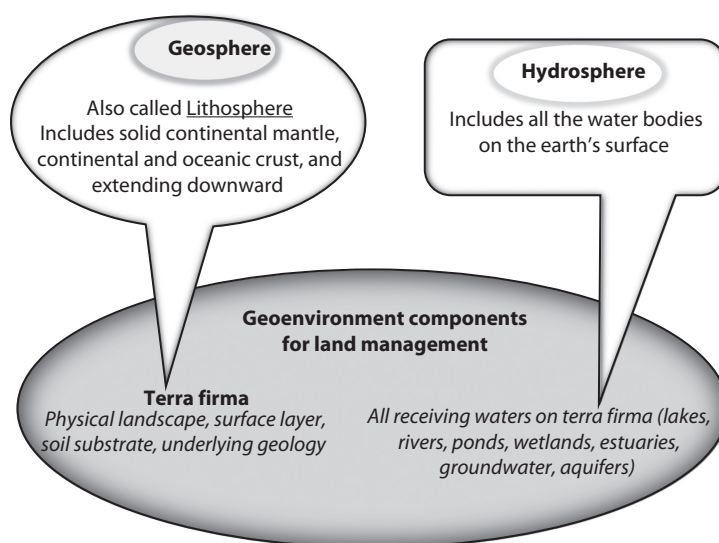


FIGURE 2.16

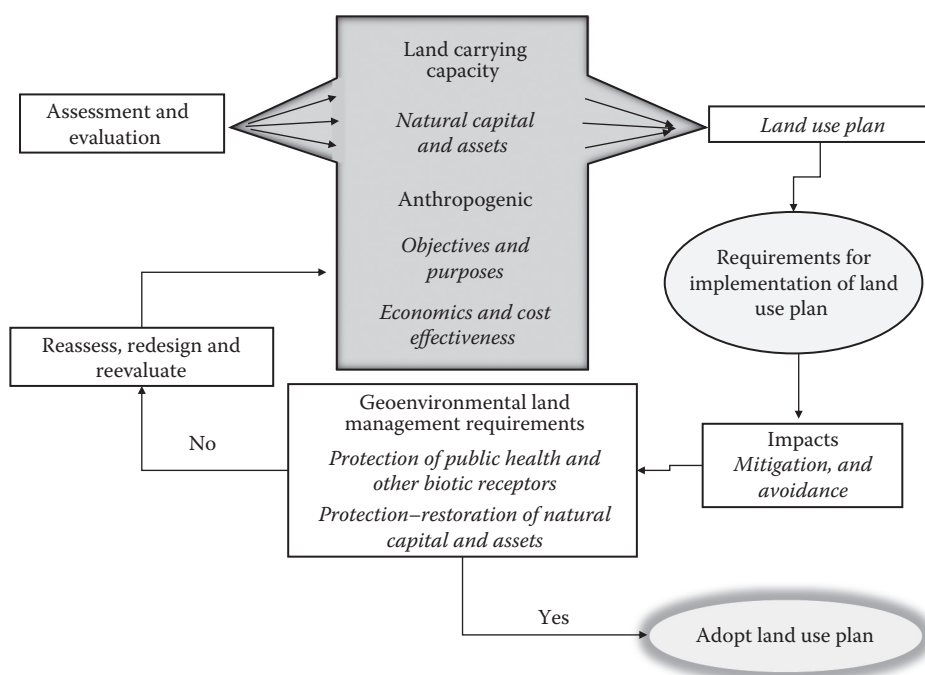
Geosphere and hydrosphere features included as geoenvironment components for land management.

the term implies, is the utilization of management practices to a land environment to meet a set of *land-use* objectives.

Because of the use of several common terms in the various geosciences and geoenvironmental communities, we will define the following terms as they relate to their use in *geoenvironmental land management*:

- *Land use*: The utilization of a land to fit a particular set of objectives or purposes. A simple example of such can be found in such usages as constructed facilities, farming, eco-parks, playing fields, forests, wetlands, etc. It is important to appreciate that land use should be considered within the bounds of proper environment and natural resource protection.
- *Land capability and functionality*: The performance capability and/or functionality of a and piece of land, i.e., what a land is capable of *doing* or what it can be used for. Land capability and functionality requires one to determine the natural capital of the land and to determine how these assets can be utilized. In the context of geoenvironmental sustainability, it follows that utilization of these assets must be consistent with the principles of sustainability.
- *Natural capital and assets*: This includes the physical attributes such as landforms and natural resources (including biodiversity). This grouping of properties is not only the most important but is perhaps the most difficult to fully delineate. Other than the obvious asset of a piece of land, e.g., mineral and hydrocarbon resources, what constitutes an asset, or a natural capital is to some extent dependent on the sets of criteria and guidelines developed for the particular problem at hand.

The manner in which a land is exploited is dictated by several factors and forces, not the least of which is *land capability*. Figure 2.17 gives an illustration of the procedure that might be used in land-use planning and implementation to satisfy geoenvironmental land

**FIGURE 2.17**

Example of procedure to be used to satisfy geoenvironmental land management issues in adoption and implementation of land-use plans.

management concerns. As with any project, the impacts to the geoenvironment must be evaluated, and procedures for avoidance and mitigation of these impacts need to be established. The end result of all of these must satisfy geoenvironmental land management requirements—i.e., they must ensure that there are no threats to public health and other biota—and that the natural capital and assets of the site are maintained. Reassessment and redesign are necessary if initial land-use plans do not satisfy geoenvironmental impact concerns. The key elements that must be satisfied are preservation of natural capital and assets.

2.8 Concluding Remarks

We have focused on contamination of the land environment as one of the key issues in protection of the natural capital and assets of the land environment.

- Geoenvironmental land management requires practise of the principles of sustainability.
- Insofar as the land environment is concerned, environmental impacts associated with anthropogenic activities can be in the form of changes in the quantity, quality, and renewal ability of the natural resources or capital items of the various features that constitute the land environment.

- Not all anthropogenic activities will result in adverse impacts on the environment.
- The degree of environmental impact due to contaminants in a contaminated ground site is dependent on (a) the nature and distribution of the contaminants, (b) the various physical, geological, and environmental features of the site, and (c) existent land use.
- Each type of land use imposes different demands and requirements from the land. The ideal situation in land utilization matches land suitability with land development consistent with environmental sensitivity and sustainability requirements.
- Groundwater is an integral part of land-use considerations.
- Causes and sources of groundwater contamination include wastewater discharges, injection wells, leachates from landfills and surface stockpiles, open dumps and illegal dumping, underground storage tanks, pipelines, irrigation practices, production wells, use of pesticides and herbicides, urban runoff, mining activities, etc.
- To evaluate and determine the nature of geoenvironmental impacts created by the presence of contaminants in the geoenvironment, one needs to have an appreciation of the nature of the contaminants and associated events that are responsible for the impacts. The various activities associated with the production of goods and services generate waste streams and products. In most instances, these waste streams and products find their way into the land environment, either inadvertently as in the case of runoffs and spills or by design, i.e., failure of constructed safe land disposal facilities.

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3

Sustainable Water Management

3.1 Introduction

As pointed out in the previous chapter, water is one of the essential ecosystem components for survival of all living species. The water component of the geoenvironment includes all rivers, lakes, ponds, inlets, wetlands, estuaries, coastal water, groundwater, and aquifers. These contribute as inputs to the oceans that make up 70% of the earth's surface water. Water is required for many needs such as drinking, agriculture, cooking, domestic and industrial uses, transportation, recreation, electrical power generation, and support for aquatic life and other wildlife. Among the many underlying reasons for increasing water shortages are (a) demand in excess of supply, (b) depletion of aquifers, (c) lack of rain and other forms of precipitation, (d) watershed and water resources mismanagement, and (e) diversion of rivers. It is noted that irrigation requirements for agriculture are increasing. Estimates indicate that more than 70% of the world's freshwater is utilized for agricultural purposes (Postel, 1999).

The importance of water has been highlighted in the Johannesburg World Summit on Sustainable Development (WSSD, 2002). "Water and Sanitation" was identified as one of their five thematic areas at WSSD 2002. The quality of water can be, and is, significantly impacted by all the other four thematic areas defined by the WSSD (2002); "Sustenance and Development," "Industrialization," "Urbanization," and "Resource Exploitation and Agriculture." Adequate quantities of good quality water are also essential for health, agriculture, energy, and biodiversity. Lack of water and poverty are intimately linked. The discussion in this chapter will focus on the uses (and misuse) of water in the geoenvironment. It will also examine some of the main elements required to address, contain, and manage stressor impacts to water quality as a step toward water management for sustainability of water resources.

3.1.1 Geoenvironment Sustainable Water Management

Sustainable water management can be defined in a similar manner to the definition for *sustainable development* articulated in Section 1.3 in Chapter 1. Accordingly, we can define sustainable water management as all the activities associated with usage of water in support of human needs and aspirations, which must not compromise or reduce the chances of future generations to exploit the same resource base to obtain similar or greater levels of yield. In the context of the geoenvironment, with particular focus on geoenvironmental engineering, we limit ourselves to the receiving waters in the geoenvironment, i.e., all water forms contained within the land surface, such as rivers, lakes, ponds, and groundwater (aquifer and soil porewater).

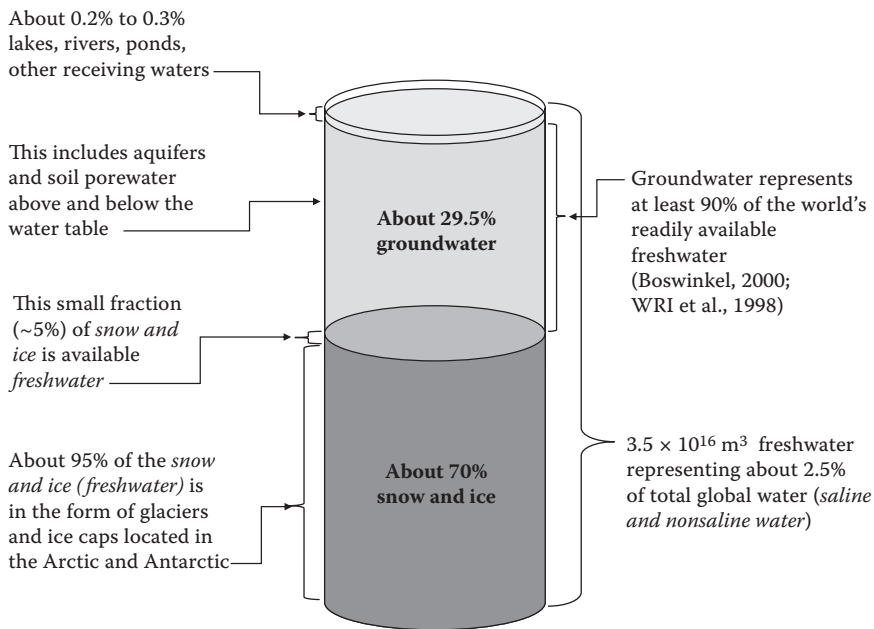


FIGURE 3.1
Sketch of distribution of global freshwater.

3.1.1.1 Water Availability and Quality

Water availability and water quality are central issues in survivability of living species—humans, animals, plants, etc. Lack of water and unacceptable water quality are significant threats to survivability. Water availability or the lack thereof is a topic that is well covered in textbooks devoted to such a subject. The problem of threats to the quality of water in the geoenvironment constitutes the central focus of discussions in this book. It has been said previously, in Chapter 2, that soil contamination does not only mean contamination of the soil solids themselves, but also contamination of the porewater, with possible extension to groundwater and the aquifers through transport of contaminants in the subsoil. Chemical stressors producing point source and non-point source contaminants (to be discussed in the succeeding chapters) will contaminate not only soils but the receiving waters. The importance in protection of available freshwater, and especially groundwater, is demonstrated in Figure 3.1, which highlights the degree of utilization of this resource by the world's population.

3.2 Uses of Water and Its Importance

Safe and adequate amounts of water are essential. The first Dublin-Rio principle has emphasized the need for sustainable water resource practices. It states that “fresh water is a finite and vulnerable resource, essential to sustain *life, development, and the environment*”

(ICWE, 1992). In other words, water is essential for these three categories. Note that the use of the term *environment* is meant to include the life-supporting functions of ecosystems, as discussed in Chapter 1.

3.2.1 Hydrological Cycle

Although it is convenient to think in terms of essentially two primary sources of drinking water—surface water and groundwater (aquifer and soil porewater)—it is more useful to bear in mind the total hydrological cycle when one wishes to consider (a) the need for water for life-support systems and (b) the impact of mankind on the sources of water. The hydrological cycle reflects the constant or continuous movement of water within the earth, on the earth, and in the atmosphere, as shown in Figure 3.2.

Beginning with the ocean and other surface water bodies—such as rivers, ponds, and lakes—together with open land surfaces, we can identify these processes as (a) evaporation and condensation, (b) evapotranspiration, (c) precipitation, (d) infiltration (percolation) from ground surface into subsurface, (e) groundwater (subsurface water) discharge into land receiving waters and oceans, (f) discharge from rivers, and (g) surface runoff. It is necessary to note that the terms *infiltration* and *percolation* are quite often used to mean the same event, i.e., entry of water into the ground surface from water on the surface, either from precipitation or from ponded water, or other similar sources. Direct anthropogenic interference in the natural hydrological cycle occurs most often in processes such as infiltration and runoff, for example, in the quality of the water that infiltrates into the ground and also the quality of the runoff that enters the receiving waters.

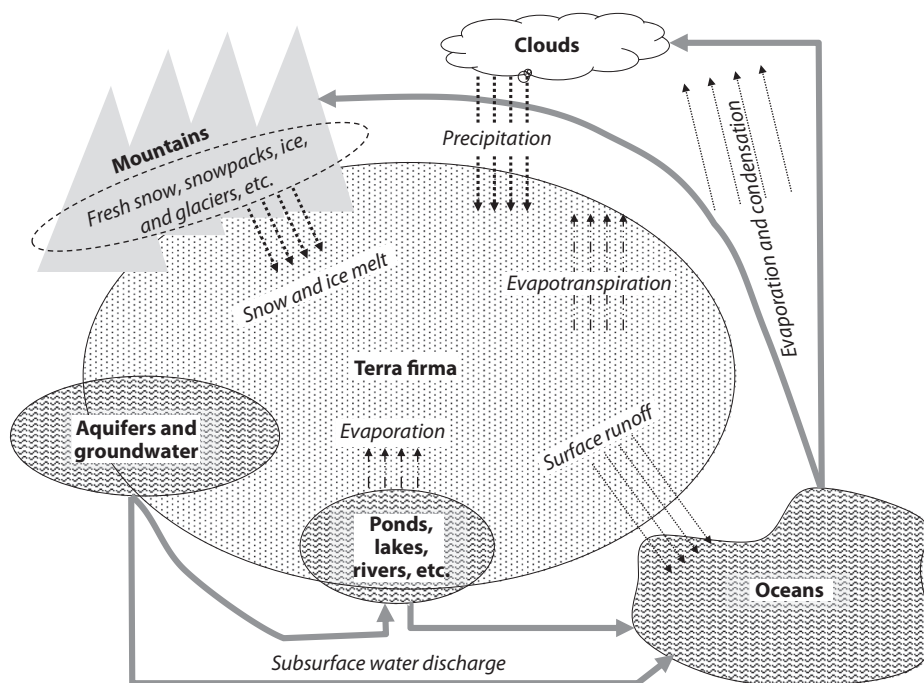


FIGURE 3.2

Sketch of basic elements and processes in the hydrological cycle. Percolation from surface into subsurface is not shown in the sketch.

3.2.1.1 Human Interference on Infiltration and Runoff

Human interference in the hydrological cycle is most significant in the processes of infiltration and runoff. The form of some of the major interferences on infiltration and their impacts, some of which are shown in Figure 1.5 in Chapter 1, are as follows:

- Development, production, and construction of impermeable surface areas: These impermeable surfaces include housing and similar structures, roads and pavements, runways and aprons, parking lots, and other generally paved surfaces constructed in the urban environment. The effect of these impermeable surfaces is to deny infiltration into the ground, hence denying recharge of any underlying aquifer. Runoffs obtained on the impermeable surfaces are generally fed to storm drains or other similar drainage discharge systems.
- Compacted surface layers: These are surfaces of natural soil compacted by agricultural and construction machinery and other similar devices. The effect of compacted surface layers is to reduce infiltration rate and infiltration capability in general. Surface runoff occurs when the rate of precipitation onto the surface is greater than the infiltration rate. Unlike the paved impermeable surfaces, these runoffs are not generally fed to storm drains or other catchment facilities.
- Soil porewater and aquifer contamination by infiltration: The term *soil porewater* is used to mean the water in the pores of the soil matrix. Normally, in compact clay soils, this porewater is not easily or readily extractable. However, in more granular materials such as silts and sands, this porewater can be harvested. Aquifers in general are seams or layers of primarily granular materials that are full of water. We use the term *groundwater* to mean both soil porewater (above and below the water table) and water in the aquifers, but mainly to denote water in the ground that is normally considered as a water resource. When it is necessary to talk about soil porewater, the term *porewater* is generally used. Contaminants on the land surfaces will be transported into the subsoil via infiltration and other transport mechanisms such as dispersion and diffusion. Pesticides, herbicides, insecticides, organic and animal wastes, ground spills, other deliberate and inadvertent discharges of hazardous and noxious substances on surfaces, etc., serve as candidates for transport into the subsoil. Contamination of groundwater will occur when communication between the contaminants and these water bodies is established, i.e., when the contaminated infiltration plume reaches the groundwater, meaning that contamination of groundwater occurs the moment contaminants reach soils containing porewater. The result is impairment of groundwater quality. Ingestion of polluted groundwater can be detrimental to human health.

As with infiltration processes, surface runoffs can occur on natural ground surfaces devoid of much human contact. This occurs when rainfall rate exceeds infiltration rate, and when natural surface cover (vegetation, plants, etc.) is so dense that it acts as a shield or umbrella. As we have seen from the preceding, natural infiltration properties of soils can be severely compromised by human activities resulting in runoffs. There are at least two types of runoffs: (1) managed runoffs where the runoffs are channeled into drains and sewers and (2) unmanaged runoffs where the runoffs take directions controlled by surface topography and permeability properties of the surface cover material. In both cases, the

runoffs will end up in receiving waters—lakes, rivers, oceans, etc. In the case of managed runoffs, there are at least two options for the runoffs before they meet the receiving waters: (1) treatment (full or partial) of the runoff water and (2) no treatment before discharge into receiving waters. The result of untreated runoffs into receiving waters is obvious—degradation of the quality of the receiving waters. When such occurs, the receiving waters will require treatment to reach drinking water quality standards. A point can be reached where the accumulated contaminants will be at a level where treatment of the degraded receiving water will not be effective—not from an economic standpoint and not from a regulatory point of view.

The combination of infiltration, and runoffs as potential carriers of contaminants into the ground and receiving waters (including groundwater) is a prospect that should alert one to the need for proper management of the sources of contamination of water resources. Treatment of water to achieve levels of quality dictated by drinking water standards is only one means for water resource management. The other has to be directed toward eliminating or mitigating the sources of contamination of water resources.

3.2.2 Harvesting of Groundwater

We have seen in Chapter 1, and in Figures 1.9 and 3.1, that only about 5% of the water in the world is freshwater. The rest is seawater. This tells us that our drinkable freshwater resource is severely limited. The graphic in Figure 3.1 informs one that although groundwater represents about 30% of the available freshwater, at least 90% of the world's population rely on this as a source of freshwater (Boswinkel, 2000; WRI et al., 1998). Infiltration and runoffs carrying contaminants serve as chemical stressors whose impacts on the solid land environment are both *soil contamination* and *contamination of groundwater*. The subject of soil contamination has been discussed in Chapter 2, and the processes and geoenvironmental engineering practices for mitigation and remediation of contaminated soils will be discussed in Chapters 9 through 11. Groundwater abstraction for drinking water purposes will require treatment aids. Since reliance on groundwater as a drinking water source is considerable, it is clear that maintaining acceptable groundwater quality is a high priority not only because of the need for treatment after abstraction, but also because once the aquifer is contaminated, clean-up of the aquifer to acceptable standards is almost impossible. When aquifers become contaminated, one key element for aquifer sustainability is lost. In effect, sustainability of that aquifer as a water resource is lost.

Depletion of aquifers is also another sustainability loss that requires attention. Depletion occurs when the rainfall is insufficient and/or aquifer recharge is exceedingly slow, i.e., input or replenishment of the aquifer is less than the output. Continued water use from that aquifer is thus not sustainable. This is occurring with more frequency as water use has increased by a factor of 6 since the beginning of the twentieth century. The amount of groundwater abstraction is estimated to be between 950 and 1000 in 2000 km³/year, representing about 25% of global water use, which increased from 100 to 150 km³/year in 1950—(Howard, 2004). According to the UN, an increase in the world's population of 80 million people per year increases freshwater demand by 64 billion m³/year (WWDR, 2012). The Ogallala aquifer in central United States was used at 140% above its recharge rate (Gleick, 1993), but since 1985, water table levels have stabilized and in some cases have risen through better water management (High Plains Underground Water Conservation District, 2014).

Freshwater is depleting rapidly in countries such as India, China, and even in the United States, rivers are drying up and water table levels are decreasing. In China, there is a lack

of water in more than 300 cities (WRI, 1994). It was estimated in the *Global Environment Outlook 3* report by the United Nations Environment Program (UNEP, 2002) that about half of the world's population will not have sufficient water by the year 2032. This would be the result of the currently unsustainable practices that are currently using about 50% of the earth's freshwater supply (UN-FPA, 2001). What will happen to the ecosphere and to human life when the population reaches 9 billion by 2100 (UNDP, 2001)? Even now, dehydration is occurring in many areas to the extent that this will affect biodiversity and increase the requirements for agricultural irrigation.

Per hectare of land, 10 million liters of water each season is required for production of 8000 kg of corn (Pimentel et al., 1996). Water use for irrigation has decreased due to improved agricultural practices. Treatment of groundwater as a scarce resource may be required. Water markets have been proposed (Dorf, 2001) as a means of valuing water as a resource. Conservation by farmers, and urban users will increase as the price of water increases.

3.2.2.1 Excessive Groundwater Abstraction and Land Subsidence

In regions where the underlying geology consists of interlayering of soft aquitards and aquifers, excessive groundwater abstraction from the interlayered aquifers can cause subsidence of the ground surface. A good case in point is the Quaternary sediments that underlie many coastal cities such as Shanghai, Bangkok, and Jakarta. In Bangkok, the capital of Thailand, for example, the city is situated on a low-lying, flat deltaic plain known as the Lower Central Plain (known also as the Lower Chao Phraya Basin)—about 30 km north of the Gulf of Thailand. The basement bedrock gently inclines southward toward the Gulf of Thailand, and the strata overlying the basement bedrock consists of a complex mix of unconsolidated and semiconsolidated sediments of the Tertiary to Quaternary geological age. The thickness of the strata ranges from about 400 m in the north to more than 1800 m in the south, with a stratigraphic profile that shows five discernible separate aquifers layers separated by unconsolidated and semiconsolidated sediments, all of which are overlain by a stiff surface clay layer. Excessive long-term groundwater abstraction has resulted in subsidence in the region. This causes severe flooding of the region. Yong et al. (1991) reported that with the drainage system existent at that time, extensive flooding lasting for periods of 6 to 24 hours occurs with rainfall exceeding 60 mm.

For coastal cities in similar situations, land subsidence due to prolonged excessive groundwater abstraction can reach the stage where the land surface will reach levels below sea level. When such occurs, unless containment dikes are built, seawater intrusion causing local flooding and contamination of the aquifers can occur. The impacts to human health in respect to contaminated water, in addition to physical problems associated with flooding can be severe. Buildings and other structures have been known to suffer considerable structural distress due to uneven settlement of footings and foundations. By some accounts, delivery of potable water from a central source located in a "safe" region is required when flood waters compromise the existent drinking water sources.

3.2.2.2 Uses of Water

By all indications, if sustainable water usage is to be obtained, water treatment and reuse will need to increase and demand will need to decrease. Decreased water quality through contamination decreases the amount of available water. In the industrialized

world, although water quality is in general good, water use is increasing. Many cities lose up to 40% of their water through leaking sewer and distribution systems (United Nations Economic Commission for Europe, 1998; Bertram et al., 2002). In developing countries, water is both scarce and unhealthy due to rapid urbanization. Water management practices must be improved to reduce scarcities and impacts on ecosystems. Factors affecting leakage include system age, main type and pressure, soil type, climate and topography, and local value of water. A program by the water regulator in England and Wales reduced water leakage from 29% to 22% between 1992/1993 and 2000/2001.

Water can also be used as geothermal energy. The sites are mainly in volcanic and seismic regions. Countries such as Iceland, Spain, France, Hungary, Japan, Mexico, Russia, and the United States (in the states of California and Hawaii) are exploiting this form of energy (Chamley, 2003). Iceland uses this form of energy for domestic heating, greenhouse cultivation, and electricity production. Exploitation can be from the steam of geysers or very hot liquids of 100°C or more. Cooled water can then be reinjected for reheating and reuse. Geothermal systems can also be utilized where groundwater at a depth of 100 m is about 15°C. This is warm enough to heat buildings in the winter using a heat pump principle. There are some hurdles that need to be overcome in exploiting geothermal energy. These include (a) transportation of warm water over long distances without major loss of heat, and (b) induced earthquakes. The advantages in the use of geothermal energy include (a) negligible amounts of contamination produced, (b) little or negligible production of greenhouse gases, and (c) almost no waste production.

As water serves many purposes, these demands can be highly competitive. Agriculture is an intensive user and thus water use must be more efficient per crop grown. Since ecosystems can be depleted for human water use, public awareness of these links is necessary if conservation and sustainability goals are to be achieved. In parallel with WSSD (2002), the *WaterDome*, which was organized by the African Water Task Force (AWTF) highlighted the importance of water and sustainable development—an imperative that was not really addressed in the Summit in Rio in 1992. They addressed the link of poverty with lack of water and sanitation, and the importance of hydroelectric dams as a means of electricity generation.

3.3 Water Quality Characterization and Management

3.3.1 Classes of Contaminants Characterizing Chemical Stressors

Organic contaminants in water will deplete oxygen required for fish and other water organisms. These contaminants generally originate from the discharge of domestic and industrial wastewaters into water bodies. Increases in population density near these water bodies generally result in corresponding increases in the levels of organic matter in the water. High levels of biological oxygen demand (BOD) or chemical oxygen demand (COD) deplete the oxygen in the water through microbial degradation of the organic matter. This depletion of oxygen can lead to severe effects on aquatic biota. Color, taste, and odor of the drinking water may also be affected.

Farming and agricultural activities have added contaminant sources such as insecticides, pesticides, fungicides, and fertilizers. It has been estimated that 38% of the agricultural land cultivated in the world has been damaged by agricultural practices by aspects

including salting, waterlogging, compaction and loss of soil structure, contamination by pesticides, decreased fertility, and erosion (Gliessman, 1998). Herbicides and pesticides are (a) persistent in the environment, (b) highly mobile, and (c) can accumulate in the tissues of animals, producing a variety of ill effects. Data on their concentrations in groundwater are quite limited. So as not to appear prejudicial, all of these contaminant sources will be identified as a group under the term *agro-additives*. These agro-additives find their way into the receiving waters and groundwater through surface runoff and through transport in the ground. Nutrients such as nitrates from animal wastes from poultry or pigs are other sources of groundwater contaminants (Figure 3.3). Agricultural contaminants are typically difficult to monitor and estimate due to their dispersion and seepage through soils into the groundwater.

High levels of nutrients (nitrogen and phosphorus) from fertilizers, detergents, and other sources can reach surface waters and lead to eutrophication and excessive algal growth. Nitrogen, in particular, and, to a lesser degree, phosphorus demand in fertilizers have grown significantly in the last fifty years (USGS, 1998). Eutrophication causes oxygen depletion in the water and production of bad odors, tastes, and colors. Nitrogen, in particular, originates from fertilizer and manure addition to the soil. Although nitrates have an important role within the nitrogen cycle, overapplication of manure and fertilizers impact negatively on plant and microorganism biodiversity. Although ammonium ions adsorb onto clay particles, nitrate compounds are easily transported. Movement of nitrates in groundwater depends on aquifer hydraulic conductivity, soil type and moisture, temperature, vegetation, and amount of precipitation. Shallow unconfined aquifers have been

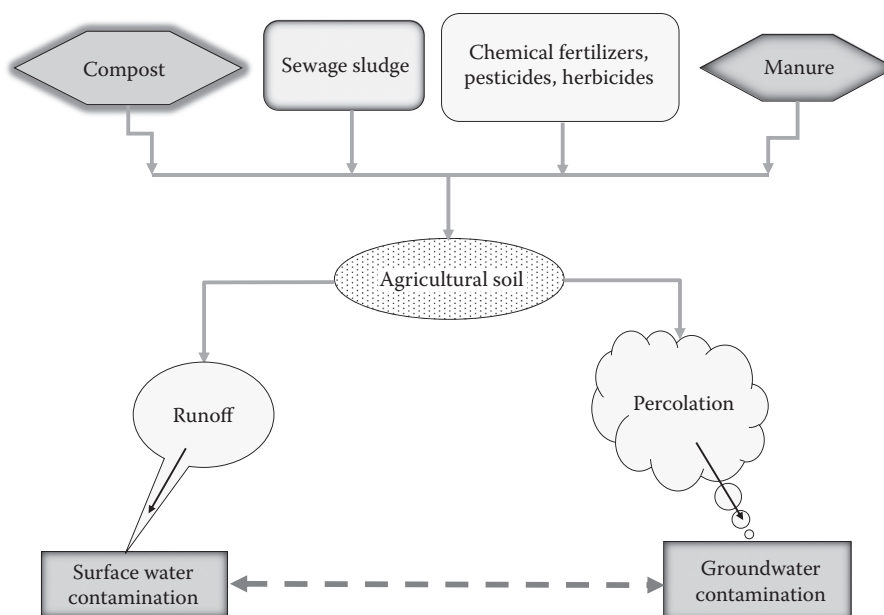


FIGURE 3.3

Contaminant sources (stressors) for surface and groundwater contamination from agricultural soil. The dashed line between groundwater and surface water contamination indicates potential contamination of groundwater from surface water or surface water contamination from groundwater.

found to be highly susceptible to nitrate contamination from agricultural sources (Burkart and Stoner, 2002).

Another major class of contaminants is microorganisms from agricultural runoff, and septic and sewage systems. Microorganisms contribute turbidity, odors, and elevated levels of oxygen demand. Drinking contaminated water can lead to severe gastrointestinal illnesses and even death. The case of Walkerton, Ontario, a small town 200 km northwest of Toronto, is an example of this. In May 2000, heavy rain washed manure into swampy land, which subsequently contaminated drinking well water. More than 2300 people became ill and 7 died as a result of drinking the contaminated well water. This is discussed further in Chapter 9.

Numerous organic compounds are potentially mutagenic and carcinogenic to humans, animals and plants. We have previously seen from Figures 1.4 and 1.5 in Chapter 1 how industrial, agricultural, and urban discharges can contaminate aquifers and surface waters. As indicated previously, the sources of these contaminants can be traced to waste streams and discharges from industrial plants, households, resource exploitation facilities, and from farms. Oil spills, are a major cause of devastation to marine and land ecosystems. Some examples of contaminant groups include pesticides and herbicides such as dichlorodiphenyltrichloroethane (DDT), aldrin, chlordane, diazinon and parathion, volatile organic compounds (VOCs) such as vinyl chloride, carbon tetrachloride and trichloroethylene (TCE), and heavy metals (e.g., chromium, cobalt, copper, iron, mercury, molybdenum, strontium, vanadium, zinc). VOCs enter the water systems as industrial and municipal discharges. Owing to their higher volatility, they are less persistent than herbicides and pesticides. Metals originate from industrial processing, runoff from mining operations and atmospheric disposition from incinerator emissions and other processes.

All the other sources of contaminants shown—i.e., discharges and waste streams—are most likely contained in storage dumps, landfills, holding ponds, tailings ponds, or other similar systems. All of these containment systems have the potential to deliver contaminants to the receiving waters (groundwater and surface waters) because of eventual leaks, discharges, and failures. Some of these will be discussed in detail in Chapter 5.

In urban regions, leakage of sewers and other wastewater sources can significantly contribute to recharge and contamination of aquifers. It was estimated in 2013 that more than 985 million m³/year of wastewater (2.6 trillion gal/year) was lost due to broken sewers in the United States (Uni-Bell PVC Pipe Association, 2011). Aquifers under cities can be highly polluted, making them unsuitable for drinking water. This is particularly significant in regions where (a) wastewater is untreated; (b) source contaminants such nitrates, ammonia, fecal coliforms, and dissolved organic carbon abound; and (c) urbanization is rapid and essentially uncontrolled.

Contamination of the surface waters and groundwater can occur as a result of industrial or municipal discharges or runoff from agricultural land, mining operations, or construction. Industrial contaminants in the groundwater such as benzene, toluene, xylene, and petroleum products originate from (a) leakage of underground storage tanks, (b) chemical spills, and (c) discharges of organic chemicals and heavy metals such as cadmium, zinc, mercury, and chromium. The numbers of affected sites in the United States have been reported to be at least 5 or more orders of magnitude (Gleick, 1993). Runoff and seepage from mining operations can contribute significant levels of heavy metals, for example, in the illustration shown in Figure 3.4 of runoff of iron from a coal mine.

**FIGURE 3.4**

(See color insert.) Iron runoff from a coal mine into canal area.

Natural sources of contaminants can also contribute to the contamination of groundwater. Salt water intrusion from coastal aquifers can also degrade groundwater quality by transporting salt into the groundwater (Melloul and Goldenberg, 1997). The arsenic contaminated aquifers in West Bengal and Bangladesh discussed previously in Section 2.2.4 in Chapter 2 provide good examples of a combined “man-and-nature” impact on the geoenvironment. Since these aquifers provide potable water for the majority of the population of Bangladesh and some significant proportion of population in West Bengal, it has been estimated that from 35 to 50 million people are at risk of arsenic poisoning. Often referred to as the singular most dramatic case of mass poisoning of the human race, the arsenic polluted aquifers serving the tube wells in the two countries contain arsenic concentrations far in excess of the prescribed limits of the WHO. Worldwide, in 2007, it was estimated that more than 137 million people in over 70 countries including the United States are affected by arsenic in drinking water (Smedley and Kinniburgh, 2002).

In the United States, a survey showed that more than 36% of the surface water does not meet water quality objectives (U.S. Environmental Protection Agency [USEPA], 1996). More recently, in the *National Water Quality Inventory: Report to Congress* for the 2004 Reporting Cycle (USEPA, 2009), U.S. states reported that of the assessed stream miles, lake acres, and bay and estuarine square miles about 44%, 64%, and 30%, respectively, were impacted sufficiently that would not allow uses such as fishing and swimming. The most common types of impairment of lakes shown in Figure 3.5 include pathogens, mercury, nutrients, and organic enrichment/low dissolved oxygen from atmospheric deposition, agriculture, hydrological modifications, and unknown or unspecified sources. Increasing population and economic growth are contributing to this problem. Major sources of contaminants are the agricultural industry and urban runoff from storm sewers. Although problematic in some locations, the presence of pesticides and fertilizers is currently not a huge concern. There is not a large amount of data concerning groundwater quality in the United States.

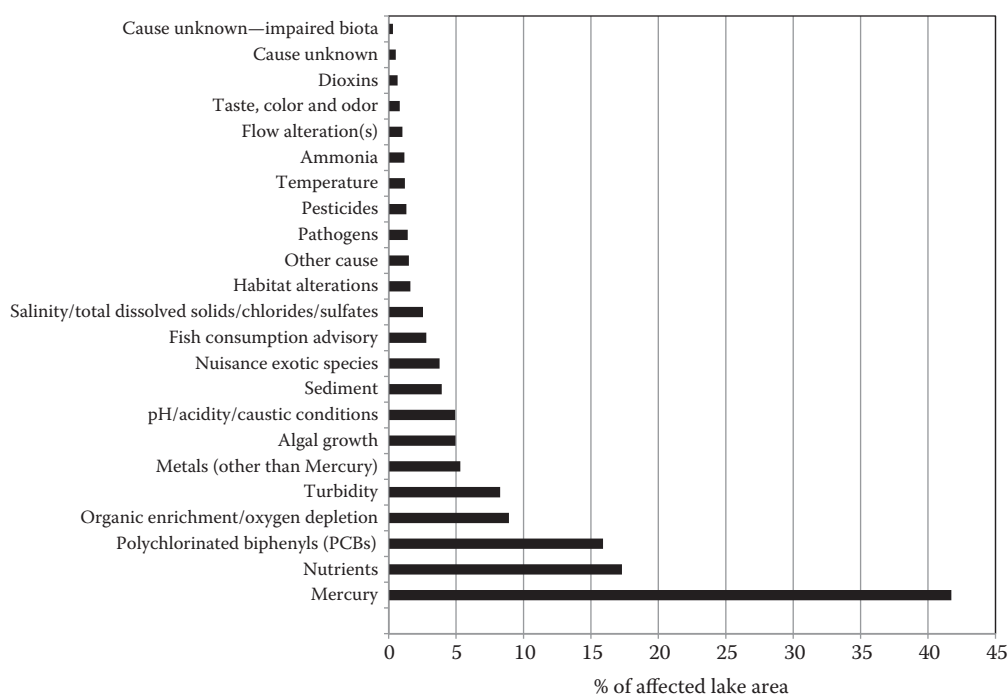


FIGURE 3.5

Percentage of lakes contaminated by various components. (Data from USEPA, *National Summary of Impaired Waters and TMDL Information*, http://ofmpub.epa.gov/waters10/attains_index.control, 2014.)

3.3.2 Monitoring of Water Quality

In industrialized countries, concern over the quality of waters in rivers has resulted in a considerable amount of public funds being invested in water quality monitoring during the last decade. Accordingly, monitoring of chemical contaminants in the environmental matrices has entered a new phase. Modifications in instrumentation, sampling, and sample preparation techniques have become essential in keeping pace with the requirements for (a) achieving low detection levels, (b) high speed analysis capability, and (c) convenience and cost efficiency.

Environmental indicators such as water quality can be used as indicators of sustainability. The term *monitoring* is used in many different ways. In the context of monitoring of a particular site to determine whether the events expected to occur in the site have indeed transpired, *monitoring* means the gathering of all pertinent pieces of information providing evidence that those events had occurred. We interpret from the definition of monitoring in the previous chapter to mean a program of sampling, testing, and evaluation of status of the situation being monitored. In the situation being monitored, a *management zone* needs to be established, as shown, for example, in Figure 3.6. To determine whether attenuation of contaminants in a contaminated site has been effective, it is necessary to obtain information pertaining to the nature, concentrations, toxicity, characteristics, and properties of the contaminants in the attenuation zone. The contaminants have residence in both the porewater (or groundwater) and on the surfaces of the soil solids, i.e., attached to the soil solids' surfaces. Residence (of the contaminants) associated with the soil solids

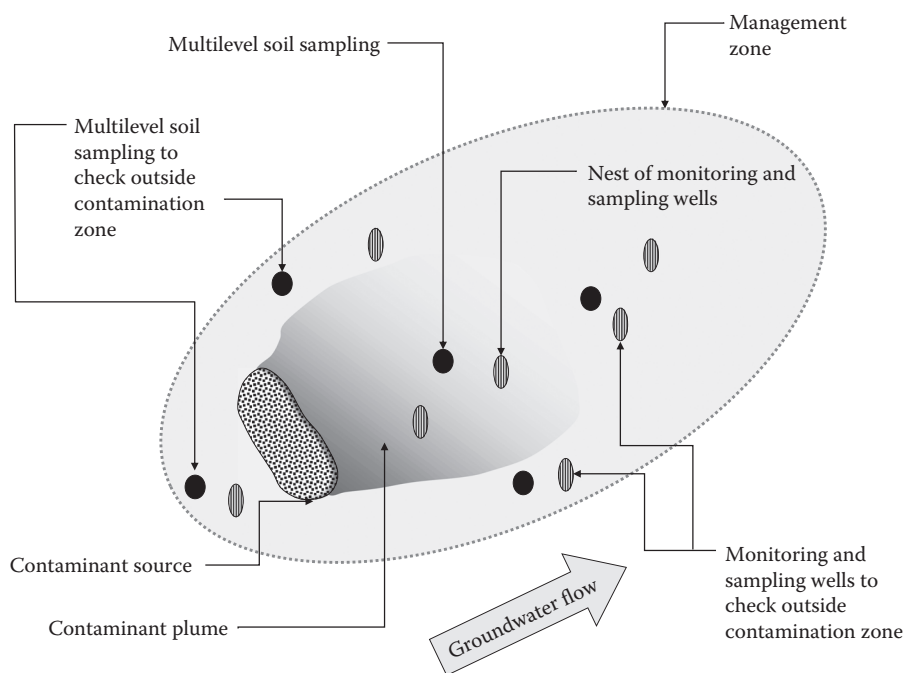


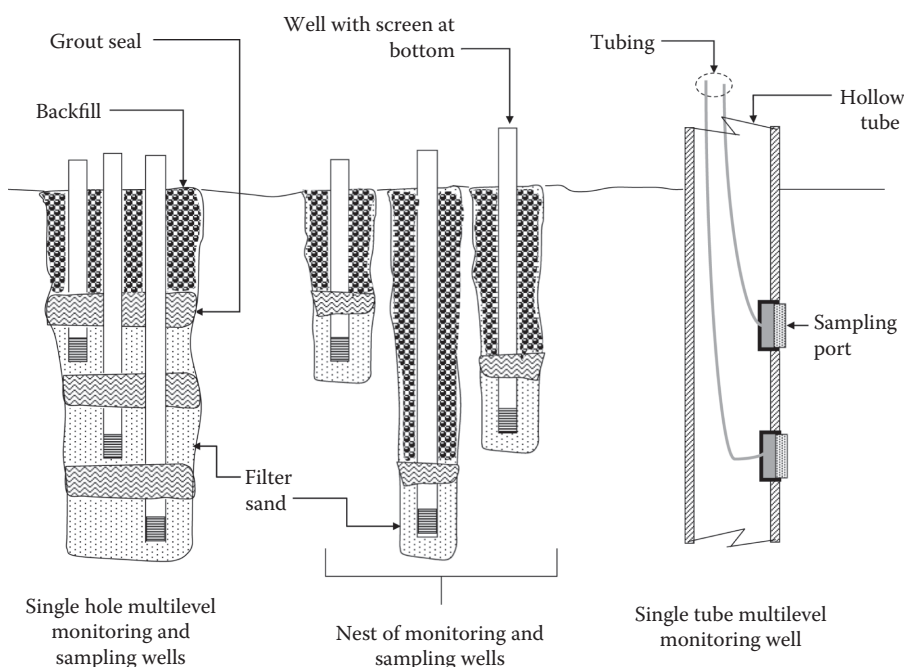
FIGURE 3.6

Plan view of distribution of monitoring wells and soil sampling boreholes for verification monitoring and long-term conformance monitoring. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

can take the form of sorbates and co-precipitates. In turn, the sorbates can be complexed with the soil solids and will remain totally fixed within the structure of the soil solids. However, the sorbates can also be held by ionic forces, which can be easily disrupted, thus releasing the sorbates.

What the preceding discussion of residence status of the contaminants tells us is that we need to monitor and sample not only the porewater or groundwater but also the soil fractions in the contaminant attenuation zone. Two types of monitoring–sampling systems are needed. For porewater or groundwater, monitoring wells are generally used. These wells are necessary to provide access to groundwater at various locations (vertically and spatially) in a chosen location. The choice of type of monitoring wells and distribution or location of wells will depend on the purpose for the wells. In respect to determination of whether natural attenuation can be used as a treatment process, there are at least three separate and distinct monitoring schemes that need to be considered. These range from the initial site characterization studies to verification monitoring and long-term conformance monitoring.

The term *monitoring scheme* is used deliberately to indicate the use of monitoring and sampling devices to obtain both soil and water samples. Figure 3.7 shows some typical devices used as monitoring wells to permit monitoring groundwater at various levels. In the left-hand group, we see individual monitoring wells with sampling ports located at different depths but grouped together in a shared borehole. This is generally identified as a single borehole multilevel monitoring well system. The middle drawing shows a nest of single monitoring wells in their own separate boreholes, and the right-hand drawing

**FIGURE 3.7**

Some typical groundwater monitoring and sampling wells. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

shows a single tube system with monitoring portholes located at the desired depths. With present technological capabilities, monitoring wells and the manner of operation have reached levels of sophistication where downhole sample analysis of groundwater can be performed without the need for recovery of water samples.

Site characterization monitoring is necessary to provide information on the hydrogeology of the site. It is necessary to properly characterize subsurface flow to fully delineate or anticipate the transport direction and extent of the contaminant plume. Determination of the direction and magnitude of groundwater flow is most important. Obviously this means a judicious distribution of monitoring wells up- and down-gradient. Proper locating of monitoring wells and analysis of the results should provide one with knowledge of the source of the contaminants and the characteristics of the contaminant plume.

Verification monitoring requires placement of monitoring wells and soil sampling devices within the heart of the contaminant plume and also at positions beyond the plume. Figures 3.6 and 3.8 show the vertical and plane views of how the wells and sampling stations might be distributed. It is a truism to state that the more monitoring and sampling devices there are, the better one is able to properly characterize the nature of the contaminant plume, assuming that the monitoring wells and sampling devices are properly located. The monitoring wells and sampling devices placed outside the contaminant plume, shown in Figure 3.6, will also serve as monitoring wells and sampling devices for long-term conformance assessment.

The tests required of samples retrieved from monitoring wells are designed to determine the nature of the contaminants in the pore or groundwater. These will inform one about

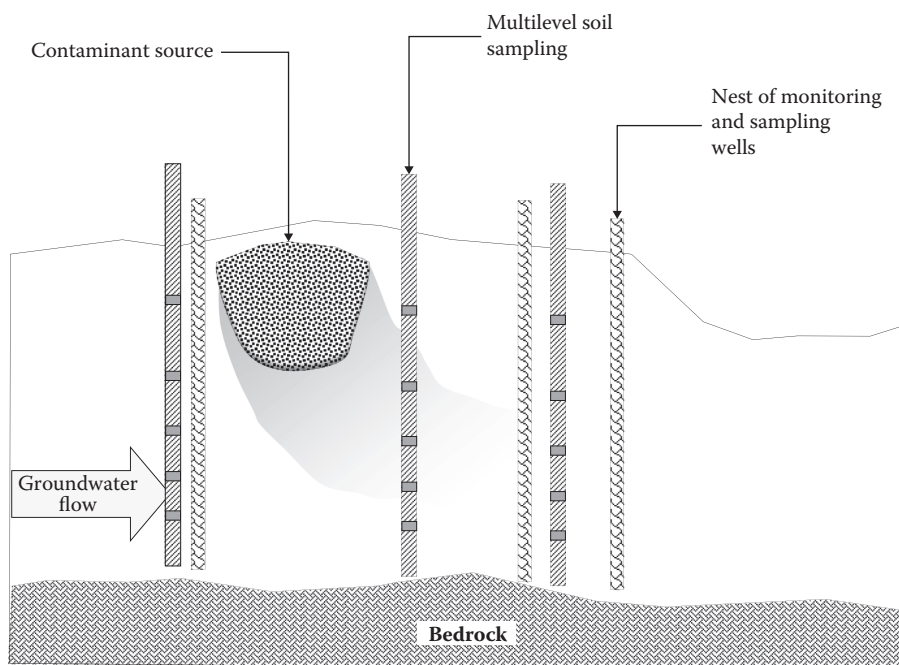


FIGURE 3.8

Simple monitoring and sampling scheme for evaluating groundwater quality. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

the concentration, composition, and toxicity of the target contaminant. For prediction of further or continued attenuation of the target contaminant, the partition coefficients and solubilities of the various contaminants are needed as input to transport and fate models. If biotransformation of the target contaminants has occurred, supporting laboratory research would be needed to determine the likely fate of the transformed or intermediate products.

3.3.2.1 Remote Sensing

Most of the existing technologies for monitoring algae and cyanobacteria rely on microscopic techniques that are laborious and highly variable. Recently, algae and algal blooms can be detected using satellite imaging systems and spectrofluorimetry (Gitelson and Yacobi, 1995). Millie et al. (2002) have demonstrated that absorbance and fluorescence spectra can be used to discriminate microalgae. This method can potentially be applied as part of in situ monitoring program.

Remote sensing by Landsat satellites has been evaluated by Zhu et al. (2002) for the Pearl River in South China, Hong Kong, and Macau region and by Han and Jordan in the United States (2005). Sea color was monitored, and the images were analyzed by an algorithm of *gradient transition*. In situ optical, chemical and biochemical measurements for chlorophyll-a and phytoplankton and other parameters correlated well with ocean color. Han and Jordan (2005) found that the first derivative spectra and the best wavelengths could correlate well for determining the chlorophyll content of biofilms.

Water quality in urban runoff can also be monitored by remote sensing. Ha et al. (2003) combined Landsat, the Korea Multi-Purpose Satellite (KOMPSAT) with two types of neural networks. Runoff, peak time, and contaminant data could be obtained to determine water quality in an urban area. In the Netherlands, a remote sensing system was tested to construct maps of water quality (Hakvoort et al., 2002). A hyperspectral scanner was set up in an airplane to retrieve information on subsurface reflectance spectra, specific inherent optical properties (SIOP) of the water components and the Gordon reflectance model using a matrix inversion technique. Data for both total suspended matter and chlorophyll were obtained when circumstances were good, and reliable data mainly only for total suspended matter under less ideal conditions. Information on dissolved organic matter levels could not be obtained. The matrix inversion technique for airborne image was particularly promising.

Significant advances have been made in the last decade concerning the levels of detection, information about contaminants including speciation and the speed of monitoring of contaminants in water, as regulatory requirements become more demanding. For example, the U.S. Groundwater Rule is being established to provide a risk-based regulatory strategy for groundwater systems that can be sensitive to fecal contamination.

Another example is the Arsenic Rule where the rule agreed that 10 µg/L of arsenic would be the standard from 2002 onward for drinking water (USEPA, 2012a). Drinking water systems must comply by 2006. Analytical methods for determining the different arsenic species include SPME and solid-phase extraction (SPE) with GS/MS, liquid chromatography (LC)/electrospray ionization mass spectrometry (ESI-MS), LC/ICPMS, and ion chromatography (IC)/inductively coupled plasma mass spectrometry (ICPMS). Field kits have also been used, particularly in Bangladesh and West Bengal. However, there have been problems with their accuracy (Erickson, 2003).

Methyl *tert*-butyl ether (MTBE) has recently been of concern because of the problem of leaking underground storage tanks, pipeline breaks, and other fuel discharges. Monitoring of this compound is now required, with detectable values that must not exceed 20 µg/L 99% of the time (USEPA, 2012b). In a study by Williams (2001) in California from 1995 to 2000, 1.3% of all drinking water samples contained detectable levels of MTBE. More than 75% were below 13 µg/L. In Germany, Achten et al. (2002) found average levels of 88 ng/L in well water and filtered riverbank samples. Lacorte et al. (2002) found that 7 out of 21 groundwater samples in Catalonia Spain had levels exceeding 20 to 40 µg/L. Methods to measure MTBE have been reviewed by Richardson (2003), including headspace, purge and trap, or solid-phase microextraction (SPME) combined with gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) analysis. Detection levels are in the order of nanograms per liter range.

Following water contamination cases such as Walkerton in Ontario, Canada, where *Escherichia coli* gastroenteritis occurred in 2000, the importance of analytical methods for microorganism detection has increased. Due to the deficiencies in the standard methods for detection of viruses, bacteria, and protozoa, particularly length of time, various new methods have been developed. These include (a) immunofluorescent antibodies techniques, (b) fluorescent in situ hybridization, (c) magnetic bead cell sorting, (d) electrochemiluminescence, (e) amperometric sensors, (f) various polymerase chain reactions (PCR), RT-PCR, and (g) realtime PCR methods (Straub and Chandler, 2003), and (h) immunomagnetic separation. Richardson (2003) has also indicated that several reviews have been published using mass spectrometric techniques for characterization of microorganisms.

Analysis of herbicides and pesticides is also of interest because of their effects on human health and the environment. A field kit has been evaluated by Ballesteros et al. (2001) for

analysis of triazine herbicides in water samples. Detection levels by this ELISA-based technique are 0.1 µg/L for atrazine and 0.5 µg/L for triazine. Other methods have now been developed to analyse enantiomeric pesticides. Studies were performed by enantioselective GC/MS from 1997 to 2001 on a lake that received agricultural runoff in Switzerland (Poiger et al., 2002). Pre-1998, samples showed the dominance of the racemic metolachlor, whereas samples collected in 2000 to 2001 showed a clear dominance of the *S*-isomer. This coincided with the commercial switch from the racemic to the *S* form for agricultural use. Pharmaceutically active compounds and other personal care products have also been identified in surface runoff from fields irrigated with wastewater treatment effluents (Pedersen et al., 2002).

Methods such as GC, HPLC, GLC, and atomic absorption spectrometry (AA) are accurate, and limits of detections are continually decreasing due to combined techniques (e.g., GC/MS, LC/MS, CE/MS, CE/ICP-MS, and ICP-MS). Polar compounds, prior to LC/MS were extremely difficult to detect. Improved methods of sample preparation have reduced solvent usage and are more environmentally friendly and rapid. Although efforts have also been made to automate and simplify many of the technologies, they must continue to enable more widespread use of the technology. Recoveries from SPE will need to improve to enable one to obtain more reliable data from this technique. More extensive testing needs to be done with real environmental samples, not just standards, to more fully understand interferences within the samples. This will enable one to (a) monitor water quality, (b) determine the origin or source of biological and chemical contaminants, and (c) determine the transport and fate of the contaminants in the environment.

3.3.2.2 *Biomonitoring*

Biomonitoring is used to indicate the effect and extent of contaminants in the water. It includes determining changes in species diversity, composition in a community, and in the mortality rates of a species. Buildup of contaminants in the tissues of individuals can also be evaluated, in addition to physiological, behavioral, and morphological changes in individuals. The effect of specific contaminants is difficult to determine. Biomonitoring involves the determination of the numbers, health, and presence of various species of algae, fish, plants, benthic macroinvertebrates, insects, or other organisms as a way of determining water quality (USEPA, 2000). Knowledge of background information is essential. Attached algae (known as periphyton) are good indicators of water quality since they grow on rocks and other plants in the water. The advantages for using these as indicators are (a) high numbers of species are available, (b) their responses to changes in the environment are well known, (c) they respond quickly to exposures, and (d) they are easy to sample. An assessment could include (a) determination of the biomass by chlorophyll or on an ash-free dry basis, (b) species, (c) distribution of species, and (d) condition of the attached algae assemblages. As yet, their use has not been widely incorporated in monitoring programs.

Benthic macroinvertebrates have numerous advantages as bioindicators (protocols). They do not move very far and thus can be used for upstream–downstream studies. Their life span is about a year, enabling their use for short-term environmental changes. Sampling is easy. They are numerous, and experienced biologists can easily detect changes in macroinvertebrate assemblages. In addition, different species respond differently to various contaminants. They are also food sources for fish and other commercial species. Many states in the United States have more information on the relationship between invertebrates and contaminants than for fish (Southerland and Stribling, 1995).

Fish are good indicators of water quality because (a) they always live in water, (b) they live for long periods (2 to over 10 years) (Karr et al., 1986), (c) they are easily identifiable and easy

to collect, and (d) they can quickly recover from natural disturbances. They are also consumed by humans and are of importance to sport and commercial fishermen. Fish make up almost 50% of the endangered vertebrate species in the United States (Warren et al., 2000).

Aquatic plants (macrophytes) grow near or in water and many of them can serve as indicators of water quality. A lack of macrophytes can indicate quality problems caused by turbidity, excessive salinity or the presence of herbicides (Crowder and Painter, 1991). Excessive numbers can be caused by high nutrient levels. They are good indicators since they respond to light, turbidity, contaminants such as metals and herbicides and salt. No laboratory analysis is required and sampling can be performed through aerial photography.

Biosurveys are useful in identifying if a problem exists. Chemical and toxicity tests would then be required to determine the exact cause and source (USEPA, 1991). Routine biomonitoring can be less expensive than chemical tests over the short term but more expensive over the long term. Field bioassessment experts are required to obtain and interpret data. However, there are no established protocols. More knowledge is required to determine the effects of contaminants on populations of organisms and better coordination of background data before site contamination. Recently, data on toxicity and chemical have been combined to evaluate the sustainability of reaction pathways by Zhang et al. (2000). Risk indices were developed for aquatic life or human health as part of environmental index determination.

The USEPA (Barbour et al., 1999) has been developing a biological data management system linked to STORET, which can store biological data and associated analytical tools for data analysis. STORET enables storing, retrieving, and analyzing biosurvey data. The data can then be processed to evaluate the distribution, abundance, and physical condition of aquatic organisms, and their environment.

3.4 Sustainable Water Treatment and Management

To enable the adequacy of water resources for future generations, management practices must control the sources of contamination and limit water use. This requires sufficiency in recharge of aquifers and prevention of contamination of surface water and groundwater. Remediation of contaminated water is required, but as is well known, effective and complete remediation of aquifers is not easily accomplished. As discussed previously, the quality of both surface water and groundwater need to be protected by mitigation and management procedures. Reuse of treated waste streams, in particular, needs to be practiced in farming and agricultural activities by irrigation.

Real-time monitoring and remote sensing and graphical information systems (GIS) are essential for water management. Calera Belmonte et al. (1999) examined the use for GIS tools to manage water resources in an aquifer system using remote sensing from a satellite to determine the spatial distribution of irrigated crops and water pumping estimates. The information obtained enables the GIS to be used as a tool for monitoring and control of water exploitation for agricultural uses.

Two EPA GIS tools (USEPA, 2013) useful for water quality study purposes are BASINS and WATERS. BASINS, Better Assessment Science Integrating Point and Nonpoint Sources (BASINS), is a multipurpose environmental analysis system used by regional, state and local agencies for watershed and water quality-based studies. Water quality can be assessed at a selected stream or an entire watershed. Watershed Assessment, Tracking & Environmental Results (WATERS) is an integrated information system connected to a

larger framework known as the National Hydrography Dataset (NHD) that allows sharing across programs.

3.4.1 Techniques for Soil and Groundwater Treatment

Contamination of groundwater occurs when chemicals are introduced on or into the ground through such actions as application of pest control aids, direct and indirect discharge of liquid wastes, transport of leachates containing contaminants escaping from landfills, etc. Decontamination of the groundwater requires reduction (elimination?) of the toxicity of the contaminants by (a) sequestration, or by (b) chemically and biologically mediated transformation of the contaminants, and/or (c) removal of the noxious contaminants from the groundwater. In most instances, the groundwater of concern is porewater (water in the void spaces of compact soil). Several techniques are available to manage and control contamination of groundwater by contaminant plumes, to minimize adverse environmental and health impacts. These include (a) construction of impermeable barriers and liner systems for containment facilities, (b) remediation techniques designed to remove or reduce (attenuate) the contaminants in the ground such as soil flushing, and (c) passive procedures relying on the properties of the ground to reduce contaminant concentrations in leachate streams and contamination plumes.

3.4.1.1 Isolation and Containment

Contaminants can be isolated and contained to (a) prevent further movement, (b) reduce the permeability to less than 1×10^{-7} m/s, and/or (c) increase the strength (USEPA, 1994). Physical barriers made of steel, concrete, bentonite, and grout walls can be used for capping, vertical, and horizontal containment. Liners and membranes are mainly used for protection of groundwater systems, particularly from landfill leachates. A variety of materials are used including polyethylene, polyvinyl chlorides, asphalt materials, and soil-bentonite or cement mixtures. Monitoring is a key requirement to ensure that the contaminants are not mobilized.

Most in situ remediation techniques are potentially less expensive and disruptive than ex situ ones, particularly for large contaminated areas. Natural or synthetic additives can be utilized to enhance precipitation, ion exchange, sorption, and redox reactions (Mench et al., 2000). The sustainability of reducing and maintaining reduced solubility conditions is key to the long-term success of the treatment. Ex situ techniques are expensive and can disrupt the ecosystem and the landscape. For shallow contamination, remediation costs, worker exposure, and environmental disruption can be reduced using in situ remediation techniques.

Sequestration of contaminants can be obtained using encapsulation techniques. The common ones are known as solidification/stabilization (S/S) techniques. These are designed to detoxify and incorporate the contaminants in a solid matrix. Some metals such as arsenic, mercury, and chromium(VI) are less suitable for these techniques. Monitoring is required to ensure that the process is stable, and the contaminants are not mobilized. For inorganic contaminants, the two groups of solidification/stabilizing agents used are (1) cement, fly ash, kiln dust, clays, zeolites, and pozzolonic materials and (2) bitumen products, epoxy, urea-formaldehyde, polyethylene, and resins. Strict requirements for weathering (leachability, etc.) and durability of solidified and stabilized products have been specified by many regulatory agencies. Performance assessment of such products, as with most treatment procedures, is a standard requirement. X-ray diffraction and scanning electron microscopy may also be beneficial for examining crystalline structures.

Vitrification, a high-temperature solidification process, leads to the formation of a glassy solid, and is especially applicable for treatment of arsenic-contaminated soils since arsenic possesses low volatility. The melting ability of the contaminated soil depends on the soil's silica content. The maximum allowable oxide content in a soil containing arsenic as a contaminant is 5% (Smith et al., 1995). It is the best demonstrated available technology (BDATs) for Resource Conservation and Recovery Act (RCRA) wastes. Off-gas collection and treatment may be required. Melting of the soil leads to volume reduction upon elimination of void spaces and this backfill is required to replace subsidence.

As an example, information regarding the sustainability of arsenic immobilization could be obtained for sequential extraction techniques to evaluate the adsorption, sequestration, and bioavailability of arsenic in soils (Yong and Mulligan, 2004) before and after treatment with additives such as iron, aluminum, calcium, and manganese, cement, lime, and pozzolanic materials as was previously shown for phosphate treatment.

3.4.1.2 Extraction Treatment Techniques

To remove NAPLs from the groundwater, extraction of the groundwater can be performed by extraction pumping of the contaminated dissolved phase and/or free phase NAPL zone. Drinking water standards can be achieved with the method of treatment. However, substantial periods can be required before this occurs. To enhance the removal rates of the contaminants, extraction solutions can be infiltrated into the soil using surface flooding, sprinklers, leach fields, horizontal, or vertical drains. Water with or without additives is employed to solubilize and extract the contaminants as shown in Figure 3.9. Chemical

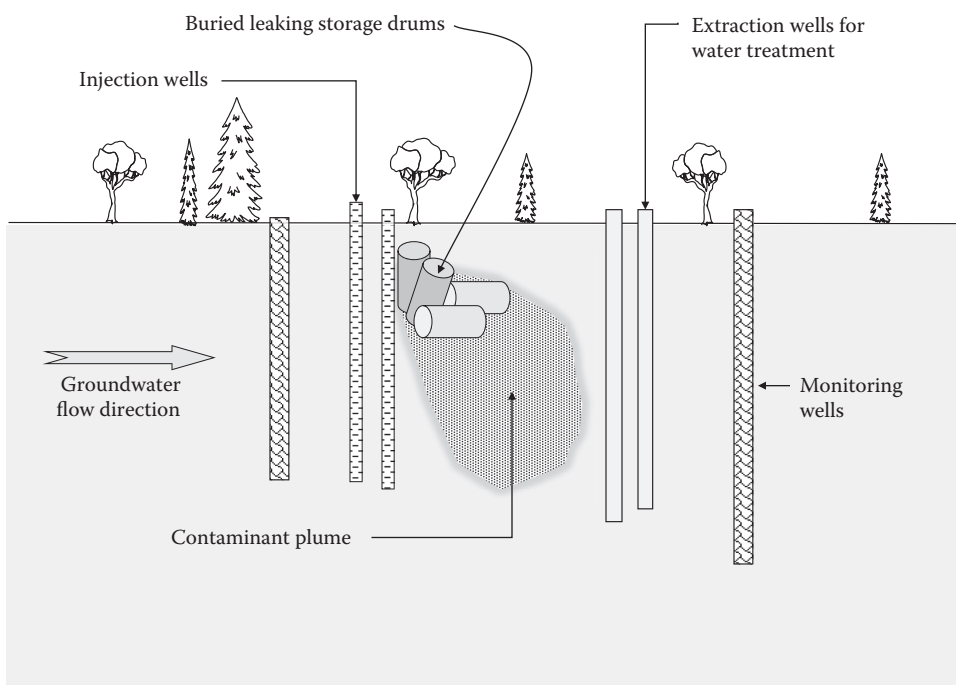


FIGURE 3.9

Schematic diagram of a soil flushing process for removal of contaminants.

additives include organic or inorganic acids, bases, water soluble solvents, complexing agents, and surfactants. Removal efficiencies are related to, and affected by, soil pH, soil type, cation exchange capacity, particle size, permeability, and the type of contaminants. High soil permeabilities (greater than 1×10^{-3} cm/s) are considered to be beneficial for such procedures.

As an alternative to groundwater pumping, soil vapor extraction (SVE) (Figure 3.10) may be utilized for the vaporization of volatile and semivolatile components in the unsaturated zone (Yong, 1998; Rathfelder et al., 1991). Soil can be decontaminated by applying a vacuum to pull the volatile emissions through the soil pore spaces. The air may be then treated at the surface with activated carbon filters, chemical oxidation, or biofilters. This technique is applicable to highly permeable soils and volatile contaminants such as gasoline or solvents. Other parameters such as the octanol–water coefficient, Henry’s law constant and solubility of the contaminant, and moisture and organic contents of the soil also affect the removal efficiencies.

Volatile components can also be removed by air sparging. In this technique, bubbles of air are injected into the groundwater to strip NAPLs and to add oxygen for in situ bioremediation. It has been successfully used for dissolved hydrocarbon plumes (Bass et al., 2000). Reduction of the NAPL zone may then allow natural attenuation processes to proceed. Bioventing is a variation of this technique where lower aeration rates are used to promote aerobic biodegradation instead of volatilization.

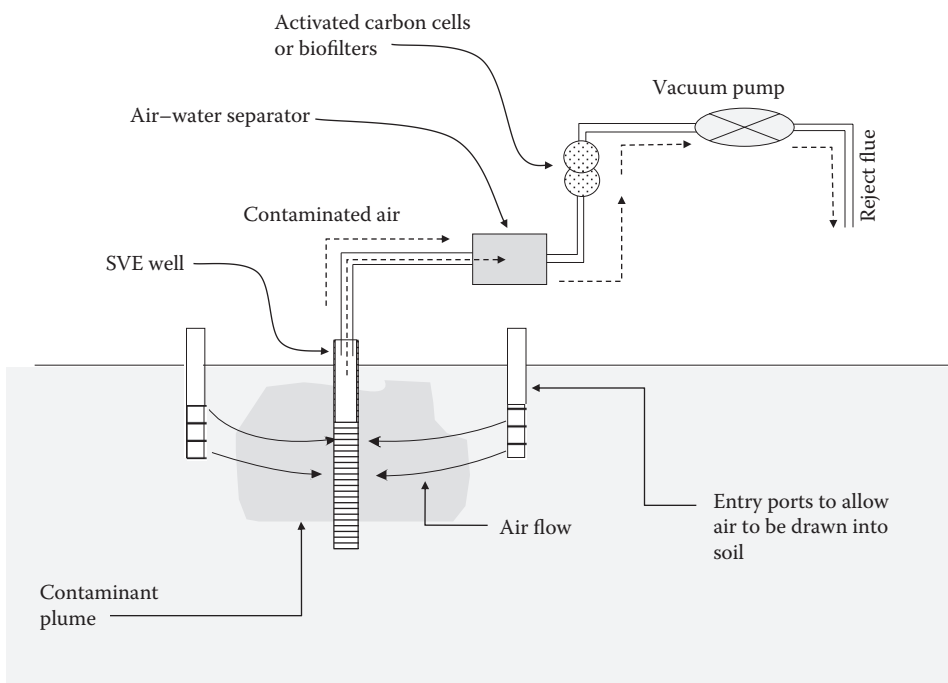


FIGURE 3.10

Schematic of a SVE process. A series of SVE wells can be introduced into the ground, connected in series or in parallel. The number of SVE wells that can be introduced will depend on the capacity of the vacuum pump system. (Adapted from Yong, R.N., *Compatible Technology for Treatment and Rehabilitation of Contaminated Sites*, Nikken Sekkei Geotechnical Institute, Japan, NNGI Report No. 5, pp. 1–33, 1998.)

Phytoremediation is the use of plants to remove, contain, or render harmless environmental contaminants. Constructed wetlands use aquatic plants such as water hyacinths to remove nutrients and contaminants from water. The various mechanisms involved in phytoremediation include (a) phytoextraction, (b) uptake of contaminants through the roots and subsequent accumulation in the plants, (c) phytodegradation, (d) metabolism of contaminants in the leaves, shoots, and roots, (e) release of enzymes and other components for stimulation of bacterial activity or biochemical conversion and rhizodegradation, and (f) mineralization of contaminants in the soil by microbial activity in the rhizosphere. Phytoremediation is a low cost in situ technology that causes minimal disturbance, and is aesthetically pleasing. It is acceptable to the public and generates low amounts of waste. This technology is presently being developed for a treatment of a wide variety of organic and inorganic contaminants. Better understanding of contaminant uptake by the plants, development of hyperaccumulators, and increased field testing are needed.

3.4.1.3 Electrokinetic Applications

Electrokinetics involves the use of electrodes and electrical current to mobilize inorganic contaminants. It is more effective for treatment of silty soils than for clay soils where energy requirements can be substantial. Energy levels must be higher than the energy that binds the contaminants to the soil. This processes involved have been described in detail by Yong (2001). Electro-osmosis and electrophoretic phenomena are the principal mechanisms in the treatment process. Conditioning fluids are required to enhance contaminant ion movement, and electrode dissolution or fouling is a substantial problem.

3.4.1.4 Natural Attenuation

The attenuation of contaminants, including those caused by assimilative processes of soils, refers to the reduction of concentrations and/or toxicity of contaminants, including those contaminants during transport in soils. This process is discussed in detail in Section 10.2 in Chapter 10 where the use of soils as a waste management tool is addressed. For the present, we will examine some of the phenomena pertinent to the present context of water and groundwater controls. Reduction in concentrations and toxicity of contaminants in the groundwater can be accomplished by (a) dilution because of mixing with uncontaminated groundwater, (b) interactions and reactions between contaminants and soil solids that can lead to partitioning of the contaminants between the soil solids and porewater, and (c) transformations that reduce the toxicity threat posed by the original contaminants. Short of overwhelming dilution with groundwater, it is generally acknowledged that partitioning is by far the more significant factor in attenuation of contaminants and/or pollutants.

Natural attenuation refers to the situation when attenuation of contaminants results because of the processes that contribute to the natural assimilative capacity of soil. This means that contaminant attenuation occurs as a result of the natural processes occurring in the soil during contaminant–soil interaction. Broadly speaking therefore, natural attenuation refers to natural processes occurring in the soil that serve to reduce the toxicity of the contaminants and/or the concentration of the contaminants. These natural processes of contaminant attenuation include dilution, partitioning of contaminants, and transformations. They involve a range of physical actions, chemically and biologically mediated reactions, and combinations of all of these.

According to the U.S. National Research Council (NRC), the sustainability of natural attenuation is dependent on the sustainability of the mechanisms for immobilizing or

destroying contaminants while the contaminants are being released into the groundwater. A mass balance analysis can be used to estimate the long-term destruction or immobilization rates (NRC, 2000). For hydrocarbons, the availability of electron acceptors or donors may be evaluated to determine the sustainability of remediation techniques such as natural attenuation for hydrocarbons. However, in the case of metals and metalloids such as arsenic, this approach is only applicable if the attenuation is biologically driven.

Monitored natural attenuation (MNA), because of its adherence to “remedy by natural processes” necessitates a proper understanding of the many principles involved in the natural processes that contribute to the end result. Monitoring of the contaminant plume at various positions away from the source is a key element of the use of MNA. Remembering that this (MNA) is a contaminant and soil-specific phenomenon, one generally tracks a very limited number of contaminants, and specifically the ones considered to be the most noxious. Historically, more attention has been paid to documenting the properties and characteristics of the contaminants. By and large, the contaminants tracked have primarily been the organic chemicals including, for example, chlorinated solvents (PCE, TCE, and DCE), and hydrocarbons such as benzene, toluene, ethyl benzene, and xylene (BTEX).

When active controls or agents are introduced into the soil to render attenuation more effective, this is called *enhanced natural attenuation* (ENA). This is to be distinguished from engineered *natural attenuation* (EngNA), which is probably best illustrated by the permeable reactive barrier (PRB) shown in Figure 3.11 and the barrier-liner system shown in Figure 3.12. ENA refers to the situation where, for example, nutrient packages are added to the soil

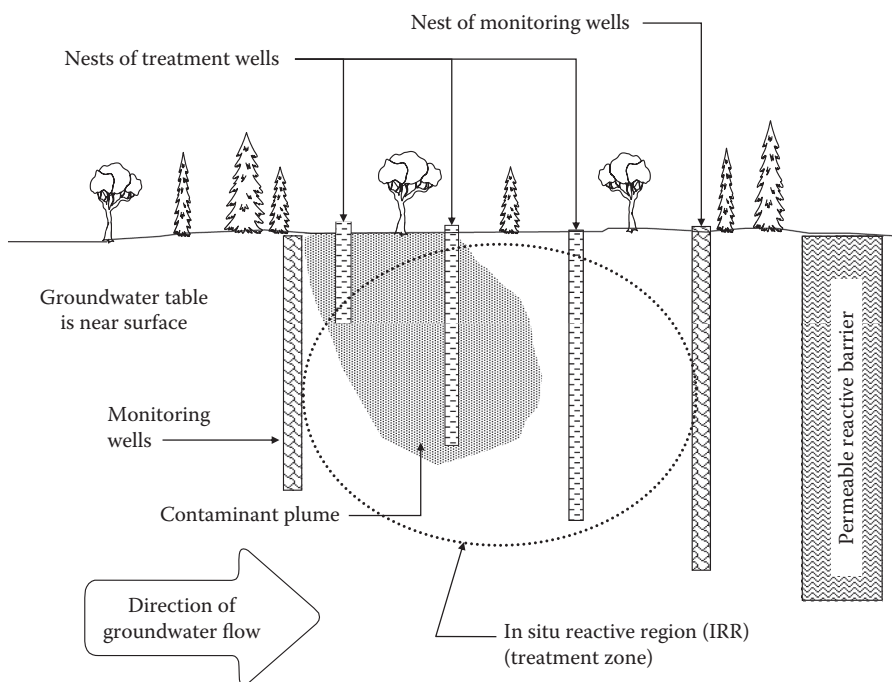


FIGURE 3.11

Enhancement of natural attenuation using treatment wells. Treatments for enhancement can be any or all of the following: geochemical intervention, biostimulation, and bioaugmentation. Treatment occurs in the contaminant plume and down-gradient from the plume. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

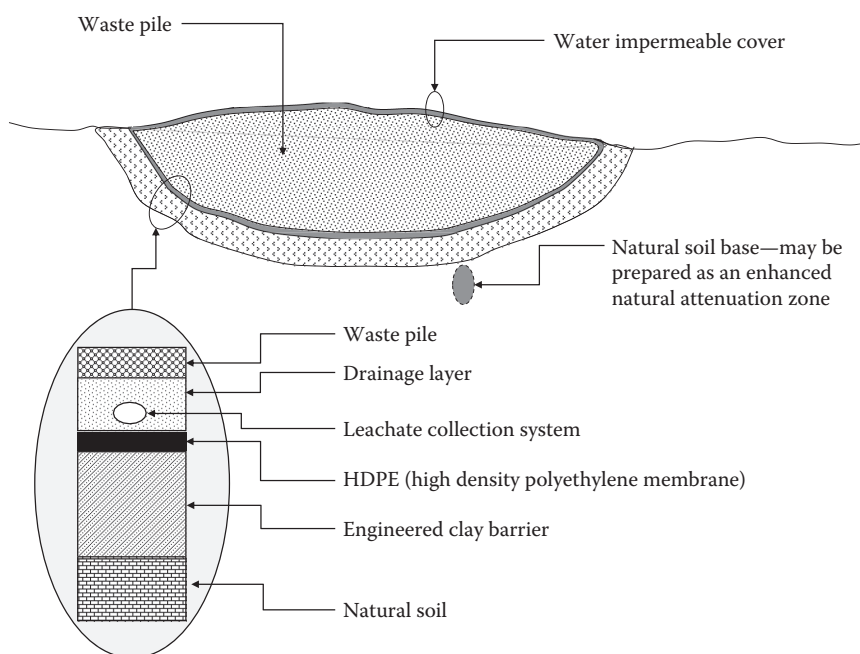


FIGURE 3.12

Contaminant attenuation layer constructed as part of an engineered barrier system. The dimensions of the attenuation layer and the specification of the various elements that constitute the “filter, membrane, and leachate collection system” are generally determined by regulations or by performance criteria. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

system to permit enhanced biodegradation to occur, or where catalysts are added to the soil to permit chemical reactions to occur more effectively. ENA could include biostimulation and/or bioaugmentation. These subjects are discussed in greater detail in Chapter 10.

3.4.1.5 Biostimulation

Probably the simplest procedure for improving the intrinsic bioremediation capability of a soil is to provide a stimulus to the microorganisms that already exist in the site. This procedure is called *biostimulation*, i.e., adding nutrients and other growth substrates together with electron donors and acceptors. The intent of biostimulation is to promote increased microbial activity with the set of stimuli to better degrade the organic chemical contaminants in the soil. With the addition of nitrates, Fe(III) oxides, Mn(IV) oxides, sulfates, and CO₂, for example, anaerobic degradation can proceed. This technique is used for sites contaminated with organic chemical contaminants and is perhaps one of the least intrusive of the methods of enhancement of natural attenuation. The other method of enhancement that falls in the same class of “less-intrusive” enhancement procedure is bioaugmentation.

3.4.1.6 Bioaugmentation

If the native or indigenous microbial population is not capable of degrading the organic chemicals in the soil, for whatever reason, e.g., concentrations, inappropriate consortia, other microorganisms can be introduced into the soil. These are called exogenous

microorganisms. Their function is to augment the indigenous microbial population such that effective degradative capability can be obtained. If need be, biostimulation can also be added to the bioaugmentation to further increase the likelihood of effective degradative capability. We need to be conscious of the risks that arise when unknown results are obtained from interactions between the genetically engineered microorganisms and the various chemicals in the contaminated ground. The use of microorganisms grown in uncharacterized consortia, which include bacteria, fungi, and viruses can produce toxic metabolites (Strauss, 1991). In addition, the interaction of chemicals with microorganisms may result in mutations in the microorganisms themselves and/or microbial adaptations.

3.4.1.7 Enhanced Natural Attenuation

We show in Figure 3.11 a direct application of ENA as an in situ remediation process. Enhanced treatment of a region (spatial and vertical) of the site down-gradient from the contaminated site permits the ENA to function as planned. The treated region is called the in situ *reactive region* (IRR) or *treatment zone*, and can be used in conjunction with other treatment procedures. Figure 3.11 illustrates the use of the IRR as a treatment procedure for the contaminant plume in the region in front of the PRB. Treatment procedures using treatment wells or boreholes and associated technology include

- Geochemical procedures such as pH and *Eh* manipulation
- Soil improvement techniques such as introduction of inorganic and organic ligands, introduction of electron acceptors and donors
- Various other biostimulation procedures and bioaugmentation

The choice of any of these, or a combination of these methods of augmentation, will depend on the type, distribution, and concentration of contaminants in the contaminated site, and also on the results obtained from microcosm and treatability studies.

3.4.1.8 In Situ Reactive Regions—Treatment Zones

We have seen from Figure 3.11 an example of the use of a treatment zone, known also as an IRR, i.e., the region immediately in front of the PRB. The purpose of an IRR is to provide not only pretreatment or preconditioning in support of another treatment procedure, but also as a posttreatment process for sites previously remediated by other technological procedures. In the drawing shown in Figure 3.11, we show the IRR used in support of the PRB treatment procedure. Other treatment procedures can also be used in place of the PRB. The presence of heavy metals in combination with organic chemicals in the contaminant plume is not an uncommon occurrence. One could, for example, envisage using IRR as a treatment procedure in combination with a subsequent procedure designed to fix or remove the metals.

In application of IRR as a posttreatment process, one is looking toward the IRR as the *final cap* for some kind of design or technological process for remediation of a contaminated site. This is generally part of a multiple-treatment process—as opposed to the use of IRR in a pretreatment or preconditioning process. A good example of this is the use of pump-treat procedure as the first phase of the remediation program, followed by the IRR as a posttreatment process where the treated contaminant plume will receive its final cleanup. The efficiency of cleanup using pump-and-treat methods rapidly decreases as greater contaminant

extraction from the groundwater or porewater is required. It is not unusual to remove some large proportion of the contaminants from the groundwater or porewater, and to leave the remaining proportion to be removed via natural attenuation processes in an IRR.

3.4.1.9 Permeable Reactive Barriers

The intent of a permeable reactive barrier is to provide treatment as a remediation procedure to a contaminant plume as it is transported through the PRB so that the plume no longer poses a threat to biotic receptors when it exits the PRB. Figure 3.13 shows a funnel and gate arrangement of a PRB application where the contaminant plume is channeled to the PRB gate by the impermeable walls. Transport of the contaminant plume through the PRB allows the various assimilative and biodegradative mechanisms of the treatment wall to attenuate the contaminants. The PRB needs to be strategically located down-gradient to intercept the contaminants.

PRB are also known as treatment walls. The soil materials in these walls or barriers can include a range of oxidants and reductants, chelating agents, catalysts, microorganisms, zero-valent metals, zeolite, reactive clays, ferrous hydroxides, carbonates, and sulfates, ferric oxides and oxyhydroxides, activated carbon and alumina, nutrients, phosphates, and soil organic materials. The choice of any of these treatment materials is made on the basis of site-specific knowledge of the interaction processes between the target contaminants and material in the PRB. Rapid clogging or deactivation of the material must be avoided. Site geology, geochemistry, and microbiology, in addition to contaminant concentrations

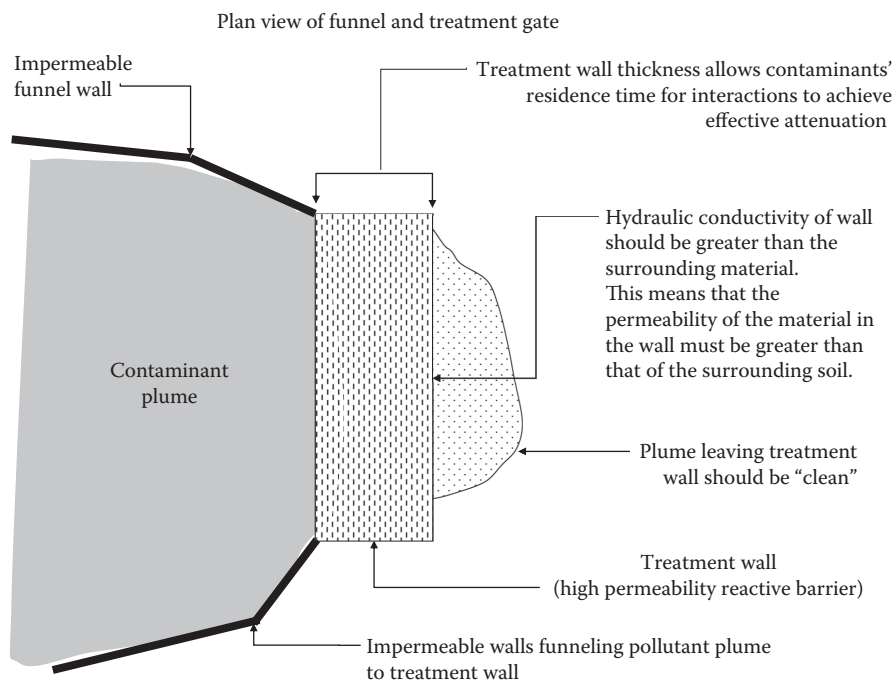


FIGURE 3.13

Funnel and gate arrangement of PRB treatment of contaminant plume. Funnel effect is provided by the impermeable walls that channel contaminant plume transport to the PRB gate. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, 310 pp., 2004.)

and properties, must be determined. Laboratory tests and treatability studies are essential elements of the design procedure for the treatment walls (PRBs). When designed properly, a PRB provides the capability for assimilation of the contaminants in the contaminant plume as it migrates through the barrier. In that sense, PRBs function in much the same manner as IRR—except that the region is a constructed barrier. Some of the assimilative processes in the PRB include the following:

- Inorganic contaminants: sorption, precipitation, substitution, transformation, complexation, oxidation, and reduction
- Organic contaminants: sorption, abiotic transformation, biotransformation, abiotic degradation, biodegradation

Use of natural attenuation for management of contaminant transport and transmission in soil: We have at least three ways in which natural attenuation can be used to manage and/or control the transport of contaminants in soil. These include MNA, ENA, and EngNA. These have various benefits and are used as effective tools in the control and management of contaminant and contaminant leachate plumes, and especially in specific bioremediation schemes. More detailed discussions of these can be found in Chapter 10.

Other techniques such as air sparging are employed to volatilize the VOCs from the groundwater. Biological techniques can also be combined with the extraction techniques in biosparging (Figure 3.14) and bioslurping processes. Essentially, both techniques add another component to the bioventing technique, for example, shown as the solvent extraction procedure in Figure 3.10. In the bioslurping technique, another dimension to the SVE process is added using vacuum-enhanced pumping to recover free product (NAPLs).

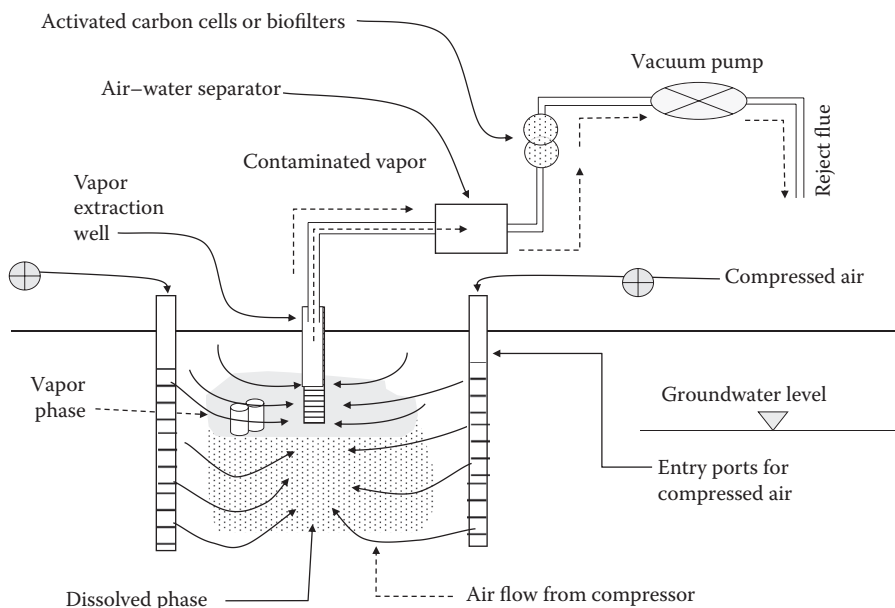


FIGURE 3.14

Schematic of a biosparging process in combination with SVE. Note that a series of compressed air wells and SVE wells can be introduced into the ground, connected in series or in parallel. Obviously, the number of wells that can be introduced will depend on the capacity of the compressor and vacuum pump systems.

3.4.1.10 Ex Situ Processes

For extracted groundwater, treatment is required before discharge or utilization of the abstracted groundwater as drinking water. These techniques are usually quite extensive, involving extraction of substantial groundwater. Standard physical, chemical, or biological wastewater treatment techniques are utilized. Physical–chemical techniques include physical and/or chemical procedures for removal of the contaminants including precipitation, air stripping, ion exchange, reverse osmosis, electrochemical oxidation, etc.

Techniques for groundwater treatment for arsenic and waste considerations are highlighted in Table 3.1. Treatment methods need to minimize the wastes produced to ensure that these processes are sustainable. To evaluate the sustainability of these methods, several factors including materials, energy, transportation, and waste management requirements for the treatment process need to be taken into consideration. One of the principal methods is ion exchange. However, in some cases, simple ion exchange techniques are insufficient. An example of this is As(III). Oxidation of this form to As(V) must be required and performed with a preoxidation filter. Although this method is highly efficient, disposal of a toxic arsenic waste from the regeneration of these filters and the ion exchange resins as a result of the water treatment procedures impacts the sustainability of these processes. These purification activities generate significant wastes that can severely impact the environment, causing more harm than good. Due to the problems of arsenic in the groundwater, economic solutions need to be found to ensure the safety of the drinking water.

Several common treatment technologies are used for removal of inorganic contaminants, including arsenic, from drinking water supplies. Large-scale treatment facilities often use conventional coagulation with alum or iron salts followed by filtration to remove arsenic. Lime softening and iron removal also are common, conventional treatment processes that can

TABLE 3.1

Comparison of Technologies for the Remediation of Arsenic Contaminated Groundwater

Technology	Waste Stream	Treatment of Waste	Disposal Options
Coagulation/filtration	Ferric sludge, redox sensitive, 97% water content	Dewatering and drying	Landfill after dewatering, brick manufacture (Rouf and Hossain, 2003)
Activated alumina with regeneration	Alkaline and acidic liquids	Neutralization and precipitation with ferric salts	Sewer, residual into landfill
Iron oxide filters	Exhausted adsorbent, redox sensitive, <50% solids, passes TCLP test ^a	No treatment	Landfill, immobilization, brick manufacture (Rouf and Hossain, 2003)
Ion exchange	Liquid saline brine	Precipitation with ferric salts	Sewer, brine discharge, landfill for residual, possible recycling of brines
Membrane techniques such as reverse osmosis or nanofiltration	Concentrated liquids	None performed	Sewer or brine discharge

Source: Adapted from Driehaus, W., Technologies for arsenic removal from potable water. In J. Bundschuh, P. Bhattacharaya, and D. Chandrasekharam (eds.), *Natural Arsenic in Groundwater: Occurrences, Remediation and Management*, Taylor & Francis, London, pp. 189–203, 2005.

^a TCLP refers to the Toxicity Characteristic Leaching Procedure (see Figure 7.4 and discussion in Section 7.3.5 in Chapter 7).

potentially remove arsenic from source waters. Treatment options identified by EPA include ion exchange, reverse osmosis, activated alumina, nanofiltration, electrodialysis reversal, coagulation/filtration, lime softening, greensand filtration, and other iron/manganese removal processes, and emerging technologies not yet identified (USEPA, 2003). New combinations of materials as sorbents such as granular activated carbon (GAC) supported nano scale zero-valent iron (nZVI) are being developed (Chowdhury and Mulligan, 2013). Treatment facilities or alternative water sources are required. We can see that this treatment method, along with the others do not eliminate the arsenic source before delivery and that other methods must be developed to accomplish this. Other groundwater methods such as oxidation can lead to the formation of toxic by-products and sludge. These will require disposal.

Methods for treatment of MTBE include bioremediation, granular activated carbon (GAC), air-stripping, ozonation, ozone/hydrogen peroxide, or phytoremediation (Richardson, 2003). These include ion exchange, reverse osmosis, activated alumina, nanofiltration, electrodialysis, coagulation/filtration, lime softening, greensand filtration, and other processes. Thermal techniques include pyrolysis and super critical water oxidation. For a detailed discussion of standard chemical and biological treatment processes, readers are referred to various textbooks dealing with wastewater treatment, e.g., Metcalf and Eddy (2003).

Previously, effluent quality was the only basis for evaluating treatment capabilities of water treatment processes. Capital, energy, nutrient, and other requirements need to be included to determine if the process under consideration is sustainable for future generations. Recycling of resources needs to be practiced as much as possible. Mulder (2003) compared the sustainability of nitrogen removal systems that included (a) conventional activated sludge systems, (b) an activated sludge system that relies on autotrophic nitrogen removal, (c) algal or duckweed ponds, and (d) constructed wetlands (Figure 3.15). The author used six sustainability indicators: production of sludge, energy consumption, resource recovery, space requirements, and N_2O emissions. They determined that the system that combines nitrification and anaerobic ammonia oxidation (autotrophic nitrogen

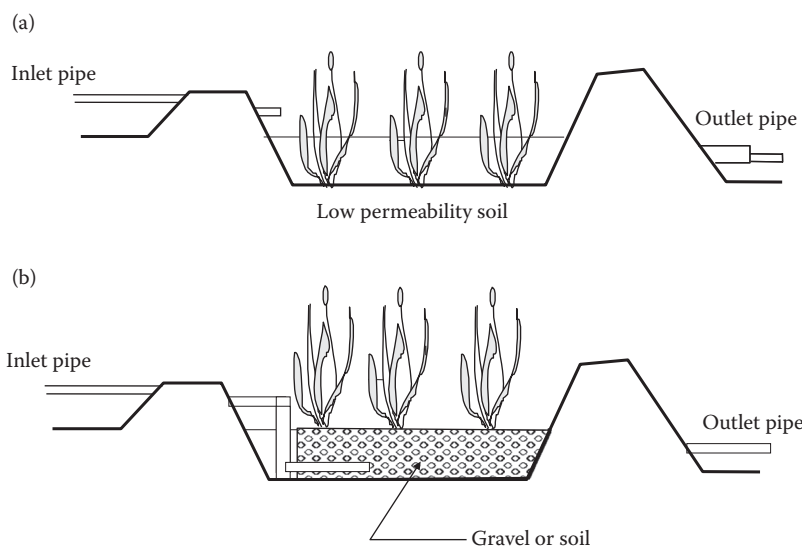


FIGURE 3.15

Overview of (a) surface and (b) subsurface flow constructed wetlands. (Adapted from Mulligan, C.N., *Environmental Biotreatment*, Government Institutes, Rockville, MD, 395 pp., 2002.)

removal) is the most sustainable because (a) organic matter is not required, (b) sludge production is low, and (c) nitrogen removal is high.

More extensive efforts have been performed by Alimahmoodi et al. (2010). It is a decision support tool (GoldSET) developed to incorporate sustainable development principles into engineering projects. It has a new wastewater treatment module that allows the application of sustainability principles through the tool to projects within the wastewater context to provide an assessment of different project options against a number of quantitative and qualitative sustainability indicators for the four dimensions of sustainability: environment, society, economy, and technology. Indicators provide a way of describing the situation surrounding the project, along with an associated weighting scoring scheme allowing the relative importance of each indicator to be reflected. The scoring scheme assigned to each indicator provides a mechanism to assess the performance of each option with respect to the indicator, producing a comparative graphical result of each option's sustainability performance. The developed module allows for both detailed design–engineering phase option assessments and design selections, and for more general project planning decisions, or future upgrades prioritization decisions.

3.4.2 Groundwater and Water Management

An effective groundwater management policy must first involve an evaluation of present practices—beginning with a determination of (a) the basic needs for the water and (b) laws and regulations that need to be established to ensure water quality and quantity. As shown in Figure 3.16, one must first determine if adequate quantities of groundwater

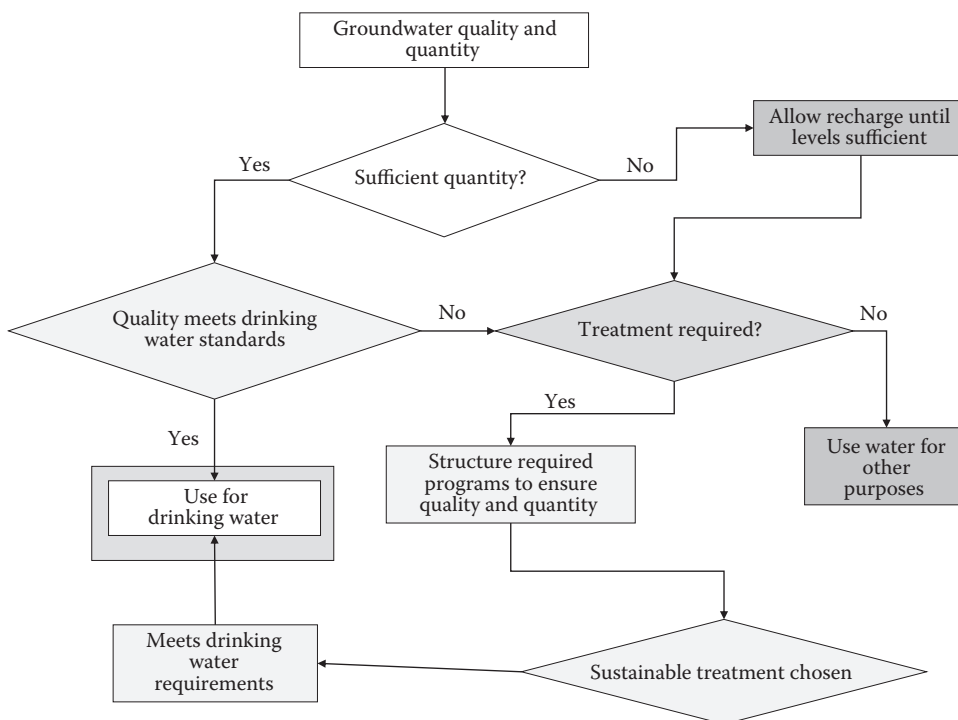


FIGURE 3.16

Flow diagram for groundwater management for drinking water purposes.

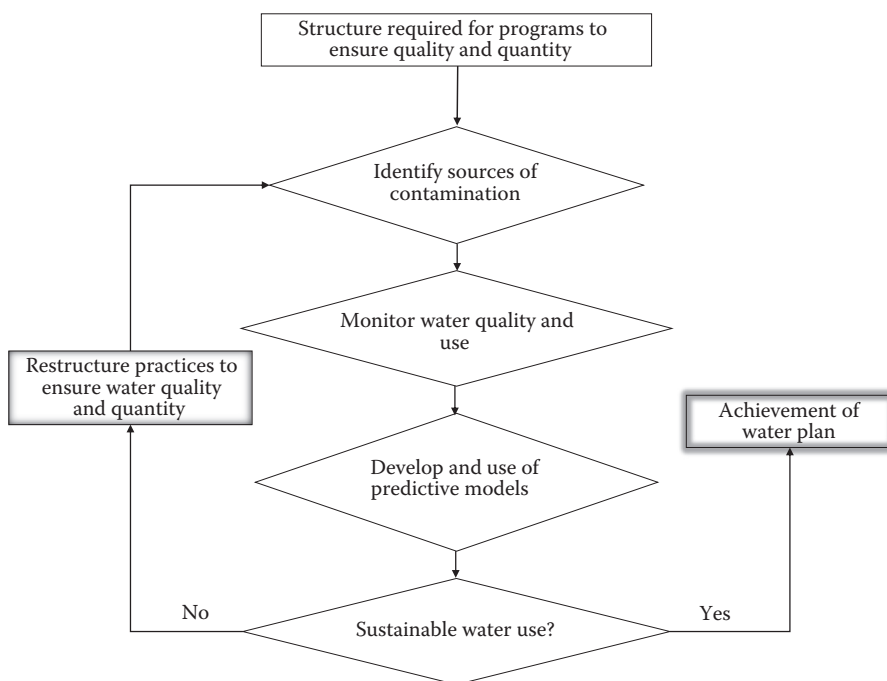
are available to meet the required needs. If not, one needs to manage the system to allow for recharge before depleting this resource. If water budget analyses show that the quantities are sufficient, the quality of the groundwater will then need to be determined. It may be adequate for industrial or irrigation purposes without treatment or perhaps with in situ treatments, as indicated previously. Drinking water quality may require further treatment. Most often this is accomplished by extraction pumping and treatment with a suitable sustainable method—to avoid harming aspects of the environment to protect others. Evaluation of the most sustainable water treatment processes can be performed through procedures similar to that previously described.

Twelve Principles of Green Engineering have been suggested to engineers as a way to improve the sustainability of industrial processes (Anastas and Zimmerman, 2003). The second principle is particularly relevant for the prevention of water contamination: “It is better to prevent waste than to treat or clean up waste after it is formed.” In other words, processes should be designed to reduce water use and the amount of contaminants that reaches the water so that the water will not have to be treated later on. In the past, many models have been developed for prediction of the impact of certain chemicals in the environment such as the transport of contaminants from point and non-point sources (Mihelcic et al., 2003). However, they have not focused on how to reduce or prevent the contamination. End of pipe solutions were the main waste management strategy until recently when green engineering has become more prominent.

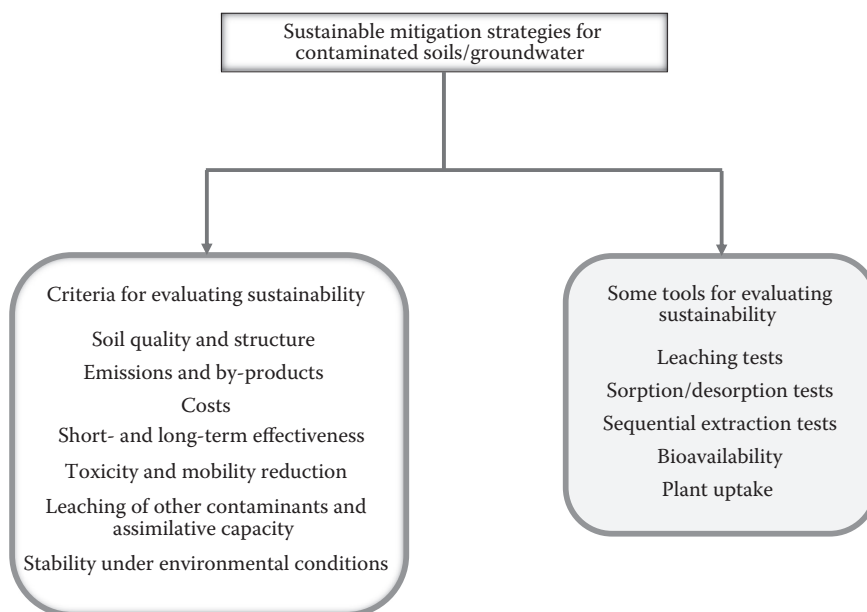
Upon determination of impaired water quality, strategies would need to be developed to prevent the introduction of the contaminants. Groundwater and surface water monitoring and GIS systems, as mentioned previously, will enable the development of the management strategies. The GIS would incorporate all aspects of land use include the types of ecosystems, landscapes, and water use. Monitoring will include determination of the quantities of water, the quality in terms of nutrient and contaminant contents and biological monitoring as described previously. Models would need to be developed to predict water discharge and recharges. All the information could then be combined to determine the water management strategy for avoidance of water contamination and optimal water use (Figure 3.17). All of these cannot be achieved, however, if the society is not educated concerning water usage and its importance. Legal guidelines must also be issued and followed to protect the quantity of resource water.

3.4.2.1 Evaluation of the Sustainability of Remediation Alternatives

Attention is focused on the problem of arsenic-polluted groundwater because contamination of groundwater from arsenic is a major threat to human health, and because this is both a man-induced and a naturally occurring phenomenon. In choosing the remediation technologies to treat this problem, it is necessary to factor in the targets, exposure routes, future land use, acceptable risks, legislation, and resultant emissions. A schematic illustration of the criteria and tools for evaluating technologies and protocols for environmental management of contaminated soils and groundwater is shown in Figure 3.18. Specific comments are included in Table 3.2 for the various technologies. Other factors that need to be considered to evaluate site remediation technologies include (a) disturbance to the environment, (b) energy use and consumption, (c) solid wastes generated, (d) emissions of contaminants and greenhouse gases into the air, and (e) water and materials used.

**FIGURE 3.17**

Flowchart demonstrating development of a program to ensure sustainable water quantity and quality.

**FIGURE 3.18**

Criteria and tools for evaluating technologies and protocols for environmental management of contaminated soils and groundwater.

TABLE 3.2

Comparison of Remediation Technologies in Soil and Groundwater

Technology	Cost ^a	Long-Term Effectiveness	Toxicity Reduction	Mobility Reduction
Containment	Good	Low	Low	Good
Solidification (in situ)	Avg.	Avg.	Low	Good
Solidification (ex situ)	Avg.	Avg.	Low	Good
Vitrification	High	Good	Low	Good
Biological treatment	Avg.-high	Low	Good	Good
Soil washing	High	Good	Low	Low
Soil vapor extraction	Avg.	Good	Good	Good
Pyrometallurgical extraction	High	Good	Low	Low
Electrokinetics	Avg.	Good	Low	Low

Source: Adapted from Evanko, C.R. and Dzombak, D.A., *Remediation of Metals-Contaminated Soils and Groundwater*, Technology Evaluation Report TE 97-01, October, GWRTAC, Pittsburgh, PA, 1997.

^a "High" is in the range of \$300 to 900/tonnes, "average" from \$100 to 300/tonnes, and "low" is up to \$100/tonnes. Avg. denotes average.

3.5 Concluding Remarks

Water is of utmost importance because without water, living species would perish. The demand and use of water can often produce situations that result in conflicts between humankind and the environment. Degradation or impairment of water quality results from various usages associated with processes and activities associated with farming, natural resources harvesting, industrialization, and urbanization. Management and education in sustainable water usage are required, and sources of contamination must be eliminated to maintain water quality and supply for future generations. Water must be conserved and managed properly for preservation of biodiversity. Failure to do so will result in the diminution of the capability of the geoenvironment to provide the basis for life support. Various remediation tools have been developed to treat water once it has been contaminated. The choice of any of these techniques requires examination of resource depletion, energy requirements, and emissions—if the aspirations of water sustainability are to be fulfilled.

The record shows that outside of the global distribution of water resources, the two great threats to the availability and quality of water resources (surface water and groundwater) are (1) overuse of the available water resources and (2) contamination of these same water resources. Overuse problem arise from poor management practices and lack of knowledge or ignorance of the nature of the various water budget items and how they contribute to the health of the available water. Control and/or mitigation of the impact of contamination of available water resources from the many contaminant sources are measures that must be undertaken as critical procedures in structuring water sustainability protocols and requirements.

Although implementation of remediation technology to improve compromised or impaired water quality is an admission that management and controls on water resource contamination have failed, it is nevertheless a remedy that needs more attention and research. Development of more capable technology to clean contaminated water resources is necessary—to meet the critical demand for clean water from the consumers. Since aquifers or

groundwater in general serve as primary water resource for many developed and remote communities, it is imperative that protection of groundwater quality be mandated as the first priority by regulatory agencies. This in essence requires (a) attention to the many forces that individually and collectively produce the contaminants that find their way into the groundwater resource and (b) control, treatment, and remediation technology to manage these forces.

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4

Industrial Ecology and the Geoenvironment

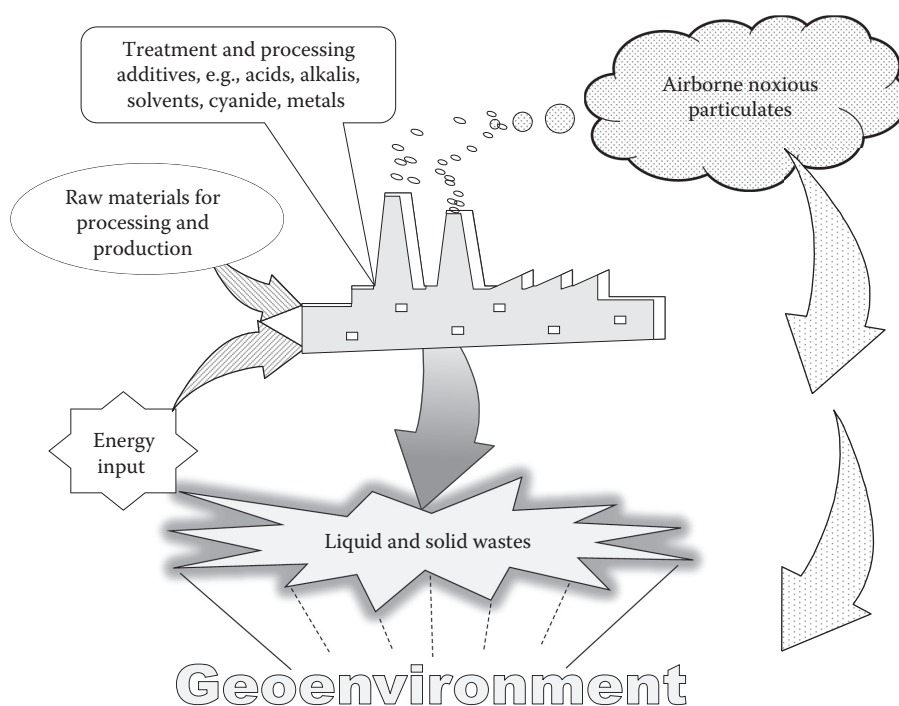
4.1 Introduction

Chapter 1 pointed out that the geoenvironment is an essential resource base that directly and indirectly provides the essential elements of life support for humankind and other living species. The different industries and associated activities undertaken, e.g., agroindustry, mining, forestry, manufacturing, energy, service industries, to respond to the needs and demands of humankind and other living species are therefore dependent on the health of the geoenvironment. Considering *industry* to be the primary driver for the various life-support systems needed to sustain life, it stands to reason that one needs to ensure that activities associated with *industry* do not materially degrade the geoenvironment.

Industrialization, as commonly defined, is the process whereby *industry* becomes a dominant component in a socioeconomic order. The term *industry* is used here in the broadest sense to mean *the work undertaken (in a plant or facility) to produce goods using machines and/or technological aids*. A vital component of industrialization is the group of industries called *manufacturing industries*. These industries are essential to the health of the economy and to the life-support systems of a vibrant society. However, it is contended that many industrial activities conflict with the goals of a sustainable geoenvironment, a contention that arises from the perception that (a) nonrenewable natural resources (materials and energy) are required to fuel the engine of *industry*, (b) nonrenewable source materials are used in the production or manufacture of goods, and (c) the smokestack emissions and discharge of liquid and solid wastes from these industries are harmful to both human health and the environment (Figure 4.1).

There are two particular geoenvironment milestones that need to be observed in respect to *industry* and its activities: (1) exploitation of renewable and nonrenewable natural resources housed in the geoenvironment must be conducted with sufficient prudence so as not to degrade the geoenvironment and also so as to allow future generations to continue to benefit from these resources (see Chapter 1); and (2) the discharge of waste products into the geoenvironment should not cause harm to the geoenvironment (see Chapter 2). In short, one must be conscious of the need to protect the geoenvironment and to ensure that its natural capital continues to be maintained, i.e., the functionality and health of the various constituents, compartments, elements, and units be preserved.

The discussion in this chapter concerns the geoenvironment and its role in the industrial activities mounted to provide for the needs of humankind and other living species. We will consider the interactions on the geoenvironment by activities associated with manufacturing and service industries. Since the purview of this book addresses resource use from the geoenvironment framework and not from the industry perspective, we will concentrate our attention on the land aspects of geoenvironment problems posed by *industry*.

**FIGURE 4.1**

Interactions between manufacturing industries and geoenvironment. Primary issues are energy usage, deposition of smokestack and other airborne noxious particulates, and discharge of liquid and solid wastes.

4.2 Concept of Industrial Ecology

The term *industrial ecology*, which stems from the initial concept of *industrial ecosystems* in a study reported by Frosch and Gallopoulos (1989), utilizes a *systems* approach to environment protection and natural resources conservation as sustainable development objectives in processes involved in industrial production. By treating the industry–environment as an intertwined system, *industrial ecology* focuses its attention on the total picture of (a) renewable and nonrenewable natural resources exploitation and conservation at the one end (front end) of industry activities, (b) efficient industrial production through technology and resource conservation, and adherence to the 4Rs (recycle, recovery, reduction, and reuse of waste products), and (c) environmentally conscious management of emissions and disposal of waste products from industrial activities at the other end. In an ideal world, industrial ecology is a holistic approach to industrial production of goods, i.e., it takes into account the goals of environment protection and resources sustainability, while meeting its goals of production of goods and other life-support systems to the benefit of consumers. These goals fit into the framework geoenvironment protection and preservation/conservation of the natural resources housed within the geoenvironment.

4.2.1 Geoenvironmental Life Cycle Assessment

There are a number of protocols and/or methodologies that have been developed to implement the objectives contained in the concept of industrial ecology. Considering industrial

ecology in respect to the geoenvironment itself, we can regard the majority of these methodologies to stem from the *life cycle assessment* (LCA) of a particular industry or set of industries in question. The idea of using life cycle assessment or life cycle analysis of a particular item (industry, element, product, hardware, etc.) is not new or novel. LCAs are common tools for evaluation of items of interest. They include evaluation of economic costs over the life cycle of a particular piece of equipment or hardware, material, or mass flow over the life cycle, and encountered risks.

In respect to the geoenvironment, and the goals that define a sustainable geoenvironment, the principal focus of *geoenvironmental life cycle assessment* (GLCA) methodologies is the impact of the various activities and products associated with industrial production on the health of the geoenvironment. A good example of how GLCA requires a different perspective of life cycle costing and evaluation is in the field of soil improvement using cementing agents. Soil cement has been used for improving the support capability of a particular piece of ground for over 60 years. It has even been used as a type of low-cost tertiary road in many countries. The problem that one faces is in respect to the geoenvironment and the need to protect its resources. Because of the relative inexpensive nature of the product (soil–cement road production), and because of the apparent facility in producing a soil–cement road, many have been built without much regard for their effective use and durability. The end result of a rapidly deteriorating system of tertiary roads is a highly impacted geoenvironment landscape, i.e., highly degraded soil quality. Restoration of the soil to its original soil functionality requires removal of the cementing agent, and the costs and penalties associated with the restoration must be included in the GLCA. The discussion in Chapter 12 points the way toward a more sustainable means for soil improvement, thereby minimizing and even eliminating adverse impacts on the geoenvironment.

As commonly perceived, the ultimate goal of industrial production is the transformation of raw or source materials into finished goods and products for the benefit of society. The agents or tools for industrial production include manufacturing industries such as upstream, midstream, and downstream industries. Upstream industries produce raw or source materials that feed midstream and downstream industries, such as those discussed in Chapters 5 and 6, to produce their goods as finished products or as inputs or source materials for further downstream industry use. The petrochemical and agroprocessing industries are good examples of downstream industries. The source or raw materials for the petrochemical industries include oil and gas produced or obtained from oil and gas production upstream industries. Similarly, the source (raw) materials for the agroprocessing industries include the products from agricultural and livestock production generated by the upstream agro industries.

For an assessment or analysis of the life cycle of a particular set of products on the health of the geoenvironment, one needs to begin with the upstream phase and end with the final downstream phase. The illustrative example shown in Figure 4.2 for consumer goods involving metal products depicts the various entities that a GLCA would include. Note that insofar as the geoenvironment-related issues for the life cycle assessment are concerned, the illustrated elements in Figure 4.2 deal only with the beginning and “end-of-life” of the consumer product. The individual GLCA of each of the industries and elements involved, beginning with the upstream industry and ending with the landfill itself are not included in the illustration. The GLCA and related discussion for the upstream mining, extraction, and processing industry shown as in Figure 4.2a can be found in Chapter 5, Figure 5.1. The extent of detail that a GLCA could consider can be very short or very long, depending on such factors or issues as magnitude of the project, economics, time, public

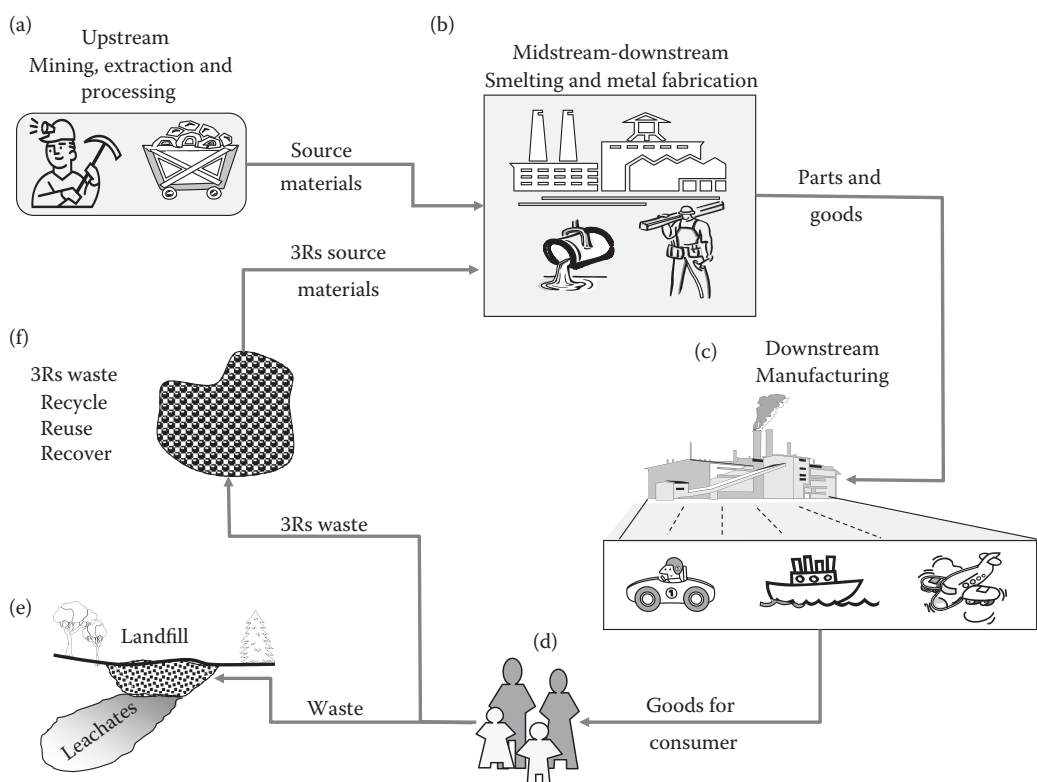
**FIGURE 4.2**

Illustration of life cycle events for consumer goods involving the use of metal products. The start of life cycle is at the upstream end (a), and the end of the cycle is when the consumed product ends up as waste for landfilling (e) or for recycle, reuse, and recovery (f). Note that the individual life cycle events for the various industries, upstream (see Figure 5.1 in Chapter 5) to downstream, are not shown in this figure.

and corporate awareness of issues involved, and anticipated severity of geoenvironmental impact.

4.2.2 Geoenvironment Impacts and Sustainability

In this chapter, we will be examining the dilemma of the apparent antagonistic actions from the activities of manufacturing industries established to meet societal needs in respect to geoenvironmental sustainability indicators and/or goals. The problem reduces to a simple resolution of the required actions needed to accommodate the goals of societal and geoenvironmental sustainability, i.e., the coexistence of societal and geoenvironmental sustainability aims and requirements. A clearer understanding of the interactions between the manufacturing industries and the land environment will allow for management strategies and ameliorative and preventative actions to be implemented. These should serve to promote harmony between societal and geoenvironmental sustainability goals.

The discussion in Chapter 1 has pointed out that almost any external physical/chemical input or external sets of activity in the ecosphere will more than likely have indirect or even direct impact on the geoenvironment and its ecosystems. This is particularly true when it comes to the various activities associated with the midstream and downstream

industries dealing with the manufacture of goods. Included in the group of midstream–downstream industries are (a) life-support industries such as the agro, forest, mining, fisheries, and energy producing industries and (b) production industries producing such varied goods as automobiles, pharmaceuticals, urban infrastructures, etc.

Although strictly speaking, service industries are not considered as downstream industries because they do not produce goods, we include them in the discussions in this chapter because these industries provide services (as goods) to the consumer. Two simple examples of sources of potential geoenvironmental problems from service industries are (1) medical services (e.g., hospitals) and (2) military services (e.g., munitions handling and storage).

The *industry* concerns addressed in this chapter center around *land use in an industrial context*, i.e., land use in the context of activities in development of, and in support of the various kinds of life-support, manufacturing–production, and service industries. The industries discussed in Chapters 5 through 7 will give examples of the interactions of various upstream and downstream industries with the geoenvironment. Since downstream industries are the consumers of the raw goods and products from upstream industries, their interactions with the geoenvironment are more in terms of “what comes out from the processing and transformation end.” The nature and composition of the outputs (airborne noxious particulates, liquid, and solid wastes) will be direct functions of (a) the nature of the product being produced, (b) the nature and composition of the source material used for the production of the product, (c) the process technology and the kinds of treatments and additives used in the process technology, and (d) the various controls on emissions, wastes and wastewaters, treatments, and management of the production technology and system.

Given the wide extent of the various kinds of industries, it is clear that within the context of *geoenvironmental sustainability*, a discussion of all of them would not be possible or desirable. Instead, the examination of the effects of land-use and geoenvironmental management requirements will confine itself to a few representative industries in the three groups of downstream industries. It is important to stress that the terms *effects* and *impacts* are not used in a negative sense. The nature of impacts ascribed to activities and events runs the gamut from beneficial through benign (neutral) to negative, depending on (a) the activity or event and (b) the indicators, markers, and criteria used to evaluate or assess the results of the impact or impacts. Whether impacts from a specific set of activities or events will add to, or subtract value from, the particular ecosystem in the geoenvironment is the question that needs to be answered. It is important to recognize that a comprehensive listing of all the impacts on the ecosystems of the geoenvironment accruing from a particular set of activities is not possible, to a very large extent because of the lack of knowledge of all the various items, activities, and interactions that comprise a functioning ecosystem. Chapter 2 has discussed many of these concerns.

4.3 Upstream, Midstream, and Downstream Industries

The various kinds of industries that exist run the gamut from (a) those that produce raw goods to those that provide finished products to (b) service industries providing a variety of services. As mentioned previously, upstream industries are primarily those devoted to production of the raw materials that need processing and transformation by midstream

and downstream industries before reaching the consumer. Agricultural activities in aid of food production, for example, constitute upstream industrial activities, whereas food preparation and food processing using materials from agricultural activities can legitimately be considered as downstream industries. Downstream industries run the gamut from industries devoted to preparation of source materials as items and parts for manufacturers to transformation into final consumer products. For example, the production of automobiles requires countless numbers of parts such as tires, engines, electronic parts, chassis, side panels, etc. Many of these parts are produced as downstream products by industries devoted to production of vital elements and parts for more intricate products. The following definitions apply:

- Upstream industries are those industries that produce the raw goods and source materials for downstream industries. Examples of these have been given in Chapters 5 and 6. Production of food, i.e., agricultural production of food (wheat, corn, barley, livestock, etc.), and mining and processing of metal ores are good examples of upstream activities and industries. The raw products can be used by the individual consumer and can also be used as resource material for midstream or even downstream industries.
- Downstream industries include (a) those industries that use the raw goods produced by the upstream industries and prepares them as resource material for other downstream industries. Technically speaking, these can be called midstream industries. However, this term is not a popular term. A good example of this is the metal fabrication and processing industry discussed in the next section; and (b) production and assembly plants and industries that produce consumer goods and products that are directly utilized by the individual and collective consumers. These are the industries that transform source materials into consumer goods. Good examples of these are buildings, bridges, automobiles, leather goods, newsprint, electronic products, etc.

The subject of interest in the following sections relates directly to the net effect of the activities associated with these varied types of industries on the geoenvironment. The material covered in these sections will focus on some industries to highlight or demonstrate the particular geoenvironmental land use in question. At that time, we will want to examine some of the major consequences and impacts of these interactions on the geoenvironment, with the aim of seeking solutions that would permit us to satisfy many of the geoenvironmental sustainability requirements.

Figures 1.5 and 1.12 in Chapter 1 show that many of the activities and industries required to provide for human sustenance and needs will have direct interaction with the geoenvironment and will incur major impacts on the geoenvironment. For the purpose of examination of geoenvironmental interaction by downstream industries, we will group them into groups of industries and/or activities associated with the following:

- *Mineral mining and processing industries:* The upstream industries are those that deal directly with extraction of the raw materials required for the metallurgical industries. The downstream mining–processing industries are the metallurgical finishing and manufacturing–production types of industries. Also included are the nonmetal mineral processing industries such as cement production, phosphoric acid production, etc. The GLCA for the upstream industries can be found in the next chapter.

- *Agroprocessing industries:* The various interactions and actions of the upstream agroindustry will be discussed in Chapter 6. Associated downstream industries are generally classed as agroprocessing-type industries. These are the industries that transform the products from the agricultural, forestry, and fisheries industries. The two general categories are (1) food industries and (2) nonfood industries.
- *Hydrocarbon, hydro, and other energy resources:* Other energy sources include biomass, hydrogen, solar, geothermal, wind, and tidal. Electric power generation and distribution for the non-hydro power systems fall somewhere in-between upstream and downstream depending on the type of energy resource being harvested. The major downstream industries are the various kinds of petrochemical industries. It is probably safe to say that downstream utilization of the products from this group of upstream industries is perhaps the largest of any of the categories of geoenvironmental resource usage.
- *Production of goods and facilities:* These are the downstream industries that transform the products issuing from upstream industries such as hydrocarbon extraction, agricultural products, and metal ore production. The products from these downstream industries are either further transformed by other downstream industries or used directly by individual consumers.
- *Public and private services:* We classify these kinds of services as industries and as downstream industries even though they do not necessarily deliver hard goods to the consumer. The delivery of services, as goods, requires facilities and use of technology and goods that in one way or another will interact with the geoenvironment. The effects or results of these interactions need to be examined.

4.4 Mineral Mining and Processing Downstream Industries

For convenience in discussion in this section, it is understood that when we use the term *industry* this will mean *downstream industry*.

4.4.1 Metallurgical Industries

The detailed treatment of resource extraction and processing associated with mineral mining and processing of the raw earth and rock materials as upstream industries can be found in Chapter 5. For this section, we want to outline the essential items for those downstream industries established to process the metal ores, obtained from the upstream industries, that directly or indirectly impact on the geoenvironment. From the illustrative example shown in Figure 4.2 of the industries associated with mining-extraction and processing as upstream and downstream types of industries, it is noted that the *midstream-downstream* industries in the upper right corner of Figure 4.2 can be classified as either midstream or downstream industries, depending on whether the products from these industries serve as source materials for other downstream industries or whether the products directly serve the individual consumer. A good example of this is the *parts* industry, i.e., the industries that produce products such as parts and elements for other industries that will assemble the parts and elements into consumer goods (assembly plants or industries). Note that midstream industries become downstream industries when their

goods or products serve the individual consumer directly. An example of this from the diagram shown in Figure 4.2 is the production of metal consumer goods. Most reports on these industries are satisfied with the distinction between upstream and downstream types, and in general, these would be sufficient to encompass all the activities engaged in the exploitation and use of the products obtained from mining. However, the nature of the impacts on the geoenvironment can be vastly different depending upon whether it is a midstream industry that produces or prepares parts for use by other downstream industries or a downstream industry that concentrates on consumer production goods. For example, the impacts from contaminants that find their way into the geoenvironment from the metal fabrication and processing midstream industries can be more significant than in the production and assembly of their counterpart downstream industries.

Metallurgical industries cover a vast variety of processes depending on the final product issuing from the industry in question. The common practice of classifying these industries into three kinds of industries in relation to the material source used in the process and product produced, allows one to conveniently group the kinds of interaction of these industries with the geoenvironment. The midstream–downstream industries represented in the top right-hand corner drawing (Figure 4.2b), for example, are intensive users of energy. The foundries produce smoke stack emissions that are sources of (a) acid rain generation and (b) land environment contamination when noxious airborne particulates find their way onto the solid land environment. The use of wet scrubbers and/or dry collectors can reduce harmful discharge of noxious gases and airborne particulates. Some of the discharges for foundries producing steel and aluminum include the various heavy metals such as lead, zinc, manganese, chromium, arsenic, iron, nickel, and copper. For many other industries, in addition to the heavy metals, we will have a variety of organic chemicals included in the hazardous air pollutants (HAPs). A listing of many of these can be found at <http://www.epa.gov/ttn/atw/188pols.html> (USEPA 2013).

4.4.1.1 Metal Fabrication and Processing

Typical metal fabrication and processing midstream–downstream industries are those that produce value-added metals and metal goods. The types of metals include iron, aluminum, copper, lead, zinc, gold, tungsten, tin, silver, cadmium, etc., and are produced in a variety of forms. These serve as downstream products or as resource material for other downstream industries. Some of the downstream industries in this present category include (a) metals finishing industries, e.g., electroplating, anodizing, and coatings and (b) industries and assembly plants utilizing metals for production of goods, e.g., manufacture of automobiles, planes, trains, ships, ovens, refrigerators, and tin cans, to name a few.

Interactions between downstream industries and the geoenvironment are primarily in respect to energy resources needed to satisfy the energy requirements of the industries, and the handling and disposal of the waste discharges, including the inadvertent spills and overflows during processing, manufacture, and production. The demands for energy in downstream industries, especially those in the category of material preparation and finishing, are of considerable concern in the overall strategy to reach the sustainability indicators that define the sustainability goals in the energy resource field. The next chapter discusses many of these concerns and strategies. Increased efficiency in manufacturing and production technology can alleviate some of the demands on energy use in these kinds of industries.

The metal finishing industries use a significantly large proportion of toxic chemicals in their various processes to produce, for example, corrosion resistance, wear resistance,

electrical resistance, hardness, chemical resistance, and tarnish resistance metals. Figure 4.3 gives an example of the processes associated with metal fabrication. The sources of solid and liquid waste discharges are seen in the diagram. Most of the chemicals used in the metals finishing business end up as wastes. Considering that the various inputs to the processes include acids, solvents, alkalis, cyanide, loose metals, and complexing and emulsifying agents, it will not come as a surprise to note that the waste discharge and wastewaters can contain these chemicals and various other residues, especially since many of the processes include rinsing and bathing operations. These wastes predominately result from the use of (a) organic halogenated solvents, ketones, aromatic hydrocarbons, and acids during the surface preparation stage of the overall finishing process and (b) cyanide and metals in the form of dissolved salts in the plating baths during the surface treatment stage. These will all be found in the discharge streams shown in the bottom right of the diagram in Figure 4.3, as sludge, solid waste, and wastewater.

In the pig iron production process, the flue dust generated is captured by wet dust cleaners. In common with most of the typical metal finishing processes shown in Figure 4.3, steel finishing involves a number of necessary processes in the production of the desired surface and mechanical characteristics for the steel. The sulfuric acid used in most pickling processes creates hazardous by-products. Pickling solutions contain free acids, ferrous sulfate, undissolved scale and dust, and the various inhibitors and wetting agents as well as dissolved trace elements. The concentration of acids and their types largely depend on the type of iron being produced. Finishing operations generate effluents containing rolling oils, lubricants, and hydraulic oils that are in free and emulsified states. Other oils

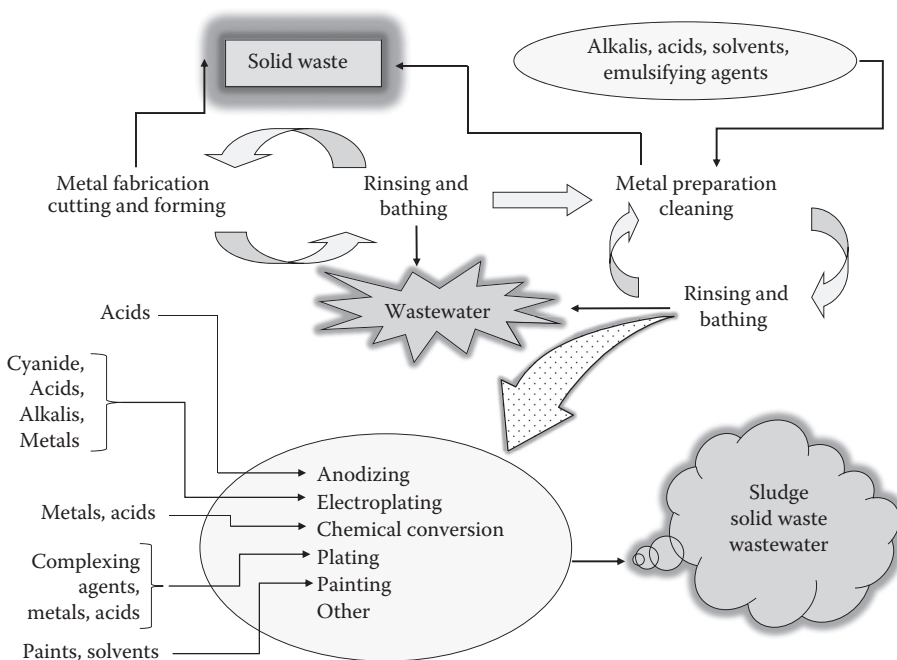


FIGURE 4.3

Processes and waste products generated in metal fabrication and preparation. (Adapted from EPA, *Profile of Metal Products Industry*, Washington, DC, Office of Enforcement and Compliance Assurance, 1995.)

found in the effluents can also originate from cold reduction mills, electrolytic tin lines, and a variety of machine shop operations.

Water leaving the wet dust cleaners usually contains anywhere from 1000 to 10,000 mg/L of suspended solids, depending upon the furnace burden, furnace size, operating methods employed, and type of gas washing equipment. Disposal of these onto the land environment will require treatment and containment to minimize ground, groundwater, and receiving water contamination. Some of these aspects will be discussed in Section 4.4.3 when sustainability targets are considered. The more detailed treatment will be found in Chapter 9.

4.4.2 Nonmetal Mineral Resources Processing

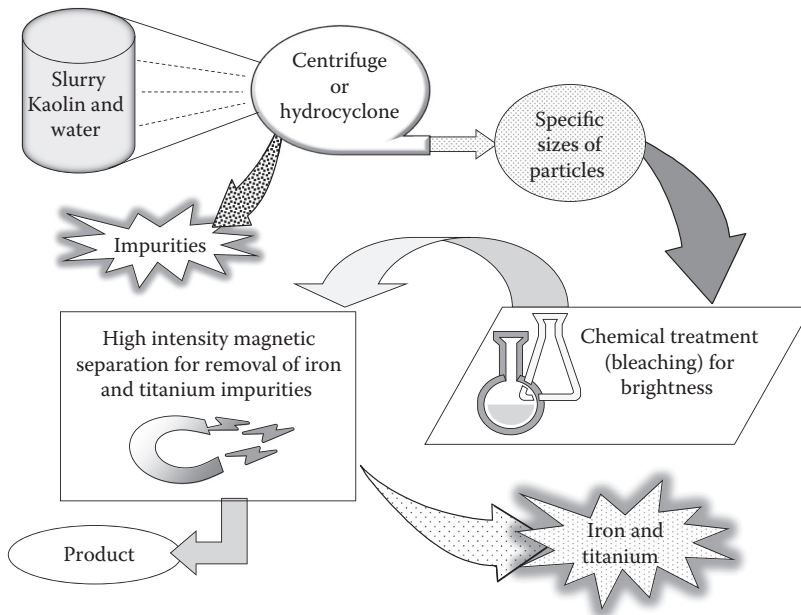
Nonmetal mineral resources include (a) clays and clay minerals, (b) crushed stone, (c) sand and gravel, (d) dimensional rock slabs such as granite and marble slabs, (e) phosphate, (f) potash, (g) gypsum, (h) peat, (i) sulfur, (j) diamond, (k) vermiculite, and natural alkali. Examples of utilization of the minerals supplied by upstream mining and processing industries include

- *Clays*—for pottery and ceramics industries; construction industries involved in the construction of roadway fills, embankments, and clay-engineered barriers
- *Clay minerals*—for paper coatings in paper industries, as catalysts for chemical industries; as expandable slurry materials (bentonites) oil exploration industries and also construction industries
- *Crushed stone, silica, sand, and gravel*—glass industries, smelting industries (silica used as flux material) concrete production industries, bituminous concrete industries, cement industries, construction industries
- *Dimensional slabs*—construction industry

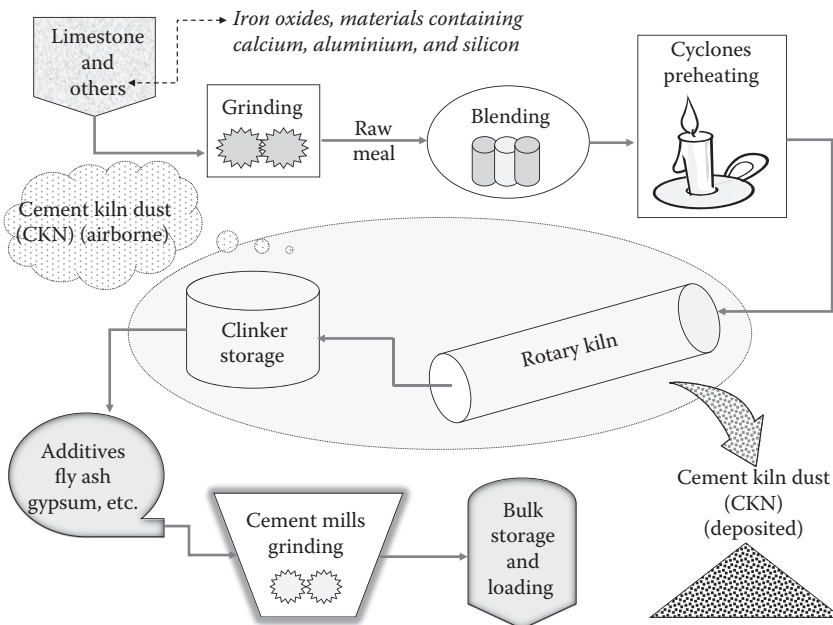
The two minerals chosen as examples to illustrate the geoenvironmental interactions of activities of downstream industries transforming nonmetal minerals obtained from upstream mining–extraction industries are the kaolin clay mineral and limestone. Figure 4.4 shows the principal steps taken to produce coatings-grade kaolin for use as kaolin-based coating pigment for the paper industry or in other industries such as latex and alkyl paints and primers. The process is not energy intensive in comparison to the metal industries and cement production industries and the discharges from the processing technique can be controlled. These discharges are the clay impurities and the iron and titanium “impurities” that are generally associated with kaolinites. The iron and titanium can be captured and reused for other applications. Insofar as geoenvironmental interactions are concerned, this downstream industrial activity is relatively benign.

The use of limestone for production of cement is shown in a simplified schematic in Figure 4.5. In respect to geoenvironmental interactions, two significant factors are evident: (1) intensive energy consumption attends almost every step of the production procedure, especially in the cyclones preheating stage and in the rotary kiln, and (2) discharge of fugitive cement kiln dust (CKN) as airborne particulates and as land discharge from electrostatic precipitators (ESPs) and other kinds of scrubbers, etc.

The significant human health issues attending the emission of CO₂, NO_x, SO₂, dioxins, and furans cannot be ignored. For example, the release of metals into the atmosphere by copper-Ni refining, fossil fuel combustion, and iron manufacture in the northern former

**FIGURE 4.4**

Production of coatings-grade kaolin using the hydrous procedure. Note that the discharge of impurities needs to be managed to ameliorate the impact on the geoenvironment.

**FIGURE 4.5**

Basic elements in manufacture of cement. Fugitive cement kiln dust (CKN) from the rotary kiln and clinker storage elements of the process will be airborne and captured CKN from scrubber systems will be deposited on land.

TABLE 4.1

Release of Heavy Metals through Effluent Discharge, Emissions, or Waste Disposal from Selected Industries

Industry	Heavy Metals Released
Fossil fuel combustion (electricity)	As, Cd, Hg, Pb, Sb, Se
Mining, smelting, metallurgy	As, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Ti, Tl, V, Zn
Petroleum refining	As, Co, Cr, Cu, Ni, Pb, V, Zn
Pulp and paper	Co, Cr, Hg, Ni, Pb

USSR has contributed up to 90% of the metal loading in the European Arctic – a very sensitive environment (Pacyna, 1995). Arsenic (As), Cd, Pb, and Zn emissions in this region contribute 4.5%, 2.4%, 3%, and 2.4%, respectively, of the global emissions. Wet and dry deposition of the metals with sulfuric acid has resulted in the accumulation of the metals in the soils, surface waters, and sediments. Acid rain enhances the environmental mobility of the metals and the bioavailability of these heavy metals. These metals may also bioaccumulate in the foods in the food chain, thus endangering the health of the consumers. Seabirds, seals, and polar bears have shown elevated levels of As, Cd, and Hg from ingesting fish and shellfish that eat contaminated algae, and plankton that accumulate heavy metals from sediments. Kansanen and Venetvaara (1991) have shown that lichens and mosses are effective bioaccumulators of heavy metals.

In 1995, more than 2 million tonnes of materials with heavy metals were emitted from a Ni-Cu smelter in Siberia. Reports indicate that the population suffers from respiratory illnesses. The precipitation of the materials in the areas has killed the lichens that affects the grazing reindeer (Klein and Vlasova, 1992). The affected area has extended up to 70 km in the SSE direction. Heavy metals may also be discharged from industrial effluents into rivers, ponds, lakes, lagoons, wetlands, and oceans. Metals generated by various industries are shown in Table 4.1. Mercury has been particularly problematic. Fish such as swordfish are known as hyperaccumulators of Hg. Fish samples in the Smithsonian Institute contain up to 500 ppb of Hg, the limit permissible by the WHO. In Lake Ontario, Hg was been found in fish exceeding this level in the early 1970s. Hg reached the lake as a result of industrial discharges.

4.4.3 Land Environment Impacts and Sustainability Indicators

The indicators that define or establish the path toward sustainability goals are specific to the activity and/or industry under consideration. One needs to define or identify the various processes or activities that impact directly or indirectly on the geoenvironment. This can be a very detailed accounting of all the activities and their outcome or could be a broad sweep of the major categories, elements, or issues. The basic elements that contribute directly as land environmental impacts for most of the types of downstream industries considered in this section (shown in Figure 4.1) include (a) deposition of airborne noxious particulates, (b) acid precipitation provoked by smokestack emissions of SO_2 and NO_x , (c) wastewater and other liquid waste discharges, and (d) solid wastes and other disposable solids. The composition, distribution of the various components in the wastes and particulates, and nature of the discharges are all functions of the type of process technology, technological efficiency, smokestack emission control, “housekeeping” efficiency, and waste management capabilities and strategies.

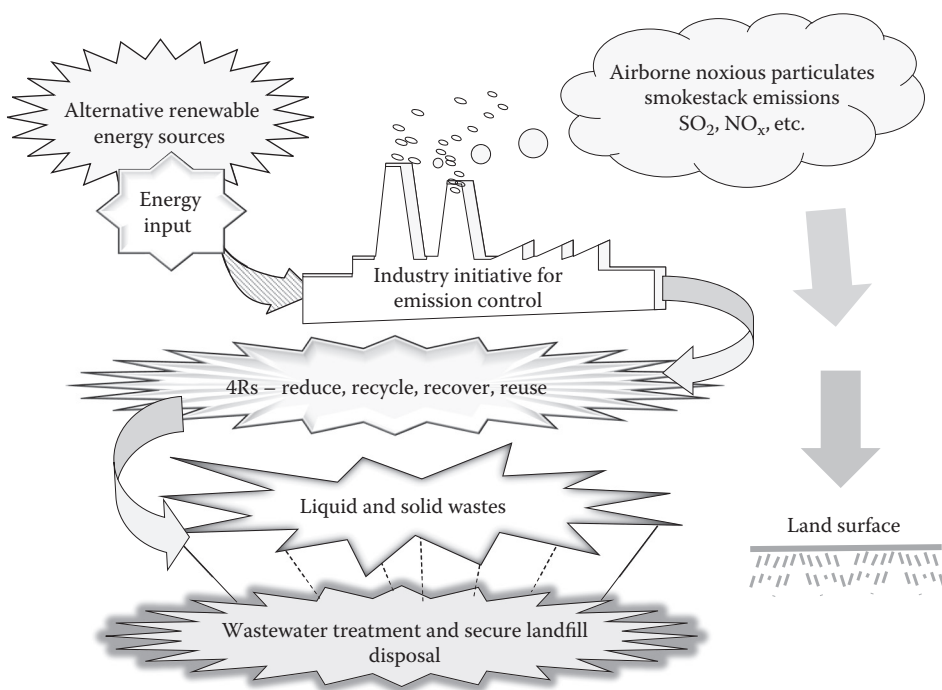
Acid precipitation impact on the surface of the geoenvironment (including the receiving waters contained in the land environment) is felt in several ways:

- a. Soil quality: The increased soil acidity will release metal ions and other positive ions bound to the soil particles, and also the structural ions such as aluminum. The mechanism for such release is found in the ionic bonds formed between the charged soil particles surfaces and the positive ions (metals and salts such as Ca^{2+} , K^+ , Na^+ , and Mg^{2+}). The sulfate and nitrate ions from acid precipitation act as counterions and have the effect of releasing the sorbed cations. Weathering of the silicate minerals will release the structural metals such as aluminum, manganese, and iron. The release of the salts Ca^{2+} , K^+ , Na^+ , and Mg^{2+} will result in nutrient depletion for plant growth and the release of aluminum especially will be harmful to aquatic life and plant growth.
- b. Biology of the forest: Reduction in rates of decomposition of the forest floor, damage to roots and foliage, changes in respiration rates of soil microorganisms.
- c. Water quality and aquatic habitats: Acidification of lakes and rivers, deposition of soil-released aluminum, species destruction, and alteration of food supply for higher fauna.

Other not so evident land environment impacts from the mining-processing downstream industries are (a) use of nonrenewable mineral resources as source material for the downstream industries and (b) excessive use of nonrenewable energy resources to drive the various processes in production of the final product. Except for the aggregate and slab production industries, metal mining and processing downstream industries, and the cement producing industries are heavy users of energy. Until alternative renewable energy resources become more available, these industries impact directly on the land environment when land energy resources are used to fuel their many process requirements. Cement kilns are perhaps the best potential users of alternative energy sources using recycled or recoverable materials. Because of the high burn temperatures required in the cement kilns, municipal biowaste, and various kinds of combustible solid and liquid wastes can be used as burn energy sources.

Land environment sustainability objectives of direct relevance to the metal mining and processing downstream industries are (a) preservation or minimal use of nonrenewable energy resources, (b) preservation or minimal use of metal–mineral resources, (c) elimination of smokestack emissions and airborne noxious particulates, and (d) 4Rs and nontoxic and nonhazardous discharge of liquid and solid wastes. Figure 4.6 shows some of the elements that can serve to drive downstream industries toward sustainability goals. Industry initiatives are needed for many of the elements shown, e.g., (a) better control on smokestack emissions and airborne particulate discharge to eliminate deposition of particulates and generation of acid precipitation, (b) more efficient use of metal–mineral resources to produce more “yield,” (c) the use of the 4Rs (reduce, recover, reuse, and recycle) strategy as part of the process efficiency technology, and (d) use of alternative renewable energy sources to aid in reduction of consumption of nonrenewable energy resources. Chapter 9 gives a brief discussion of these initiatives. A full treatment of these industry initiatives is not within the purview of this book. There exists much concern and interest in the development of these initiatives, and without a doubt, much is being done by industry to resolve these issues.

The direct connections between the impacts shown in Figure 4.6 and the geoenvironment are seen in terms of contamination of the land and water elements of the geoenvironment.

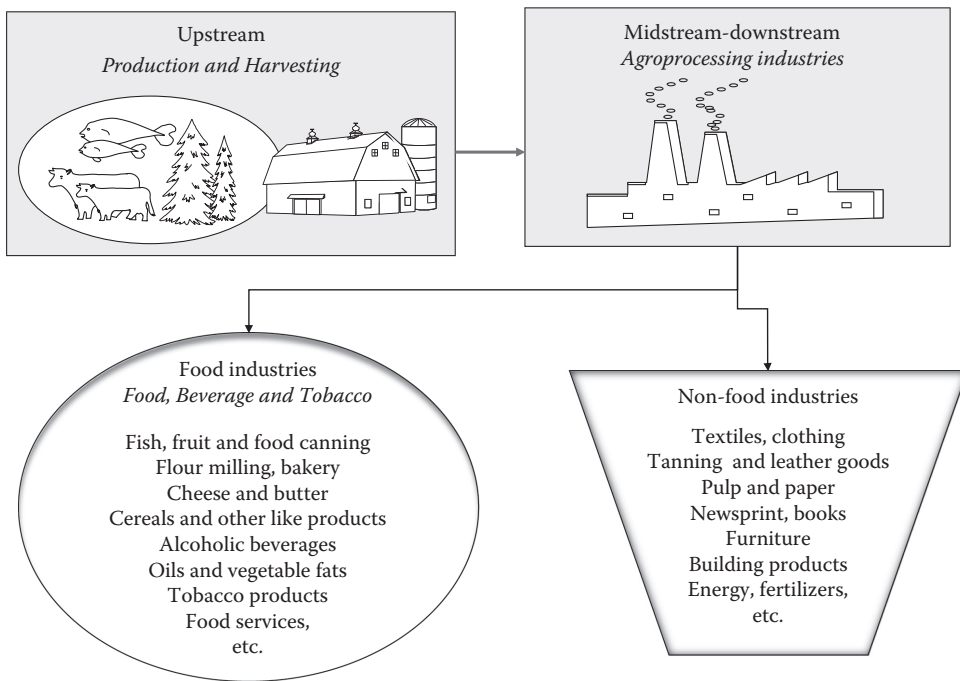
**FIGURE 4.6**

Industry initiatives for amelioration of geoenvironmental impacts.

Amelioration of the contaminant loads and protection of the land environment are necessary requirements to ensure and maintain the quality of the land and water elements of the geoenvironment. The sustainability goals for these land environment elements are (a) maintenance of the quality of the land environment and the receiving waters, (b) protection of biodiversity and natural habitats, and (c) protection of the natural (e.g., biotic and organic) and geoenvironmental (e.g., mineral and energy) resources in the region of consideration. The procedures and protocols in respect to impact minimization, avoidance, and amelioration are developed in Chapter 10, together with considerations and requirements for remediation and management.

4.5 Agroprocessing Industries

Agroprocessing industries are the group of industries that form part of the larger group identified broadly as *agroindustry*. We can conveniently divide the agroindustry into two categories: (1) agricultural production (farming), including crops and livestock (upstream industries), and (2) agroprocessing industries, including midstream and downstream industries, which can be grouped into *food* and *nonfood* industries (Figure 4.7). Details of the agricultural production industries and their relationship to the geoenvironment

**FIGURE 4.7**

Various types of midstream–downstream agroprocessing industries.

have been covered in detail in the previous chapter dealing with *Agricultural-Based Food Production Geoenvironment Stressors*. The agroindustry covers many sectors, ranging from production of the raw farm goods (e.g., crops and livestock as will be discussed in Chapter 6) to the processing and production (i.e., transformation) of end-use products, including such consumables as cheese, bread, cotton fabrics, leather goods, etc.

One of the major sources of stressors on the geoenvironment from agricultural production is the waste derived from livestock and dairy farming. Management of manure waste from livestock can be in the natural discharged form or as a liquid. The latter form of manure management—i.e., liquid manure—is seen as a major source of methane (CH_4) emission. Disposal of the natural discharged manure is most often on the land surface, thereby creating chemical stressors that will impact on soil and groundwater quality. The discussion on these stressor impacts and geoenvironmental engineering measures for management of these impacts can be found in Chapters 6 and 10.

Midstream industries deal with initial processing of products for manufacture and production from upstream agroindustries. Their products are utilized by downstream industries dealing with manufacture and production of final or finished goods. Forestry and forest products are included in the agroindustry category. The downstream industries associated with forest products include all the wood products such as pulp and paper, furniture, etc. Although the use of agents such as pesticides, fungicides, herbicides, and fertilizers is a major part of regular and intensive agricultural practices, the industries involved in the manufacture of these agents are not included in the agroprocessing or general agroindustry classification. Instead, these will be considered in the grouping of *petrochemical and chemical industries*.

4.5.1 Leather Tanning Industry

The leather tanning industry, in a sense, has an unique position in the food and nonfood agroprocessing industries in that it has to rely on the availability of an animal source for its raw material. The different kinds of leathers produced from raw hides and skins are functions not only on the production process, but also of the source material, i.e., the animal species. The variety of source material include (a) cattle, sheep, pigs, and horses for hides and (b) reptile, crocodile, snake, etc., for the more exotic leathers. The size of the total industry, together with the range in sizes of the industries and variety of raw materials (animal species) devoted to production of hides and leathers, requires one to pay attention to the impacts on the geoenvironment in the processing of the raw material into product form (see Figure 4.8). The estimates are that about 2 billion m² of leather are produced a year with a market value of about \$40 billion. When some of the leather material is processed into consumer goods, for example, leather footwear, where it is estimated that about 65% of the 2 billion m² is utilized, the market value of the produced footwear is in the order of about \$150 billion. There is an interesting counter argument that states that production of leather is in effect an environmental conservation effort since it removes the burden of disposal of the hides and skins of slaughtered animals.

There is intensive use of water mixed with various additives during the beamhouse process shown in the upper portion of Figure 4.8, and also in the many other processes accompanying tanning and fat liquor and finishing. The additives and aids used in the diverse

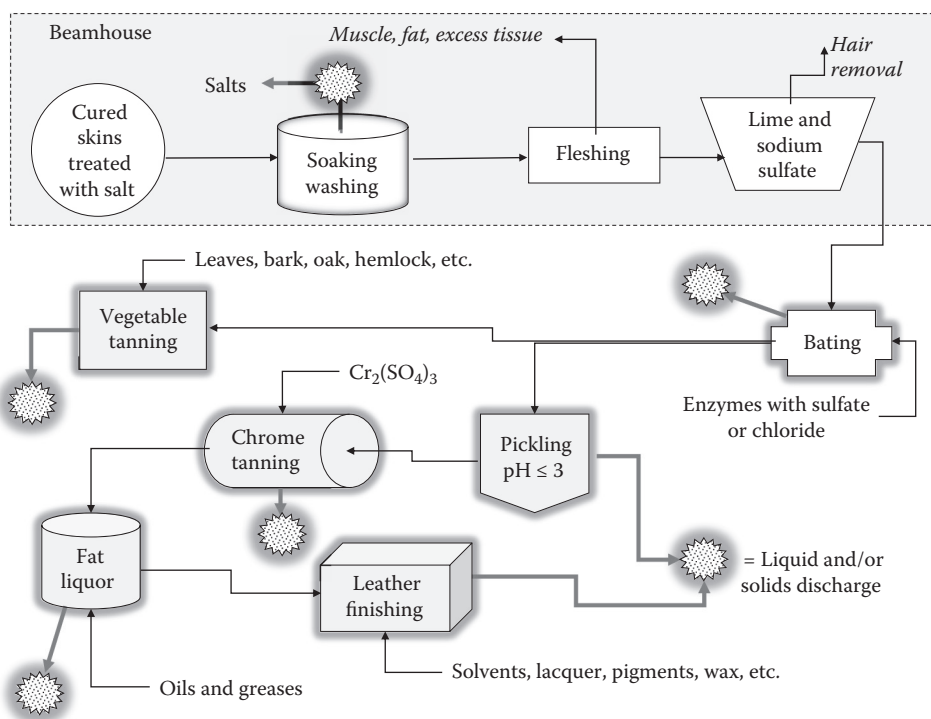


FIGURE 4.8

Major processes in leather tanning. The process used to remove hair and the outer protein layer from hides is called *bating* (middle right-hand process shown in the diagram). Note: Additives and aids used in the various processes and also the many discharge points denoted by the broader arrows.

processes include lime, sodium sulfate, enzymes, tannin, sulfuric acid, ammonium salts, sodium bicarbonate, linosulfate, trivalent chromium salts, pigments, dyes, resins, formaldehyde, glutaraldehyde, and heavy oils. The liquid discharge—i.e., wastewater—from the various processes has been reported to be from 20 to 80 m³/t of hide treated. The composition of the wastewater contains many of the additives and aids described in the preceding, with high levels of chromium, sulfide, chloride, BOD, and COD. It has been reported that residues of pesticides from hides have been found in the wastewaters, and because of the removed fats, unwanted tissue, muscle, hair, skin, and other body meat items, the solid wastes containing the decaying and decayed body parts pose severe human health threats. The treatment, handling, and disposal of the liquid and solid wastes are problems that must be addressed satisfactorily if impact on the geoenvironment is to be avoided. These will be addressed in Chapter 10.

4.5.2 Pulp and Paper Industry

Wood industries supply building materials, cellulose fiber, resins, and other pulp chemicals, and pulp and paper products. By far, the supply of building materials and pulp and paper products constitute the major portion of the overall wood industries. There is general agreement that the many thousands of pulp and paper industries in the world, when taken as a whole, constitute one of the largest contributors to water, land, and air pollution problems in the locations of those industries. Figure 4.9 shows a simplified flow diagram

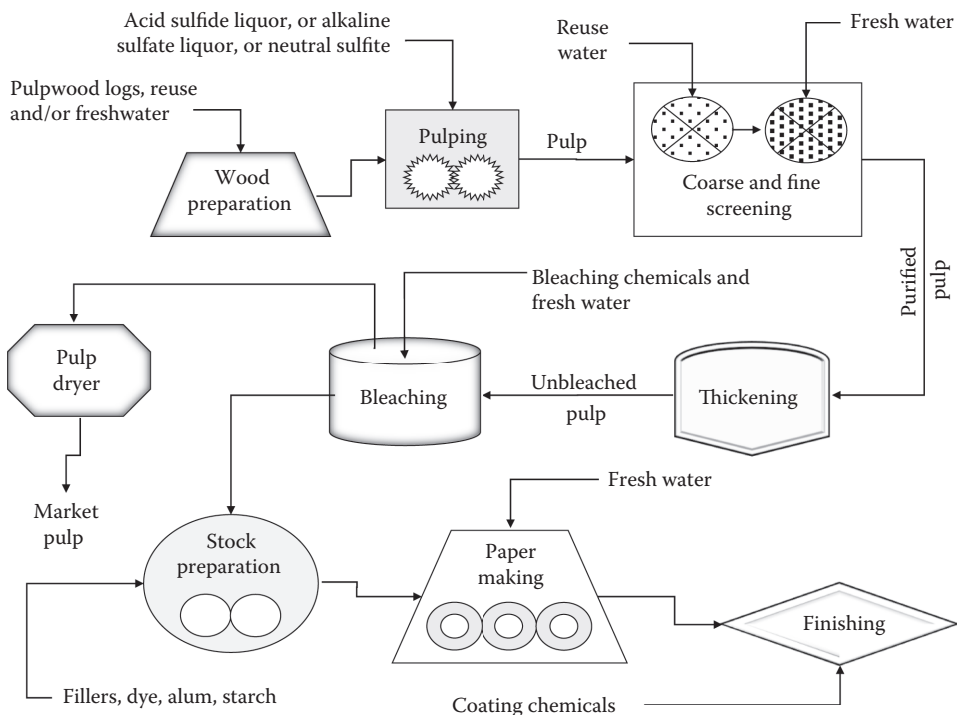


FIGURE 4.9

Simple flow diagram showing typical pulp and paper processes. Note inputs into the various processes and the extensive use of freshwater for many of the processes.

for typical pulp and paper processes. Debarking and chipping are the major operations in the *wood preparation* process. Recovery of the removed bark for subsequent use as fuel has reduced the waste discharge while decreasing energy costs. The pulping and bleaching processes contribute the more significant impacts to the geoenvironment. The various means for pulping range from mechanical, thermomechanical, and chemical. The most frequently used process is the Kraft process, i.e., the sulfate process. This chemical process (sulfate process) is not to be confused with the sulfite pulping process, which is becoming less popular as a process because the source wood species (spruce, balsam, fir, and western hemlock) are not as plentiful as the other species used for the kraft process. This kraft process generates sludges high in chromium (Cr), lead (Pb), and sodium (Na).

The various processes shown in Figure 4.9 require considerable amounts of energy input and extensive use of freshwater. Recycled water, identified as whitewater, is used to augment the water input to the coarse screening, bleaching, and wood preparation processes. For the fine screening—washing and paper machine processes, freshwater is required. Other inputs into the different processes include acid sulfite liquor, alkaline sulfate liquor and neutral liquor, chlorine-type bleaching chemicals such as hydrogen peroxide, ozone, peracetic acid, sodium hypochloride, chlorine dioxide, and fillers, dyes, alum, starch, and paper-coating chemicals. The wastewater discharges from the many processes include pulping liquor, mill washings and acid plant wastes, solvents and chlorine-based organic bleach compounds, and general wastewaters. The organochlorines discharged in the wastewater and solid wastes present some difficult toxic issues to the biotic receptors in the immediate geoenvironment. Discharged mill wastewater in the rivers causes considerable breeding problems to several types of aquatic species. Solid wastes discharged include sludges from secondary treatment plants containing inks, dyes, pigment, boiler ash, chemical processing, and waste fiber wastes including organochlorines (if chlorine has been used in the bleaching process).

4.5.3 Palm Oil Industries

Although palm oil industries may be considered as belonging in the larger group of vegetable and oilseeds processing industries, its variety of transformed products have greater application. The grouping of vegetable and oilseeds include palm, soybean, rapeseed (canola), sunflower, and cottonseed. As agroprocessing industries, palm oil industries fit into both the food- and nonfood-producing agroindustries—with application in food industries as production of nonhydrogenated and refined oils, shortening and margarine, and broad application in nonfood industries such as chemical, cosmetic (personal care), and pharmaceutical. Food industries are grouped into two kinds: (1) production of nonhydrogenated and refined oils and solid fat products (e.g., margarine, shortening, nondairy ice cream, specialty fats, chocolate) for human consumption and (2) production of animal feed (palm kernel cake and palm kernel meal) from the by products. Nonfood industries are wide ranging, from industries devoted to production of (a) personal care products (cosmetics) such as creams, soaps, and moisturizers, to (b) chemical products using epoxidized palm to produce polyurethanes and polyacrylates and palm methyl esters, glycerol, and fatty acids as source materials to produce a variety of products ranging from a diesel substitute to plasticizers. Harvesting of the palm fruit bunches and milling belong to the upstream industry category. The output from the mill is sent to the downstream refining plant and further on to the manufacturing or production plants (e.g., chemical, cosmetic, pharmaceutical).

The two different kinds of oils or fats extracted from the palm fruit come from two separate sources: (1) palm oil from the outer portion of the fruit and (2) palm kernel oil from the kernel. Refinement of crude palm oil to refined oil is required to remove the moisture

and impurities, and other items such as the oxidation products, free fatty acids, and carotenoids. The two methods for refinement include physical (steam) and chemical (alkali) refining processes. Fatty acid distillate and refined bleached and deodorized palm oil are obtained from the physical process, and soap stock, and acid oil together with the refined, bleached, and deodorized palm oil are obtained with the chemical process. Separation or fractionation into liquid and solid phases is performed by thermomechanical means.

The major areas of concern in respect to geoenvironment impacts are (a) energy consumption in the refining processes, (b) excessive water consumption, and (c) effluent and solid waste discharge. It is estimated that effluent discharge (palm oil mill effluent POME) is from two to three times that of the amount of palm oil processed. Since the discharge contains organic compounds, these can have some severe consequences on the receptors in the area of discharge.

4.5.4 Land Environment Impact and Sustainability Indicators

Land environment impacts from the upstream phases of the various sectors comprising the agroindustry (production of raw goods and source materials) will be discussed in Chapter 6. The indicators and impacts discussed in Section 4.4.3 for the metallurgical industries apply equally well to the agroprocessing industries. What has been omitted from a discussion on the impacts in the upstream agro industries and from that section is the effect of a monoculture on the land environment and the ecosystem. Survival of the natural indigenous species is often difficult, especially since it is common practice to use integrated pest management to enhance the growth of the monoculture species. Loss of soil quality and impact on biodiversity are some of the more prominent impacts.

4.6 Petrochemical and Chemical Industries

The use of inorganic and organic chemicals as source materials for downstream industries brings with it the problems of control of production operations and management of discharges during operations and discharges as waste products. There are three groups of industries that use chemicals as source materials. These include (a) petrochemical industries that work with organic chemicals, (b) chemical industries that use inorganic chemicals as their feedstock, and (c) pharmaceutical industries that use both inorganic and organic chemicals as source material. We should also note that pharmaceutical industries use a wide variety of source materials in addition to inorganic and organic chemicals. The interactions of pharmaceutical industries with the geoenvironment are not considered in this section.

4.6.1 Petrochemical Industries

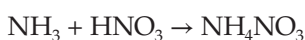
Petrochemical industries constitute the bulk of the chemical (inorganic and organic chemicals) industries in the world. The overwhelming portion of organic chemicals is derived from feedstock obtained from: crude oil, natural gas liquids, and coal. The two major processes involved in obtaining organic chemical feedstock are (1) chemical reaction and (2) purification of reaction products (USEPA, 2002). The simplest chemical reaction process is obtained in the batch reaction method where chemicals used to obtain the desired reactions and products are introduced into a reaction vessel. At completion of the reaction

process, the reaction products obtained are removed from the vessel and extraneous by-products and unreacted inputs removed (USEPA, 2002). This step is identified as product separation or purification. The techniques used involve filtration, distillation, and extraction either singly or in combination. The continuous reactions method, as the procedure implies, is a continuous reaction process technique and is suited more for greater production of reaction products, in comparison to the batch reaction method, which is used for production of smaller quantities of reaction products. As in the case of the batch method, the reaction products of the continuous reaction technique require product separation.

The feedstock obtained includes alkanes, benzene, butane, butadiene, butylenes, ethane, ethylene, methane, propane, propylene, toluene, and xylene. The feedstock organic chemicals are both end-use products and also intermediate chemicals, i.e., they serve as feedstock for production (generally by conversion processes) into other end-use organic chemicals or products. Typical end-use products include the various pesticides and fertilizers used in agriculture, the various forms and types of plastics, textiles, solvents, detergents, pharmaceuticals, appliances, synthetic lubricants, nylon, plumbing, and even chewing gum. By and large, the various kinds of plastics are perhaps the largest and most important product group emanating from petrochemical industries.

4.6.2 Chemical Industries

By definition, inorganic chemical industries manufacture chemicals that do not contain the carbon molecule. To a large extent, the feedstock or raw materials for the inorganic chemicals are mineral in origin and the products manufactured are acids, alkalis, salts, and chemicals that are used as aids in producing other products, especially fertilizers. Ammonium nitrate (NH_4NO_3), ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$), urea ($\text{CO}[\text{NH}_2]_2$), and superphosphates are some of the fertilizers manufactured. The processes involved for production or manufacture of the fertilizers, for example, vary depending on the type of fertilizer. Neutralization of nitric acid (HNO_3) with ammonia (NH_3) will yield ammonium nitrate (NH_4NO_3) through the simple reaction



Meanwhile, there are at least three different ways or sources to obtain ammonium sulfate (USEPA, 1979). These include (a) combining anhydrous ammonia and sulfuric acid in a reactor to obtain synthetic ammonium sulfate, (b) as a by-product from production of caprolactam $[(\text{CH}_2)_5\text{COHN}]$, and (c) as a coke oven by-product obtained by reacting ammonia from coke oven offgas with sulfuric acid.

The acids produced are to a large extent mainly utilized as intermediates in industrial and manufacturing activities. The fertilizer industry is a big beneficiary. Nitric acid (HNO_3) and sulfuric acid (H_2SO_4) contribute significantly to the production of ammonium nitrate and phosphate, respectively. Hydrochloric acid (HCl) is used in steel pickling, etching and metal cleaning, and hydrometallurgical production.

Perhaps one of the largest groupings of inorganic chemical industries is the chlorine-alkali group. This group produces chlorine, sodium hydroxide, sodium carbonate and bicarbonate, and potassium hydroxide. Their products are greatly utilized as intermediates in the organic chemical manufacturing industries (USEPA, 1995) ranging from (a) vinyl chloride monomer, ethylene dichloride, glycols, chlorinated solvents, and methanes for chlorine and (b) propylene oxide, polycarbonate resin, epoxies, synthetic fibers, soaps, detergents, and rayon for caustic soda. The raw or source material for the industry is both natural salt deposits and

seawater. Removal of the impurities such as calcium, iron, aluminum, sulfate, magnesium, and trace metals is required before the electrolysis process used to obtain the end product (chlorine, caustic soda, and hydrogen). The three types of cells used in the electrolysis processes for the manufacture of the products are mercury, diaphragm, and membrane.

4.6.2.1 Stressors and Impacts on Geoenvironment

The major areas of concern for land environment protection are similar to the other industries described in the previous sections. These areas are (a) deposition of smokestack (point) and fugitive (from process equipment, leaks, and spills) emissions of particulates and noxious substances including SO_x and NO_x , (b) discharge of wastewater and fugitive process waters, and (c) solid wastes. The nature of the chemicals, especially the organic chemicals, makes it critical to monitor both the acidity and chemistry of precipitations. For example, ammonia (NH_3) and nitric acid (HNO_3) have been recorded as emissions from processing for ammonium nitrate. NO , NO_2 , and SO_2 have been detected as emissions from plants producing HNO_3 and H_2SO_4 , respectively.

Wastewater from petrochemical industries manufacturing organic chemicals will contain excess chemicals (spills?), hydrocarbons, and other dissolved solids in suspended form. Also included are the wastewaters from maintenance procedures and washing of equipment. These would likely contain solvents, lubricants, and detergents. In the case of the inorganic chemical manufacturers, corresponding wastewater discharges will be obtained, except that the surplus chemicals will be inorganic chemicals. Maintenance and cleaning procedures will supply wastewater that would also contain lubricants and detergents and perhaps some solvents.

Land disposal of waste materials would generally be in a sludge form since raw materials and manufacturing processes generally do not involve solid materials. Brine muds are perhaps the greatest "solid" wastes derived from the chemical industry. These are obtained from the chlorine-alkali industry and are regularly disposed in brine mud ponds in a manner similar to the holding ponds of the mining-metal industries.

4.6.3 Land Environment Impacts and Sustainability Indicators

The impacts to the land environment from the emissions, discharges, and land disposal of the waste items are in general similar to those for the other industries described in the previous sections. The only significant difference in the case of petrochemical and chemical industries is the added chemical nature of the various emissions and discharges. The record shows that utilization of proper scrubber systems together with stringent wastewater treatment procedures have served to reduce the levels of impact to the land environment. Indicators of proper sustainability of the land environment are obviously zero threat emissions and discharges.

4.7 Service Industries

Service industries do not necessarily create tangible goods or products. By definition, they are industries that create or provide services to the consumer. The major service industries include (a) health (all aspects of medical, dental, and social services), (b) military, (c) educational, (d) government, (e) technical, and (f) financial. Because they do not really create

goods, the interactions among these industries and the geoenvironment are limited to the operational or fugitive discard of liquid and solid items associated with the service and the “tools of the trade.” Military services, for example, present an added dimension to the composition of waste streams. This relates to waste products associated with munitions and the storage and use of ammunitions. A major feature of the decommissioning of military sites is the decontamination of sites contaminated by all of these. The bulk of the discards and wastes generated by the large service industries can be classified as “institutional” wastes. This category includes the paper discards and general housekeeping items. The exception to the preceding will be the health service industry. The problem arises from services associated with the care of patients in hospitals.

4.7.1 Hospital Wastes and the Geoenvironment

Outside of the regular “housekeeping type” of waste products such as paper consumables and kitchen waste, hospitals generate wastes that classify under the category of hazardous, toxic, and infectious wastes. The contributors to these are the biomedical, radioactive, and chemical–pharmaceutical wastes. The sources for biomedical wastes include biological, medical, and pathological. Contributors to these are services associated with surgery, pathology, biopsy, laboratories, and autopsy. For the radioactive wastes, the sources include X-ray discards, liquid scintillation vials, and all other treatment procedures and equipment utilizing radioactive materials. Sources of chemical–pharmaceutical wastes include research laboratories, pathology, and histology.

The record shows that among hospital wastes, infectious biomedical wastes pose the greatest threat to human health. Management and disposal of these wastes to the land environment are critical issues. Special regulations have recently been structured by most State Regulatory Agencies concerning hospital wastes in general and infectious wastes in particular. Sorting, storage, transportation, treatment, disinfection, and incineration are some of the principal steps in the handling and disposal of these infectious wastes. Liquid infectious wastes are required to be treated before discharge and only noninfectious and nonanatomical wastes are permitted to be disposed of in landfills. Unhappily, technical and economic constraints may deny full and safe–secure disposal of these wastes.

4.8 Energy Production and the Geoenvironment

The sources of energy are of two distinct types: (1) nonrenewable and (2) renewable. The main nonrenewable source of energy is fossil fuels (hydrocarbons and coal). Another notable source of nonrenewable energy is uranium, used in the production of nuclear energy. Renewable energy sources, by definition, refer to those sources that are sustainable such as solar, wind, ocean (tidal and wave), geothermal, osmosis, and biomass. The discussion in this section deals with the impacts arising from stressors generated by the use of the nonrenewable and renewable resources in energy production.

4.8.1 Fossil Fuel Energy Production

The primary sets of concerns associated with energy production industries relying on fossil fuels can be grouped into three categories: (1) mining, drilling for extraction of the

fossil fuel (source material), and delivery of the fuel, (2) conversion of the source material into energy, i.e., energy production, and (3) transmission of the energy to the consumer (infrastructure). The discussion on the stressors and their impacts, generated from extraction of the resource, can be found in the next chapter, which deals with nonrenewable resources extraction and their stressors and impacts. The sources of stressors that will generate adverse impacts on the geoenvironment from the mining and drilling operations include mine drainage, discards and spills from mining operations, and waste streams. There are textbooks devoted to mining, petroleum, and coal mining operations and technologies, which the reader should consult for detailed discussions on how these types of industries operate.

4.8.1.1 Geoenvironment Stressors

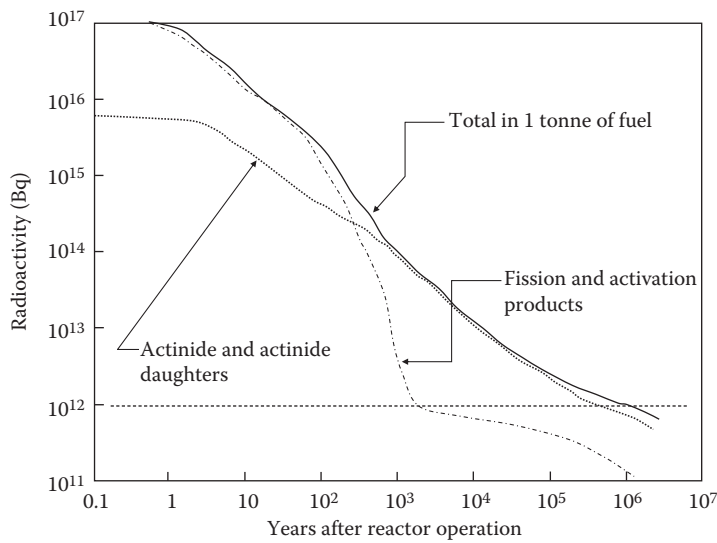
By and large, the sources of stressors associated with fossil fuel energy production can be traced to

- *Operations required in conversion of source material to energy:* The sources of stressors for energy production are essentially similar to most manufacturing–production industries, i.e., the sources are mostly related to processing, manufacturing, and production operations, with differences in composition, quantities, and quality of the discharges and spills attending each type of industry (discussed in Section 4.9 and in Chapters 5 and 6). Spills, discharges of liquid, and solid wastes constitute the major sources of stressors to the geoenvironment. Treatment and disposal technologies constitute the main elements of a sustainable geoenvironment strategy (see Chapter 10).
- *Transmission and delivery of fossil fuel, including land transport systems such as trucking, railways, and pipelines:* Assuming that the infrastructure for vehicular (trucks and trains) land transport systems are already in place, outside of the various geoenvironment-related aspects associated with construction of pipelines for transmission of liquid hydrocarbons, the main source of stressors in respect to *transmission–delivery* appears to be spills and inadvertent discharges arising from vehicular and pipeline accidents and transmission–delivery operations. These constitute major sources of chemical stressors contaminating the land compartment of the geoenvironment.

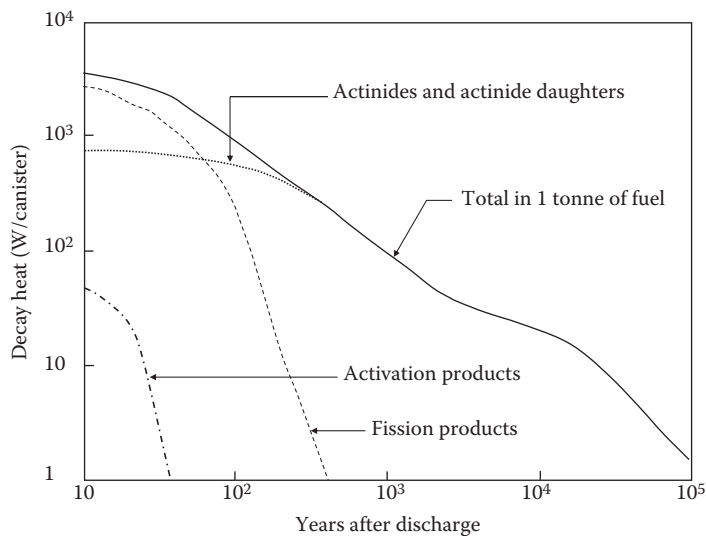
4.8.2 Nuclear Energy

The case of nuclear energy production is somewhat unique in that considerations and accounting for interactions with the geoenvironment must include the time factor as a big issue. The problem of disposal of high level radioactive waste is of considerable concern in that one needs to take into account: (a) the level of radioactivity of the spent fuel (high level radioactive waste), (b) the heat of the spent fuel, (c) the time required for the level of radioactivity of the spent fuel to reach acceptable limits, as shown in Figure 4.10, i.e., below threshold levels for exposure to humans, and (d) the time required for the heat to dissipate and to reach ambient temperature levels, as shown in Figure 4.11 (Yong et al., 2010; Pusch et al., 2011).

Figure 4.10 shows the time–decay relationship for changes in radioactivity of the fuel rods given in units of becquerel (Bq) with a burnup of 38 MWd/kg (megawatt days per

**FIGURE 4.10**

Level of radioactivity of spent nuclear fuel with a burn-up of 38 MWd/kg U as a function of time after reactor operation, i.e., after removal from active service. (Adapted from Hedin, A., *Spent Nuclear Fuel – How Dangerous Is It?* SKB Technical Report, 97-13, 1997.)

**FIGURE 4.11**

Reduction in decay heat in the spent-fuel canisters in relation to time after removal from operation. (Adapted from Swedish Nuclear Fuel and Waste Management Company (SKB), *Deep Repository for Spent Nuclear Fuel, SR97 – Post-Closure Safety*, SKB Report TR99-06, Main Report, Vol. 1, 1999.)

kilogram). Initial radioactivity is by fission and activation products. This activity decays rapidly after 100 years. Further activity appears to be contributed primarily by actinides and actinide daughters. The horizontal line shown at a radioactivity level of 10^{12} Bq represents the radioactivity for eight tonnes of natural uranium with daughters. The half-lives of uranium 235 (^{235}U), ^{236}U , ^{238}U , and iodine 129 (^{129}I), which are 7.0×10^8 , 2.3×10^7 , 4.5×10^9 , and 1.6×10^7 years, respectively, tell one, for example, why disposal or safe containment of the burned-up fuel rods is a special type of management problem for geoenvironmental engineers. It is useful to note that if one establishes a reduction in radioactivity level to the one matching natural uranium deposits (10^{12} Bq level) as the required containment level of security, this would require at least 100,000 years of “safe” containment isolation.

In addition to the problem of radioactivity, one needs to look at the heat generated by the decay heat, which is the residual power or the heat generated in the fuel after cessation of operation (Figure 4.11) in relation to the time after cessation of operations. As can be expected, the fission and activation products contribute to the heat in the canister in the first 100 plus years, after which time, the main contributor to the total heat is from the actinides and actinide daughters. The discussion of containment of these radioactive wastes can be found in Chapter 10.

4.8.3 Alternative Energy Sources and the Geoenvironment

The pursuit of alternative energy sources or means to produce energy without reliance on nonrenewable fossil fuels such as coal and hydrocarbon resources has gained considerable attention among those concerned with two principal issues: (1) generation of greenhouse gases (GHG) from present fossil fuel energy-producing plants that have been faulted for contributing directly to “global warming” and also from the means to procure the fossil fuels themselves and (2) the need to conserve nonrenewable hydrocarbon resources, i.e., using renewable natural resources. The types of industries or efforts mounted to generate energy for the consumer have earned the nickname of *green energy sources*, with the related name of *green energy production*. The proper designation is *alternative energy sources*, with the term *alternative* meaning *alternative to coal and hydrocarbon resources (fossil fuels)*. Some of the alternative energy production-type industries are hydroelectric, solar, geothermal, biomass, osmotic, wind, and ocean (tidal and waves). Strictly speaking, solar, geothermal, ocean, and wind are *nondepleting energy resources*—meaning that they are *always there*, and do not really undergo renewable processes over any specified period.

The concerns in respect to the land compartment of the geoenvironment and in regard to the sources of stressors from the use of these types of energy resources are not as severe as with the nonrenewable resource types of energy production. In common with the other types of energy production systems, the sources of geoenvironment stressors are from construction of the production systems and also from the construction and delivery of the harvested energy (transmission system). The various geoenvironment stressors are thought to be mostly physical in nature.

4.9 Contaminating Discharges and Wastes

Table 4.2 gives a very short summary of many of the contaminating substances and chemicals found in the geoenvironment as a result of deliberate discharges, spills, leaks,

TABLE 4.2

Typical Composition of Discards, Spills, and Waste Streams from Some Representative Industrial Activities and Industries

Industry	Discards, Spills, and Waste Streams
Metal manufacturing and finishing	Acids, bases, cyanide, reactive wastes, heavy metals, ignitable wastes, solvents, spent platings, oil and grease, emulsifying agents, particulates, polishing sludges, scrubber residues, complexing agents, wastewater treatment sludges
Agroindustries (food and nonfood)	Acids, bases, sulfides, chromium, hides, skins, suspended solids, pesticides, solvents, chlorine compounds, waste (fiber) sludge, dyes, pigments, kaolin clay sludge
Petrochemical and chemical industries	Acids, bases, ignitable wastes, heavy metals, inorganics, pesticides, reactive wastes, solvents, lubricants, spent catalysts, spent caustic, and sweetening agents, organic waste sludges
Hospitals—medical facilities	Biomedical wastes, infectious wastes, acids, bases, radioactive materials, solvents, heavy metals, ignitable wastes

emissions, and disposal of liquid waste and solid waste materials from the downstream service industries. For the processing and manufacturing industries, the discharges come during the processing and manufacturing stages. These include (a) inadvertent losses of raw and intermediate products and materials utilized during processing and manufacturing and (b) liquid and solid waste products associated with processing and manufacturing procedures and technology. Acids, bases, heavy metals, inorganics, organic chemicals, and solvents are common to the industries shown in Table 4.2. Many of the inorganics are composed of chemical compounds that do not contain carbon as the principal element. Most of the inorganic compounds are stable and soluble in water. They tend to have rapid chemical reactions and large numbers of elements. They are generally less complex than the organic chemical compounds. Other more specialized wastes include pesticides, herbicides, and the like, solvents, cyanides, reactive wastes.

Other than general wastewater, liquid waste streams emanating directly from downstream industries can be grouped in four categories: (1) aqueous–inorganic, including brines, electroplating wastes, metal etching, and caustic rinse solutions; (2) aqueous–organic, including wood preservatives, water-based dyes, rinse water from pesticide and herbicide containers, organic chemical production, etc.; (3) organic, including oil-based paint wastes, production of pesticides, herbicides, fungicides, spent motor oil, cleaning agents, refining, and reprocessing wastes, etc.; and (4) high-solid-content and high-molecular-weight hydrocarbon sludges.

In respect to managed liquid and solid wastes in landfills, there are two types of liquid plumes or streams that emanate from the wastepile in the landfill. The first type, which is identified as *primary leachate*, consists of the liquid waste originally submitted to the landfill combined with dissolved constituents in the wastepile. The primary leachate may be aqueous–organic, aqueous–inorganic, or organic. Leachate generated from water entering into the wastepile is defined as *secondary leachate* and is generally composed of the percolating water and solutes from dissolution products in the wastepile. This leachate may be aqueous–organic or aqueous–inorganic or a combination of inorganic and inorganic solutes and compounds in the liquid phase. Since it is not really possible to distinguish between the two kinds of leachates when they exit from the bottom and/or sides of a landfill, the general term *leachate* is used, with no attempt at categorization. The predominant liquid in a leachate may be water, an organic liquid, or a combination. The solutes and inorganic and organic chemicals in the leachate are the products of the dissolution of the materials in

the waste pile. The relative abundance of a given dissolved component is a function of the composition of the principal liquid. Neutral nonpolar organic liquids will have large carrying capacities, and will easily carry other neutral nonpolar organic chemicals. Aqueous liquids have very limited carrying capacity and will not be capable of carrying nonpolar organics in its dissolved phase. Water, meanwhile, has a relatively large carrying capacity for polar organic chemicals (they may be miscible in each other in all proportions) and for inorganic acids, bases, and salts.

4.9.1 Physicochemical Properties and Processes

Water is the carrier for contaminants in the subsoil. The movement and distribution of the various contaminants in the soil depend not only on the hydrogeological setting, but also on the interactions between the contaminants carried in the liquid phase and the soil fractions. Many of these interactions have been described in Chapter 2 as transport processes. In this section, we will look at the physicochemical properties and processes involved when the kinds of contaminants listed in Table 4.2 are introduced to the geoenvironment.

4.9.1.1 Solubility

The amount of solutes needed to reach a saturated state in a given quantity of solvent at a specific temperature is defined as the solubility of the given solvent. For considerations of ionic equilibrium in aqueous solutions, the solutes are those that fall into the class of sparingly or slightly soluble ionic solids. We define the *solubility product* k_{sp} as the equilibrium constant for the equilibrium that exists between the sparingly soluble ionic solid and its ions in a saturated solution. Because of the significant electrostatic attraction between ions, crystals composed of small ions packed closely together are generally harder to pull apart than crystals made up of large ions. For example, fluorides (F^-) and hydroxides (OH^-) are less soluble than nitrates (NO_3^-) and perchlorates (ClO_4^-).

Solubility equilibria are useful in predicting whether a precipitate will form under specified conditions, and in choosing conditions under which two chemical substances in solution can be separated by selective precipitation. Substances that are more soluble are more likely to desorb from soils and less likely to volatilize from water. Meanwhile, substances with no hydrogen bonding groups or little polar character, such as hydrocarbons or halogenated hydrocarbons, usually have very low solubilities compared with compounds such as alcohols, which are capable of interaction with water. The solubility of an organic compound depends primarily upon the sorption–desorption characteristics of the sorbate (organic compound) in association with the sorbent (soil and sediment).

4.9.1.2 Partition Coefficients

Partition coefficients were described in Chapter 2. They provide a measure of the distribution of a given inorganic contaminant—between sorption onto the soil solids and the porewater. For organic chemicals, the octanol–water partition coefficient is used to describe partitioning. The *octanol–water partitioning coefficient* (k_{ow}), which has been defined in Chapter 2 as the ratio of the amount of a solute dissolved in octanol and water in octanol–water immiscible mix. k_{ow} is well correlated with the solubility of several organic chemicals. Log k_{ow} values normally range from -3 to 7 . Highly water-soluble compounds such as ethanol, have values of $\log k_{ow} < 1$, and hydrophobic compounds, such as certain PCBs and chlorinated dioxin congeners, have values of 6 to 7 .

4.9.1.3 Vapor Pressure

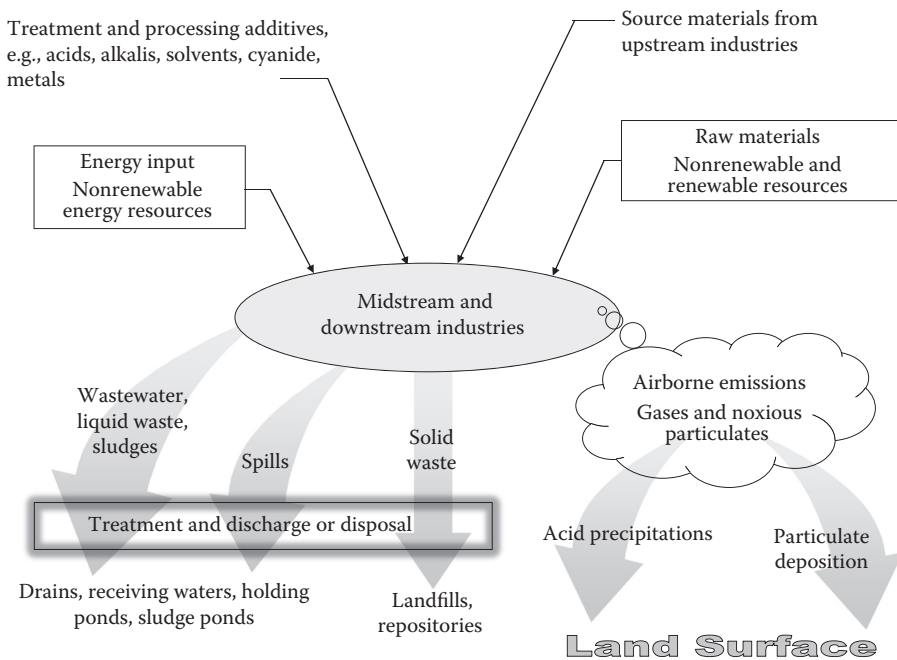
The vapor pressure of a liquid or solid is the pressure of the gas in equilibrium with the liquid or solid at a given temperature. Gasoline, for example, will evaporate rapidly since it has a high vapor pressure and is very volatile. Volatilization is a significant factor in disposal for compounds with vapor pressure greater than 10^{-3} mm Hg at room temperature. Chemicals with relatively low vapor pressures and high solubility in water are less likely to vaporize and become airborne. The transport of a compound from the liquid to the vapor phase is called volatilization. This could be an important pathway for chemicals with high vapor pressures or low solubilities. Evaporation depends on the equilibrium vapor pressure, diffusion, dispersion of emulsions, solubility, and temperatures.

4.10 Concluding Remarks

The concept of industrial ecology is very powerful—if implemented to its fullest extent. The idea that industrial activities should not only be cognizant of the need to protect the environment (and in this case, the geoenvironment) and to conserve the natural resources (both renewable and nonrenewable), but also to devise and incorporate strategies and technologies that would serve these purposes, is most refreshing and forward-looking. To that end, the use of life cycle assessment is a powerful tool. One can track all kinds of information in respect to the production and delivery of the set of goods used by the consumer. It is particularly useful in *sustainable geoenvironmental engineering practice* directed toward the application of *geoenvironment protective technology*, i.e., technology designed to protect the geoenvironment. The discussion in this chapter is designed to show the reader the importance of protection of the natural capital of the geoenvironment—from initial harvest or procurement of the resource to final manufacture—production and delivery of the consumer goods of interest. In addition, it also points out that the responsibility for protection of the geoenvironment lies with the consumer—through conservation of resources and disposal of consumed goods.

To implement the basic concepts of industrial ecology from a geoenvironment perspective, one is required to determine the connections or interactions between downstream manufacturing industries and the geoenvironment. In particular, one needs to determine the geoenvironment stressors generated from the various sources in these industries. For manufacturing and other kinds of downstream industries, the major areas requiring detailed scrutiny include (a) use of nonrenewable resources as energy input and also as raw materials for the industries, (b) spills and debris, together with liquid and solid waste discharges, and (c) gaseous and noxious particulate airborne emissions.

Figure 4.12 gives a schematic of what one might call *common denominator descriptors* for the industries and their interaction with the geoenvironment. The various input and output items shown in the schematic are common to most of the midstream and downstream industries. Although the geoenvironment perspective developed in this book does not consider industry manufacturing and processing technology, the use of nonrenewable resources as raw materials and as energy sources impact directly on the mandate of industrial ecology, and must therefore be identified as issues that need resolution. The issues of direct concern in this chapter in respect to the land compartment of the geoenvironment are shown in the bottom half of the diagram shown in Figure 4.12—identified by

**FIGURE 4.12**

Common denominator descriptor identifying interactions between midstream–downstream industries and geoenvironment. Although all the descriptors shown are central to determination of industrial ecology and sustainability indicators, the mandate for this book does not cover industry technology for manufacturing and processing (top half of diagram). The geoenvironmental concerns are directed to the issues identified in the bottom half of the diagram.

the broad arrows leading to the bottom of the diagram. From a geoenvironment perspective, the main points that require attention in establishing geoenvironment sustainability indicators as a step toward assessment of capabilities to attain geoenvironmental sustainability objectives have been stated in the preceding paragraph. These are grouped into (a) resource utilization and (b) discharges.

The discussions and examples given in this chapter have focused principally on the discharges since these are the agents—i.e., stressors—that come directly in contact with the geoenvironment. In discussing the various processes in this chapter, and in showing the diagrams for some of the processes, some appreciation of the many sources of interactions with the geoenvironment and the kinds of stressors generated can be gained. In the final analysis, these all fall into the *discharge* group of *points for study*. In the bottom half of Figure 4.12, the interactions with the geoenvironment are given as

- *Wastewater and liquid spills*: These are treated before discharge into receiving waters. The concern is in regard to whether treatment is capable of removing all the noxious and toxic substances.
- *Liquid wastes and sludges*: As noted in Table 4.2, these consist of inorganic and organic chemicals and also inorganic and organic sludges. Disposal of these in the geoenvironment is generally performed by constructing holding ponds or various kinds of secure containment ponds. Escape of these contained liquids or sludges

into the subsurface environment will pose problems to the environment and to human health and other biota.

- *Solid wastes*: These are contained in waste landfills and in underground repositories. Leachates generated can escape into the subsurface and can pose health and environmental threats.
- *Airborne emissions*: Gaseous and noxious particulates pose problems when they return to the land surface under gravitational forces and through rainfall and snowfall. The classic problems of acid rain are clear demonstrations of the *return* to land surface.

It is clear that the primary issues in respect to the discharges are the interactions of the inorganic and organic chemicals with the subsurface geological material. Chapter 2 has given a brief overview of these interactions in the context of contaminant–soil interactions. These interactions are fundamental elements that govern the transport and fate of these inorganic and organic chemicals in the ground. We will examine these further in the context of the material developed in this chapter and the previous chapters. Chapters 9 and 10 consider most of these issues in terms of land environment impacts and geoenvironmental sustainability indicators.

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5

Natural Resources Extraction: Stressors and Impact Management

5.1 Introduction

The *geoenvironmental natural capital*, which refers to the natural resources and processes, such as the biogeochemical cycles in the geoenvironment, that have or provide value to humans, can be considered to comprise two major categories: (1) renewable natural resources and (2) nonrenewable natural resources. Renewable natural resources include living resources, such as forests, plants, wildlife, marine and other aquatic species, etc., and “nonliving” resources, such soil and water. Biodiversity, as a natural resource (see Section 1.2.2) is not within the purview of this book and is therefore not included in this discussion of the natural capital in the geoenvironment. The basis for classification as a renewable natural resource is the ability of the resource to regenerate, replenish, or renew itself within a period from onset of initial resource harvesting to onset of repeat harvesting. It follows that if the resource is allowed to regenerate itself fully in the “between-harvest” period, it can be viewed as a sustainable resource. Failure to do so will render the renewable natural resource into the sub category of *exhaustible (renewable) natural resource*. In reality, most of the renewable natural resources that are exploited or harvested are exhaustible. Their ability to remain inexhaustible—i.e., sustainable—is dependent on proper exploitation–management of these resources.

The prominent nonrenewable natural resources include minerals and fossil fuels (coal, oil, and gas). The discussion in this chapter will be confined to industrial activities associated with the extraction or harvesting of nonrenewable mineral, nonmineral, and (energy) natural resources (e.g., uranium, oil sands). The materials that constitute these resources are extracted or harvested by primary upstream industries devoted to such activities as mining, excavation, fracking (rock fracturing and extraction of hydrocarbon product), mineral and hydrocarbon extraction, processing, drilling, and pumping. The outputs from these upstream industries are raw materials for their respective midstream or downstream industries (see Chapter 7).

Resource extraction and processing industries use the geoenvironment as a resource pool containing materials and substances that can be extracted and processed as value-added products. The common characteristic of the industries in this group is *processing of material extracted from the ground*. The sources of stressors, the types of stressors, and their impacts discussed in this chapter include

- Mineral–metal mining industries. Worldwide production is in the order of 1.4 billion tonnes/year for iron ore and 2700 tonnes/year of gold in 2011 according to the U.S. Geological Survey (Menzie et al., 2013). Metal extraction increased by 20% from 1980 to 2000 (Chamley, 2003). Some developed countries in Europe and Japan have completely depleted their underground resources.

- Industries involved in extraction and processing of other resources from the ground such as nonmetallic minerals (potash, refractory and clay minerals, phosphates).
- Industries devoted to the extraction and/or production of aggregates, sand, and rock for the building–construction industry and for the production of cement.
- Raw energy industries such as the extraction and recovery of uranium for the nuclear power generation industry and those industries involved in the extraction of hydrocarbon-associated materials such as the oil sands and extraction of shale gas and tight oil.

5.2 Stressors and Impacts

To institute geoenvironmental engineering practices to limit, mitigate, or prevent deleterious impacts on the geoenvironment—i.e., sustainable geoenvironmental engineering practices—it is necessary to determine the sources and types of stressors that are likely to act on or in the geoenvironment. In the case of the geoenvironment, stressors are agents (forces, stresses, processes, etc.) that are responsible for actions that impact on a particular piece of the geoenvironment. These nature or types of stressors can be physical, mechanical, hydraulic, or thermal, and can include processes that are chemical, physicochemical, and/or biogeochemical in nature. Knowledge of the sources and their related stressors allows one to determine not only the types of impacts but also the ultimate fate of the impacted body.

It is impossible to describe in detail the manner of operation of the different types of industries—not only because of their diverse natures, but also because of the different models for operational efficiency and success. The discussions presented in this and all remaining chapters in this book will only provide some of the main basic elements of operation of some of the industries involved, together with some of the main sources of stressors and their likely stressor-impacts. It is not the intent, nor is it feasible, to document a complete list of stressors and their impacts—not only because it is not realistically feasible, but also because not all the impacts are impacts on the geoenvironment. The later sections in this chapter will provide information on the nature of the impacts on the geoenvironment together with suggestions as to how these impacts can be mitigated or managed. Activities mounted in conjunction with harvesting of energy resources such as the development of oil-producing wells, natural gas wells, extraction of bitumen from oil sands, dams, and hydroelectric facilities, also contribute their share to the potential impacts list. Not all the potential impacts are directly due to the discharge of wastes and contaminants in leachate streams or wastewaters. The discussion in this chapter will focus primarily on the mineral and nonmineral (including oil sands) mining and processing upstream industries, and industrial activities dealing with underground in situ hydrocarbon extraction, i.e., industries dealing with exploitation of nonrenewable natural resources.

5.2.1 Mining-Related Activities

Activities associated with the mining, extraction, and on-site processing of extracted natural resource material (mineral and nonmineral) contribute significantly to the inventory of

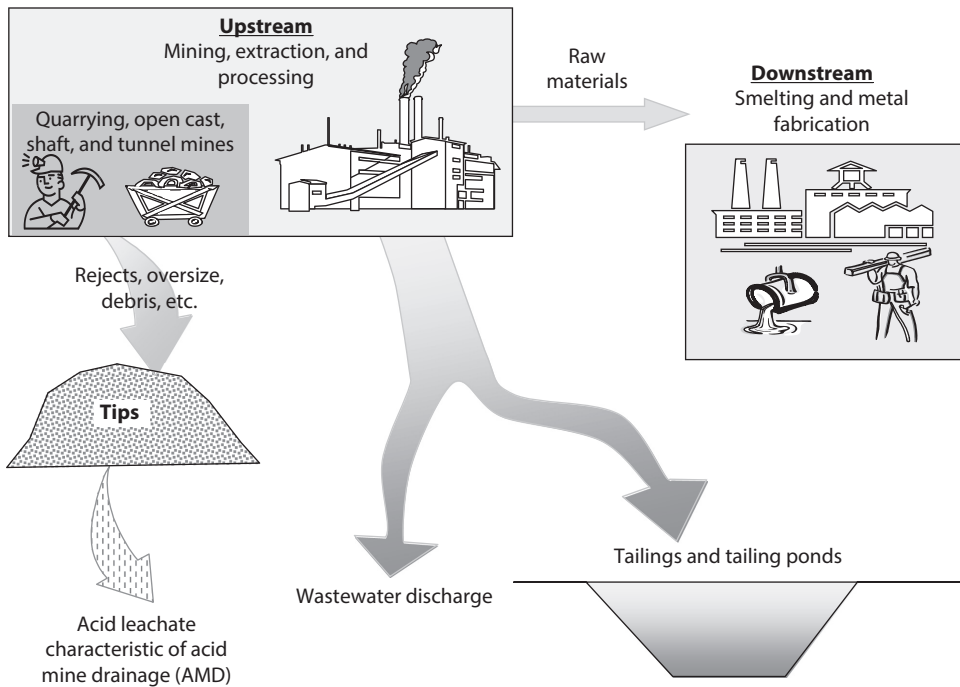
**FIGURE 5.1**

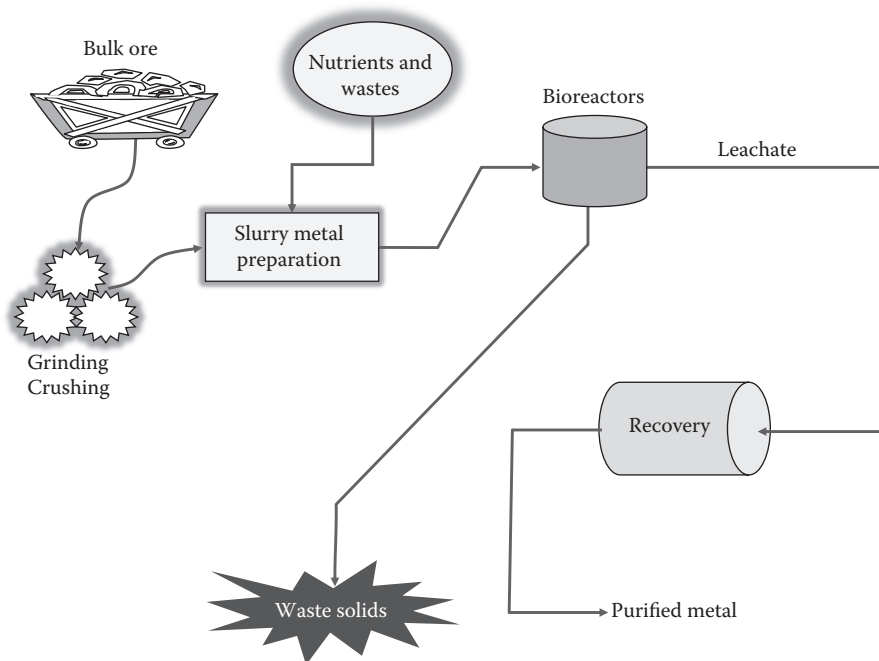
Illustration of some of the major features associated with mining and natural resource extraction. The example shown is typical of metalliferous mining–extraction operations.

potential impacts to the terrestrial ecosystem. In the United Kingdom, for example, more than 200 years of mining of coal and iron ore left 500 million tonnes of residual waste from coal and iron and steel manufacturing as sterile waste tips (Barr, 1969). These tips are the result of the removal of more than 52 million tonnes of coal from the underground. Ground subsidence, water pollution, and toxic gas emissions are other impacts. Not only do these tips constitute blights on the landscape but they are also hazards when slide failures occur. There are historical reports of such failures that have resulted in human casualties. Figure 5.1 shows a simple generic illustration of operations associated with mining and extraction of metal mineral resources. Individual mineral extraction and/or beneficiation processes will differ between different types of minerals and their host ores—creating their own types of stressors and associated impacts. Specific examples will be discussed in a later section.

The two principal groups of activities of the natural resource extraction process includes (1) mining for procurement of host rocks containing the desired ores and (2) extraction and processing the host rocks to obtain the desired minerals (generally called beneficiation). As shown in Figure 5.1, the result of these two groups of activities are generation of rejects and other debris that end up as *heaps* and discharge of tailings slurries and wastewater.

5.2.2 Biohydrometallurgical Processes

Bacterial leaching of metals from mining ores, also called bioleaching, is a full-scale process that can be performed by slurry reactors or heap leaching (Figure 5.2). Mining wastes

**FIGURE 5.2**

Flowsheet of a biometallurgical process.

include low-grade ores, mine tailings, and sediments from lagoons or abandoned sites. Low pH values lead to solubilization of the metals in the mining ores. Elemental sulfur or ferrous iron may be added as bacterial substrates. Reactors such as Pachuca tanks, rollings reactors, or propeller vessels have been used (Tyagi et al., 1991).

Heap leaching is more common since it allows the large volume of wastes to be treated in place (Boon, 2000). To enhance this process, aeration can be forced through the pile. Alternatively, hydrophilic sulfur compounds can be added (Tichý, 2000). *Thiobacilli* bacteria are responsible for the oxidation of inorganic sulfur compounds. Applications include metal dissolution of low-grade sulfide ores, generation of acidic ferric sulfate leachates for hydrometallurgical purposes, and removal of gold by oxidation of pyrite by bacterial sulfide production. The extraction of metals from low grade metals ores and refractory gold ores is a multibillion-dollar business worldwide (Rawlings, 1997). Bacterial solubilization by oxidation of the sulfide minerals, pyrite, and arsenopyrite, enhances gold extraction by the traditional method of cyanidation. The solubilization mechanisms have been debated extensively, however.

Biohydrometallurgical processes are highly efficient and cause fewer environmental problems than chemical methods (Torma and Bosecker, 1982). For slurry processes, oxidation rate per reactor volume, pH, temperature, particle size, bacterial strain, slurry density, ferric and ferrous iron concentrations need to be optimized. Bioleaching is very effective for recovery of gold from refractory gold pyrite and copper from chalcopyrite. The feasibility of the recovery of metals from a mining residue has been shown by *Aspergillus niger*, which exhibits good potential in generating a variety of organic acids effective for metal solubilization (Mulligan and Kamali, 2003). Organic acid extraction effectiveness is enhanced when sulfuric acid was added to the medium. The study by Mulligan and

Kamali (2003), which used wastes such as potato peels, leaves, corn husks, and wood shavings and different auxiliary processes to evaluate efficiency and/or reduction in costs, found maximum solubilization of 68%, 46%, and 34% for copper, zinc, and nickel, respectively (Figure 5.3). Additionally, iron co-dissolution was minimized with only 7% removal.

Rhamnolipid biosurfactants (biodegradable and of low toxicity) have also been added to mining oxide ores, to enhance metal extraction (Dahr Azma and Mulligan, 2004). Batch tests were performed at room temperature. Using a 2% rhamnolipid concentration, 28% of the copper was extracted. Addition of 1% NaOH with the rhamnolipid enhanced the removal up to 42% at a concentration of 2% rhamnolipid but decreased at higher surfactant concentrations. Sequential extraction studies were also performed to characterize the mining ore and to determine the types of metals being extracted by the biosurfactants. Approximately 70% of the copper was associated with the oxide fraction, 10% with the carbonate, 5% with the organic matter, and 10% with the residual fraction. After washing with 2% biosurfactant (pH 6) over a period of 6 days, it was determined that 50% of the carbonate fraction and 40% of the oxide fraction were removed by the biosurfactant.

Further experiments have been performed with biosurfactants and mining residues in relation to arsenic (Arab and Mulligan, 2013). Results indicated that washing the mine tailing samples with 1% rhamnolipid or sophorolipid arsenate As(V), the dominant species of arsenic, to As(III). By comparing the reduction power of these two biosurfactants we can conclude that sophorolipids are more successful in converting As(IV) to As(III) (the more soluble form of arsenic). Rhamnolipids with different concentrations were able to mobilize higher amounts of arsenic from the mine tailing than the sophorolipids. There was also a positive correlation between mobilization of arsenic and iron. The results from the present study show sophorolipids and rhamnolipid as highly efficient agents for the removal of arsenic and other heavy metals from soil and mine tailings. However, there is a need for further research on enhancing the process of arsenic and heavy metal mobilization.

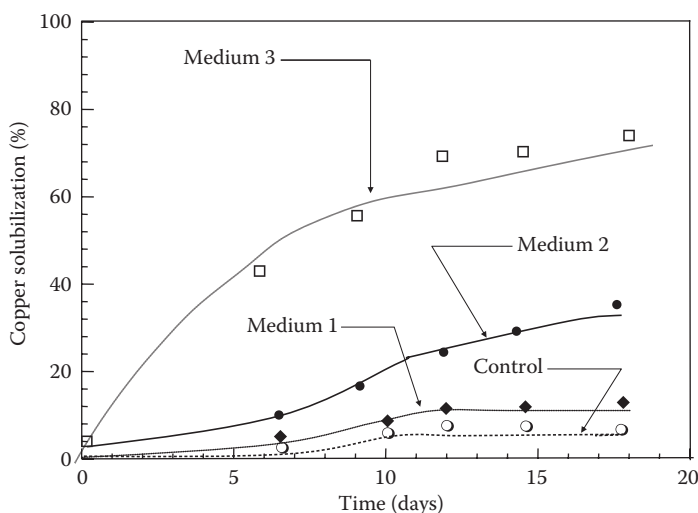


FIGURE 5.3

Effect of dilute acid pretreatment on leaves and sawdust on copper removal by *A. niger*. The control is dilute acid, with medium 1 (40 g/L potato peels and dilute acid), medium 2 (40 g/L sawdust and dilute acid), and medium 3 (40 g/L leaves with dilute acid) (Mulligan and Kamali, 2003).

Pintail Systems (Aurora, CO) has developed a biological process (USEPA, 1999) for the removal of cyanide in a heap leach process. Native microorganisms were extracted from the ore and tested for cyanide detoxification potential. Those identified were kept for bioaugmentation purposes. Pilot tests were performed to simulate pile conditions and determine detoxification rates, process parameters, and effluent characteristics. Once the test was complete, sufficient quantities of bacteria were applied to the heap. Metals were biomineralized during the leaching process. This process can be used for spent ore heaps, waste rock dumps, mine tailings, and process water from silver and gold mining operations. The technology has been evaluated in the Demonstration Program and two full-scale cyanide detoxification projects were completed.

An anaerobic treatment process was developed by Geo-Microbial Technologies (Ochelata, OK). The technology is called anaerobic metals release (AMR) instead of aerobic acidophilic bacteria that form acids and solubilize metal sulfides. This acidification can contaminate streams and lakes. In contrast, the AMR technology uses *Thiobacillus* with a denitrifying culture at neutral pH. The anaerobic conditions were controlled by the nitrate levels in the leaching solutions, which allow solubilization of the metals. All nitrates were consumed in the process. The metals are removed from the leachate by standard methods and the effluent is recycled. Levels of sulfide-reducing bacteria and sulfides are kept to a minimum. The technology was demonstrated in a 1994 SITE Emerging Technology Program.

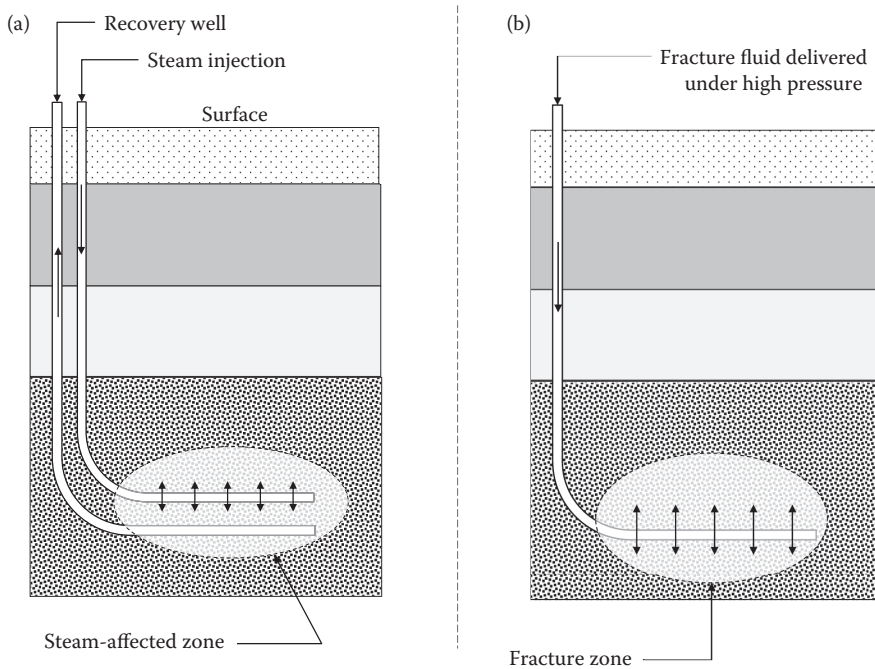
5.2.3 Underground In Situ Hydrocarbon Extraction

The activities of interest in deep underground in situ hydrocarbon extraction include (a) steam-based recovery of bitumen using the steam-assisted gravity drainage (SAGD) process or a process known as the cyclic steam stimulated (CSS) process and (b) hydraulic fracturing of deep underground shale and other geological formations containing natural gas or tightly held oil for extraction of the hydrocarbon products.

The SAGD technique is a steam-assisted heavy recovery process where parallel wells drilled into the deep underground are separated a few meters apart—with the top well providing steam to the surroundings, and the bottom well serving as a collection well capturing the gravity-assisted flow of the fluidized heavy oil as illustrated in Figure 5.4a. The steam that is fed through the upper well to soften the heavy bitumen is delivered at pressures below the fracture pressure of the host rock—thus allowing the fluidized or softened bitumen to flow under gravitational forces into the collecting well below.

In the other technique, as the name implies, the CSS process uses a somewhat similar procedure, i.e., introduction of steam into the geological formation of interest to soften the contained bitumen. However, instead of utilizing gravity drainage of the softened bitumen into a parallel well below, the same well that provided the injected steam is used to extract the softened bitumen—meaning that only a single vertical or horizontal well per location is drilled. In short, the CSS technique uses the same well for both steam injection and for extraction of the product bitumen. The cyclical procedure of steam injection followed by extraction of the bitumen previously softened by the steam injection gives this procedure its name CSS process.

Figure 5.4b shows the basic elements of the process commonly known as *fracking*, i.e., hydraulic fracturing of the host rock containing the hydrocarbons of interest (oil or natural gas). As with the CSS technique, a single horizontal well (per location) is drilled. A common technique is to use a perforating gun inserted to the end of the well to initiate small cracks in the penetrated host rock by detonating small charges. Subsequent crack

**FIGURE 5.4**

Elements of steam-assisted gravity drainage (SAGD) process for recovery of heavy bitumen (a) and hydraulic fracturing of shale or other hydrocarbon-containing geologic feature (b). Note that capture of the released hydrocarbons in fracking process is affected by other capture wells.

generation is brought about using high-pressure fracking fluids. The types of fracture-fluid commonly used consist of water and sand or other products capable of producing physical actions necessary to keep the produced fractures open to allow for recovery of the hydrocarbons of interest (natural gas or *tight oil*). This sand–water mix will generally contain various types of chemicals, such as (a) water-soluble gels, (b) chemical additives that have the capability of maintaining fractured openings open, (c) additives needed to inhibit bacterial growth, and (d) chemicals required to maintain efficiency of delivery of the fracturing fluid such as surfactants, corrosion inhibitors and friction reducers.

5.2.4 Sulfide Minerals and Acidic Leachates

We consider the case of production of acidic leachates from mining and extraction of sulfide minerals as a separate issue from the detailed discussions that begin in Section 5.5.2. This is because of the significant problems and stressors generated by sulfidic metalliferous rocks, and by their impacts on the geoenvironment—the most common or prominent issue being the generation of acid mine drainage (AMD) and the release of arsenic from their host rock ores.

5.2.4.1 Acid Mine Drainage

The sulfide minerals in the host rock in the mines and in the ores such as iron sulfides, pyrites, arsenopyrites, chalcopyrites, pyrrhotites, sphalerite, and maracasites present severe

environmental problems when they are exposed to water and oxygen. Figure 5.5 gives an illustrative example of what happens when pyrites (FeS_2) are exposed to oxygen and a source of water. Although oxygen and water are the two primary ingredients needed for the development of the phenomenon commonly described as AMD, it must be noted that microorganisms contribute significantly to the processes by way of catalyzing iron oxidation, especially at pH levels below 3.5 (Manahan, 1990). The cycle of acid contact and oxidation of the pyrite example shown in the diagram continues so long as oxidation processes can proceed.

In the series of chemical reactions reported by Manahan (1990), beginning with the oxidation of pyrite, the processes proceed as follows:



It is noted that because of the low pH levels, further iron oxidation of the pyrite can be aided by various iron-oxidizing bacteria, as follows:

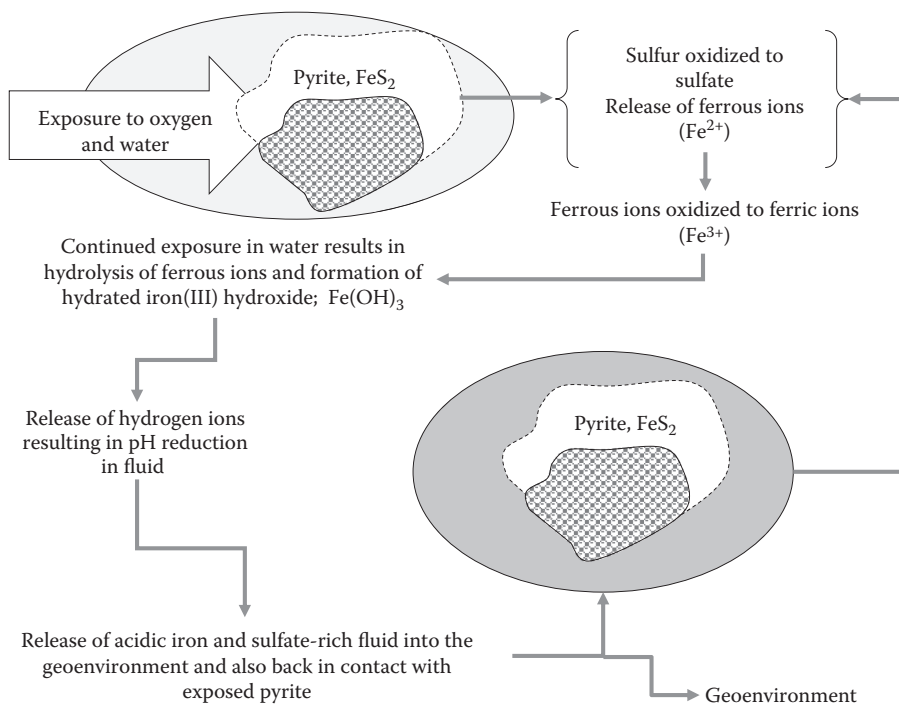
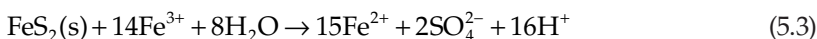


FIGURE 5.5

Effect of exposure of pyrite to oxygen and water. Continued exposure to water will result in the generation of iron hydroxide (yellowboy) and acidic solution that will be harmful to aquatic plants, animals, and will also release heavy metals previously held by the soil. Similar reactions shown in the diagram will also occur for sulfides of copper, lead, arsenic, cadmium, and zinc.

At pH values well above 3, Manahan (1990) reports that Fe(III) precipitates as hydrated Fe(III) oxide $\text{Fe}(\text{OH})_3(\text{s})$.



Release of the acid fluid into the land environment within the mining site will allow the fluid to come in further contact with other exposed pyrites. The generation of acidic leachate rich in iron and sulfate (known as *yellowboy* $\text{Fe}(\text{OH})_3(\text{s})$) is characteristic of the outcome of the various processes that accompany oxidation of the sulfur and iron in the pyrite. So long as there is a source of these in the host rock and ores and so long as these continue to be exposed to water, generation of *yellowboy* will continue unabated. The presence of sulfate-reducing bacteria in soil and water will exacerbate the problem. These bacteria are anaerobes that use sulfate as electron acceptors.

Although the generation of the acidic leachate, commonly known as AMD or acid rock drainage (ARD), constitutes a major negative impact from mining operations, the cascading or domino effects that accrue from AMD can be severe. The domino effects arising from discharge of the leachate into the environment include (a) severe health threats to aquatic species, native habitat, and plant life, (b) pollution of groundwater and drinking water, (c) deterioration of soil quality, and (d) release of trace metals and heavy metals previously retained by the soil solids in the ground. Information reported in the Interstate Mining Compact Commission study (IMCC, 1992) showed that for five western states in the United States, there were (in 1992) about 130,000 inactive and abandoned mine sites. In a later study, Skousen et al. (2000) report that approximately 20,000 km of streams and rivers in the United States have been degraded by AMD and that 90% of AMD reaching streams originate from abandoned mines. This makes the problem of attaching ownership of the problem and for cleanup of the sites and streams and rivers somewhat difficult.

The extent of acid generation at mine sites (underground mines, openings, leach ores, spent ores, etc.) is a function of several factors. These include (a) type and concentration of sulfide minerals in the host ore and in the spent ores and leach piles, (b) the host rock, (c) availability of oxygen, (d) site hydrogeology, (e) pH of the water in the system, and (f) presence or absence of bacteria, e.g., *Thiobacillus ferrooxidans*.

5.2.4.2 Arsenic Release

Oxidation of the mineral sulfides may result in the solubilization of trace metals and heavy metals, effectively releasing them and allowing them to be mobile in the liquid phase. It is not uncommon to find evidence of arsenic, cadmium, cobalt, copper, lead, manganese, nickel, and zinc as released metals. Arsenic poisoning of groundwater and aquifers has been reported in many parts of the world. This problem has gained considerable publicity and has been reported as “the largest mass poisoning of a population in history” (Smith et al., 2000) in relation the poisoning of the tubewells in Bangladesh and West Bengal, as previously mentioned in Chapters 1 and 3. In this particular case, information available points to the presence of naturally occurring arsenopyrites (FeAsS) and arseniferrous iron oxyhydroxides in the substrate material as being the immediate source materials for the arsenic. If oxygen is available in the groundwater, oxidation of the arsenopyrites will release the arsenic. Some reports have speculated on the use of tubewells as a means for introduction of oxygen into the subsoil strata. In the absence of oxygen, the processes associated with reductive dissolution of the arseniferrous iron oxyhydroxides will release arsenic while increasing the bicarbonate concentrations. This will result in arsenic pollution of the groundwater. The reports given by

TABLE 5.1

Arsenic Concentrations Measured in Canadian Mine Tailings

Mine	Location	Concentration (mg/kg)	Reference
Copper mine	Murdochville, QC	500	Wang and Mulligan, 2006
Gold mine	Musselwhite, ON	63	Wang and Mulligan, 2006
Copper–zinc mine	Val d’Or, QC	270	Wang and Mulligan, 2006
Iron mine	Mont-Wright, QC	<0.70	Wang and Mulligan, 2006
Lead–zinc mine	Bathurst, NB	2200	Wang and Mulligan, 2006
Gold mine	Marathon, ON	270	Wang and Mulligan, 2006
Con mine	Yellowknife	25,000	Ollson, 1999
Giant mine	Yellowknife	4800	Ollson, 1999
Negus	Yellowknife	12,500	Ollson, 1999
Rabbit Lake	Northern Saskatchewan	56 to 9871	Moldovan et al., 2003

Appelo (2008) provide a comprehensive recounting of the worldwide occurrence of arsenic together with the geochemistry, problems, and impacts.

Mine tailings and effluents usually contain high concentrations of arsenic and are of concern as potential sources of environmental contamination. Arsenic occurs naturally in a wide range of minerals in soils in several forms of inorganic compounds. The most common arsenic-containing minerals are arsenopyrite or mispickel (FeAsS), realgar (AsS), and orpiment (As_2S_3). It has been reported, for example, that due to local mining and mineral processing, the annual total fluvial input of arsenic to the Moira Lake in Ontario, Canada, was approximately 3.5 tonnes (Azcue and Nriagu, 1995).

In mine tailings, arsenic occurs in various forms such as arsenopyrite (FeAsS), arsenian pyrite (As-rich FeS_2), arsenates, and association with iron oxyhydroxides. Wang and Mulligan (2004) measured the arsenic contents of six Canadian mine tailings. ICP-MS analyses indicated that the highest arsenic concentrations reached 2200 mg/kg in tailings from a lead–zinc mine at Bathurst, NB. These and others are shown in Table 5.1. Many other countries such as Thailand, South Korea, Ghana, Greece, Australia, Poland, the United Kingdom (Kinniburgh et al., 2003), and the United States have also experienced significant arsenic contamination associated with mining activities. McCreadie et al. (2000) have found arsenic concentrations up to 100 mg/L in the porewater extracted from tailings in the province of Ontario. Donahue and Hendry (2003) showed that dissolved arsenic concentrations within the tailings could vary from 9.6 to 71 mg/L. As with the reporting of Appelo (2008), the reports contained by Bundschuh et al. (2005) provide detailed accounting of the occurrence of natural arsenic in groundwater in many different parts of the world, together with suggested methods for management and remediation of the problem.

5.2.5 Sustainability and Resource Exploitation

It is abundantly clear that the harvesting of nonrenewable natural resources discussed in this chapter is not going to satisfy “resource sustainability” from the viewpoint of renewal or regeneration of the natural resource material. Extraction of these resources from the ground will deplete them, and will therefore fail a key sustainability issue—replenishment or renewal of supply. The primary geoenvironmental engineering concern in this respect is to (a) apply or implement engineering measures that will minimize and/or

mitigate stressor impacts generated by the activities associated with harvesting of these resources and (b) develop and implement remediation technology to restore impacted lands to pre-impact states.

The issues pertinent to sustainable practices in geoenvironmental engineering in respect to nonrenewable resource extraction operations fall within the jurisdiction of land use, i.e., sustainable land use. In most instances, activities generally associated with extraction of nonrenewable natural resources such as base metals begin with operations designed to extract the host ore from the ground through open-pit and/or underground mining (tunnel and shaft mining). Ores extracted from base metal mines include (in alphabetical order) copper, gold, iron, lead, molybdenum, platinum, silver, uranium, and zinc. The predominant base metal ores are those that contain copper, iron, lead, and zinc. These are primarily obtained from lode deposits using both open-pit and underground mining techniques. Beneficiation, ore dressing, and mineral extraction will generate waste materials in addition to processing wastes and discharges that find their way into the land environment. The nature of these and their impacts on the land environment and particularly with land use constitute the major concern in this chapter. The danger that one faces is the cascading or domino effect generated by these activities and discharges.

In respect to the deep underground in situ extraction processes illustrated in Figure 5.4, the various processes (SAGD, CSS, and fracking) have their proponents and opponents, vis-à-vis environmental impacts, etc. Although the issues between the different parties are important considerations, these are not germane to the discussions in this chapter. What is of importance is the identification of the stressor sources, the types of stressors produced, and their impact on the geoenvironment. In these cases, the impact problems are associated with fugitive contaminated water, i.e., water not captured as recycled-treated water used for steam injection and/or used as fracking fluid. The vulnerability of neighboring aquifers to contamination is a key element in information gathering. These pieces of information are important because they will provide the clues for development of geoenvironmental engineering practices necessary to mitigate the adverse impacts. The emphasis on *sustainable geoenvironmental engineering practice* is necessary because there are actions that can be undertaken to reduce and even minimize adverse geoenvironmental impacts. These, however, are *operational actions*, i.e., actions that are associated with the implementation of the processes themselves.

5.3 Resource Extraction and Stressor Impacts

The discussions in this section relate to four categories in this grouping of resource extraction and processing industry operations. These categories include those industries dealing with (1) ores in metalliferrous mining for recovery of various types of metals, etc., (2) ores from nonmetal resource mining and processing such as aggregates, clays, etc. (3) hydrocarbon resources extracted from the ground such as oil sands (formerly known as tar sands), and (4) deep underground in situ extraction of tight oil and shale gas. These are operations mounted to process the ores or liquid/gaseous resources recovered from the various forms of mining and drilling activities. The products obtained from these industries serve as raw materials for their associated downstream industries. The associated downstream industries are discussed in detail in Chapter 7.

5.3.1 Mining-Related Industries

5.3.1.1 Pit Mining

The first two categories mentioned in the previous section can be considered jointly as *mining-related industries*. For these (mining-related) industries, there are typically three types of interactive contact with the geoenvironment. There are at least two different types of mining: (1) surface mining or open-pit mining and (2) underground mining. Mining sites are characterized by piles of waste rock, huge pits, and AMD. Decommissioning procedures often must include remediation and closure strategies—requirements that have not been imposed in the past. Remediation through decontamination, isolation, or immobilization may be required for contaminated areas. For closure of open pits, two simple strategies that have been employed: (1) refilling of the pit with clean material for new land-use options and (2) harmonizing with the surroundings. Before open-pit filling, consultation is needed to ensure that the geological heritage is not destroyed. Maintaining formations is essential for research and teaching purposes or education of the public. Waste storage in these pits used to be a common practice. However, because the base of the quarries is often relatively permeable, groundwater contamination from waste leachates can result. If the pit is left for recreation or as a monument, slope stability must be ensured. Flooding of the pit can be quite beneficial. Waring and Taylor (1999) have proposed this as a method that is low cost and passive for preventing AMD by eliminating exposure of the sulfide minerals to atmosphere and hence denying oxidation of these minerals. Reservoirs can be used for fishing or wildlife or recreation or restoring biodiversity, and vegetation may also be introduced. Mines could also be sealed against seepage of rainwater and snow, and drainage systems should be developed to divert water away from the tailings and thus reduce AMD problems.

The issues of prime importance in respect to the geoenvironment and its sustainability relate to (a) the actual mining operation itself and its impact on the surficial environment and (b) the various waste products issued from mining and resource extraction operations. Most mining wastes are associated with recovery processes of host rock material for production of natural resources such as metal and nonmetal ores and products. These include aluminum, iron, copper, gold, lead, molybdenum, silver, tungsten, uranium, zinc, coal, asbestos, gypsum, barite, syenite, potash mineral, salt mineral, bitumen (from oil sands, “tight rocks,” shales, etc.) quartz, limestone, sand and gravel, and stone. In addition to solid wastes generated during the mining process, liquid wastes in the form of tailings and other process liquid waste streams associated with mining and milling operations are obtained. These need to be considered as sources of stressors that could impact on the geoenvironment. Specific and detailed examples of various mining activities and milling processes can be found in mining–milling textbooks dedicated to the study of these subjects.

5.3.1.2 Discharges from Beneficiation and Processing: Stressor Sources

Procedures and processes required to extract minerals from the ores obtained in mining operations vary according to the kinds of minerals being extracted. These procedures and processes fall under the category of *beneficiation operations* and *mineral processing*. These operations are designed to physically separate the mineral of interest from the surrounding nonmineral elements commonly called gangue, and to use various means to recover the mineral of interest. Operations included in *beneficiation* and *mineral processing* are (a) ore preparation—crushing and grinding (commonly known as *comminution*), washing;

(b) mineral recovery—including such processes as dissolution, filtration, calcining, roasting, leaching, concentration, separation, solvent extraction, electrowinning, and precipitation. The generalized procedure shown in Figure 5.6 describes the main elements of most of the processes used.

Variations (of procedure) from the main elements can be expected between different operating companies because of differences in mode of operation. Bulk ore transported to the processing and extraction plant needs to be crushed to smaller fractions where specific chemicals and additives are added. The resultant mixture is then subjected to the required mineral extractions processes, as required. The points of interest in regard to interactions of the mining–milling activities and industries with the geoenvironment shown in Figure 5.7 include debris from mining, and liquid and solid waste materials from beneficiation and processing. These discharges can be considered to be sources for various kinds of stressors.

In respect to stressors and impacts on the geoenvironment, the major sources of stressors are the heaps, wastewater, and tailings ponds. The types of stressors originating from these sources physical, chemical, physicochemical, and biogeochemical (see Figure 5.7). Collapse and subsidence of heaps are major problems. The heaps and tailings basins are also subjected to movement and have inflicted substantial damage in towns where the tailings have liquefied and flowed into towns burying houses and people. Noxious and toxic releases from dissolution, bacterial activity, and subsequent runoff also cause damage. The acid water is carried into ground and surface water thereby threatening the health of humans, animals, and the local flora.

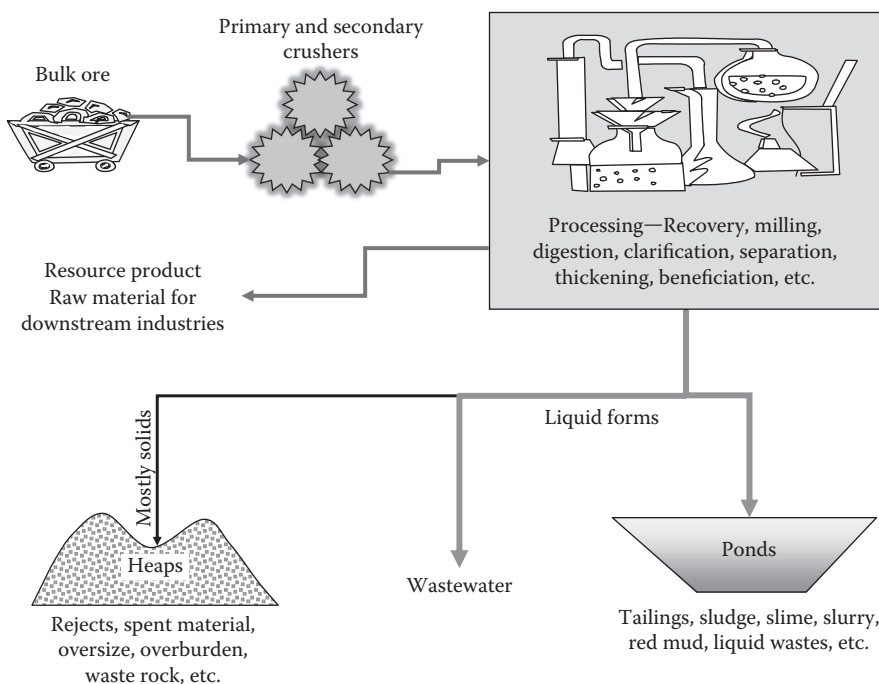


FIGURE 5.6

Generalized resource extraction–recovery process. Specific details of additives, digestion, beneficiation, etc., will vary according to types of resources (minerals, nonminerals, hydrocarbon) being extracted. Discharges to the geoenvironment will take the general forms shown in the diagram.

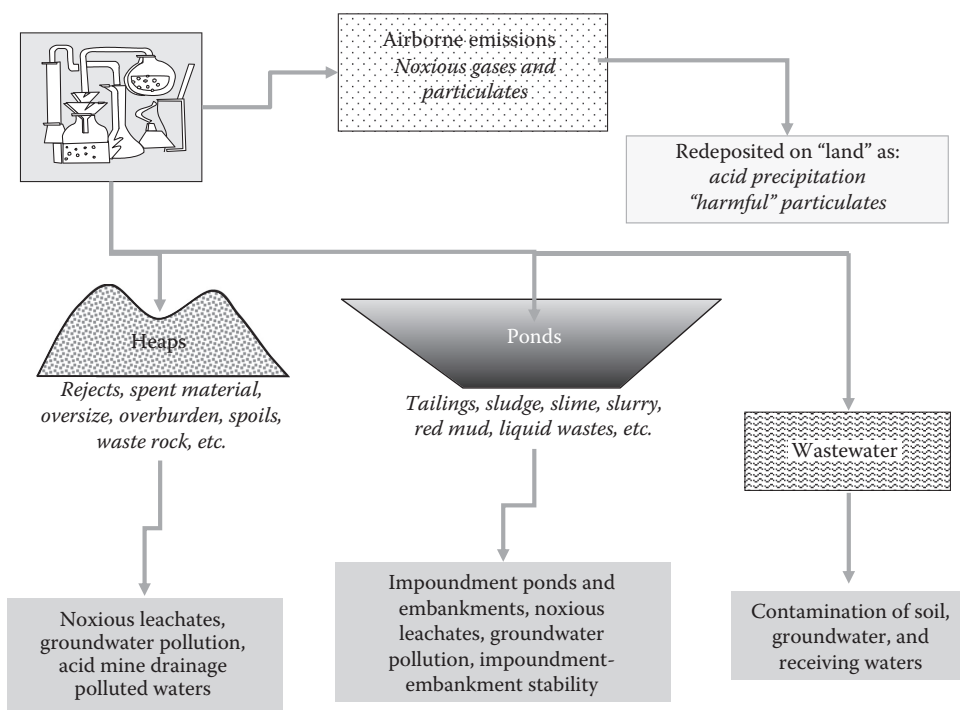


FIGURE 5.7

Discharges from resource recovery operations and some of their more significant impacts on land use and the geoenvironment. The ponds containing the slurry tailings could also be dammed-up valleys or even abandoned mine pits.

Dust inhalation by humans may also lead to cancer and other illnesses such as asbestosis and silicosis. Bioaccumulation of mercury, lead, and other heavy metals in the food chain may also be significant. Kobayashi and Hagino (1965) reported that the runoff of cadmium from a zinc mining waste in the 1950s led to accumulation in the Jintsu River that was used for drinking water and irrigation of rice fields and that *itai-itai* disease afflicted the population living in the area. Secure disposal, cleanup, and management of drainage eliminated the disease.

5.3.1.3 Solid Waste Materials and Stressors

The principal sources of solid waste materials issuing from extraction of the various minerals are waste rocks, ore spoils, and overburden. There are two types of geoenvironmental impact problems from the stressors associated with the disposal of solid waste materials: (1) physical-mechanical and (2) chemical, physicochemical, and biogeochemical. In the first case—i.e., physical-mechanical—stability of the heaps and tailings dams is a major concern.

Historical evidence shows numerous failures of these physical structures arising from simple slope instabilities to landslides and/or liquefaction triggered by excess porewater pressures. A chronology of some major tailings dam and heap failures compiled by WISE (2013) can be seen in <http://www.wise-uranium.org/mdaf.html>. The compilation includes

a whole series of cases of dam or heap failures associated with industries extracting products such as copper, nickel, manganese, fluorite, bauxite, gold, phosphate, etc., ranging from 1960 to 2012. By and large, the major stressors responsible for the slope failures and various other types of instability are (a) excessive forces or stresses in the structures (heaps and tailing dams) due to size and weight of the heap—inconsistent with the design stability of the structures, and (b) excess porewater pressures developed as a result of infiltrating rainwater or other sources—due to the lack of provision for slope protection facilities against infiltration and/or drainage system and pore-pressure shedding devices within the structures. Other examples of failures of tailings dams and their consequences can be seen in Table 5.2.

Chemical and biogeochemical stressors originating from heap and tailing dam sources can be traced to the nature of the host ores and the leaching solutions used to extract the

TABLE 5.2

Examples of Failures of Tailings Dams

Name	Tailings Dams Failures		Countries	Date
	Effects	Cause and Trigger		
Osarizawa mine	374 deaths from failure of the 60-m-high tailing dam	Increase in the height of the tailings dam due to excess copper production and heavy rainfall	Akita, Japan	November 20, 1936
Mochikoshi mine	Cyanide compound flowed out into the Kano River	Failure of the tailings dam caused by the Izu-Oshima Kinkai earthquake	Shizuoka, Japan	January 14, 1978
Church Reck tailings dam	Failure of uranium tailing dam, contaminating the Navajo Nation reservation and the Colorado River, ending in contaminating parts of Arizona and Nevada	Unidentified failure	New Mexico, USA	July 19, 1979
Baia Mare tailing dam	Cyanide spill (leakage) near Baia Mare, Romania, into the Someş River by a gold mining company has been called the worst environmental disaster in Europe since the Chernobyl disaster	Dam failure attributed to excessive snowfall	Romania	January 30, 2000
MAL Magyar Alumínium Termelő és Kereskedelmi Zrt. (aluminum smelting factory)	69,700 kL of highly alkaline red-mud waste containing heavy metals flowed out and contaminated the surrounding land and river, with 9 dead and more than 120 injured	Failure of the tailings dam not fully identified	Hungary	October 10, 2010
Oya mine	40,000 m ³ of soils including arsenic flowed out and contaminated the land and port	Failure of the tailing dam caused by the 2011 earthquake off the Pacific coast of Tōhoku	Miyagi, Japan	March 11, 2011

minerals from the ores. In respect to metalliferous mining situations, sulfide minerals are found in most of the host ores. Commonly used ores for extraction of lead and zinc ores are galena (PbS) and sphalerite (ZnS). In the case of iron, the ores are in oxide and sulfide forms. These include magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite ($\text{Fe}_2\text{O}_3\text{H}_2\text{O}$), siderite (FeCO_3), and pyrite (FeS_2). Although copper sulfide minerals are found in such minerals as chalcopyrite (CuFeS_2), covellite (CuS), chalcocite (Cu_2S), and bornite (Cu_5FeS_4), the most common source of copper ore exploited in present mining operations is chalcopyrite (Simons and Prinz, 1973). Oxide minerals include chrysocolla (CuSiO_3), malachite (Cu_2CO_3), azurite ($2\text{CuCO}_3\text{Cu}(\text{OH})_2$), tenorite (CuO), and cuprite (Cu_2O).

Using extraction of copper as an example, solid waste material discharges include the overburden material such as soil, debris and unconsolidated material, oversized material, and waste rock (rejects), spoil heaps, leach ore obtained from leaching of copper oxide mineral ores, and other solid by-products and wastes issuing from the recovery process. It is estimated that on the average, about 100 tonnes of waste material are generated in the extraction of 1 tonne of copper. Using the 100:1 ratio of waste material for each tonne of recovered copper as an example, we can surmise that for the various mineral extraction industries in the world, this would mean that hundreds of millions of tonnes of waste materials are generated in a year. All of these materials will need proper management and disposal. This is particularly significant because the rejects and other ores in the piles contain trace amounts of sulfide minerals. These will contribute to the generation of AMD problems. Not all the solid heaps are waste heaps. In operations where sulfur recovery is obtained, open-air storage on site is not an uncommon procedure. Figure 5.7 shows some of the more significant impacts to the geoenvironment, and also impacts on land use. The significant impacts from the presence of solids as rejects, oversized, etc., on land use include storage, noxious leachates, acid generation (AMD), and runoffs leading to acid pollution of watercourses, groundwater, and land surface.

5.3.1.4 Liquid Waste Streams, Discharge, and Stressors

There are essentially three categories of liquid waste streams associated with mining–mineral extraction industries. These include

1. Mine water and waste streams generated in a mining operation due to hydrological drainage from the mining site, and percolation from waste rock and mill tailings piles, and surface runoffs. Although containment of mine water and generated waste streams in abandoned mines have been previously practiced, present worries of acid mine generation have led to prevention of excess water entry into abandoned mine sites. Extraction pumping of mine water serves to remove a potential source for generation of acid in the mine. However, without the benefit of capping and sealing of mine shafts and openings, it is inevitable that some water will be introduced into the mines, resulting ultimately in the problem identified as AMD.
2. Liquid waste streams from processing plants such as solutions or liquids containing solvent extraction sludge, spent electrolytes, spent leaching solutions, spent solvents, and used oils. In general, the liquid wastes are contained in ponds, and are often referred to as solution ponds, pregnant ponds, holding ponds, etc. Pregnant (solution) ponds are those that contain some of the minerals, and solution ponds are those that are presumably devoid of these minerals.

3. Slurry tailings discharge consisting of water and a wide range of inorganic and organic dissolved constituents obtained from the remnants of reagents used in the recovery processes and fine fractions of the host ores. Impacts on land use consist of large open containment facilities such as dammed-up valleys and ponds containing sludges and slimes that pose health and safety threats to animals and humans, runoffs from the containment facilities, embankments for the impoundments used to contain the sludges and slimes and leachates that contaminate ground, groundwater, and receiving waters. Most of the slurry tailings' containment facilities contain slurries and slimes that will not exhibit liquid–solids separation, i.e., the solids in these facilities will not readily sediment or settle to the bottom of the containment structure. Typical of the types of tailings ponds are red-mud ponds, tar sands sludge ponds, phosphatic clay ponds, etc. Many of these ponds contain slurries and sludges that are toxic in nature. Their presence will pose potential safety and health threats to the human population within the immediate area. The strategies for maintaining and operating containment facilities are discussed in the next subsection.

As opposed to the discussion on tailings dam instability in the previous section, holding ponds embankment stability can be a problem if the containment embankments become too high and are subject to drawdown pressures when large fluctuations occur over a very short period in the height of the slurry or sludge in the pond. This has happened in instances when containment ponds are emptied quickly. Collapse of the embankments can lead to failure of structures located near these embankments. This particular issue is a geotechnical problem that can be corrected with proper design and management techniques.

5.3.2 Underground In Situ Hydrocarbon Extraction

We have previously described underground in situ hydrocarbon extraction to mean the extraction of natural gas from shale and similar geological formations, oil (tight oil) or heavy bitumen in deep geological deposits (using the SAGD technique or the CSS process). The procedures common to all of these underground in situ extraction techniques is the requirement for deep drilling, in most instances, to obtain horizontal wells at the depths required for extraction of the desired product hydrocarbon. The discussion of sources of stressors and resultant impact that follows is confined to those sources associated with the extraction of the product hydrocarbons in the already drilled horizontal wells.

5.3.2.1 Fluid Usage and Stressors

Common to the three types of underground in situ extraction processes is the use of high volumes or quantities of water—with or without additives. Either with or without prior addition of additives, water obtained after its accomplished purpose, is contaminated, i.e., the utilized water is a source for chemical stressors. In the case of steam-injection water used for softening the bitumen in the host material, contamination of the water by the hydrocarbons released or fluidized by the steaming process occurs—thereby rendering the used steam water a source of chemical stressors. In the case of fracking fluids used for extraction of shale gas, for example, the additives used in the fracking fluid constitute the sources for chemical stressors. Although the industries involved in the implementation of these processes make every effort to recover the water used for

the steam-assisted in situ processes and/or the fracking process for treatment at their respective surface treatment facilities, not all the contaminated water is recovered. It is the nonrecovered (fugitive) water that constitutes the source of stressors to the immediate geoenvironment.

5.4 Tailings Discharges

Central to the extraction of resource material contained in the ores obtained in mining is fine grinding of the ores—as the preliminary stage of the beneficiation process. The common elements of the various techniques used in the beneficiation processes include both fine grinding and washing–flotation and finally, at some stage in the beneficiation process, separation of the resources from the finely ground material. Flotation and other methods of resource separation (e.g., magnetic) are required. The end result of all of these processes is the generation of liquid wastes containing a suspension of the finely ground material. This liquid waste is generally defined as *tailings waste slurry* or *slurry tailings*. It can be well appreciated that the generous quantities of tailings are reflective of the significant amounts of water needed in the processing of the finely ground ore material for beneficiation.

5.4.1 Containment of Tailings

Slurries, slimes, sludges, and red-mud ponds are all names that are given to the general class of slurry tailings discharged from beneficiation processes—the choice of which depends on the nature of the tailings being discharged. These slurry tailings cannot be directly discharged into the land environment not only because (a) they contain suspended fines and (b) their chemical nature will most likely be toxic to the environment and public health. In short, discharge of these kinds of tailings will have detrimental impact on the land ecosystem. Some of the main reasons for containment of these slurry tailings are

- *To avoid pollution of the land surface environment.* This is one of the principal reasons for containment, and is generally coupled with other specific disposal–containment strategies.
- *To provide permanent containment of the tailings.* This strategy generally includes several kinds of scenarios, ranging from *permanent ponds* to totally reclaimed solid land surfaces, e.g., a multistage strategy for treatment of tailings pond sludges as a land reclamation process (Yong, 1983a, b).
- *To recover water for reuse in the beneficiation processes as process recycle water or other mine-site requirements.* This requires implementation of treatment of the supernatant—assuming that liquid–solids separation is effective in producing sedimentation of the suspended fines in the slurry tailings.
- *To permit secondary recovery from the storage pond.* This strategy presumes that some residual resource is contained in the slurry tailings waste, and that secondary recovery of this resource can be obtained when appropriate technology becomes available, and when the economic climate is favorable.

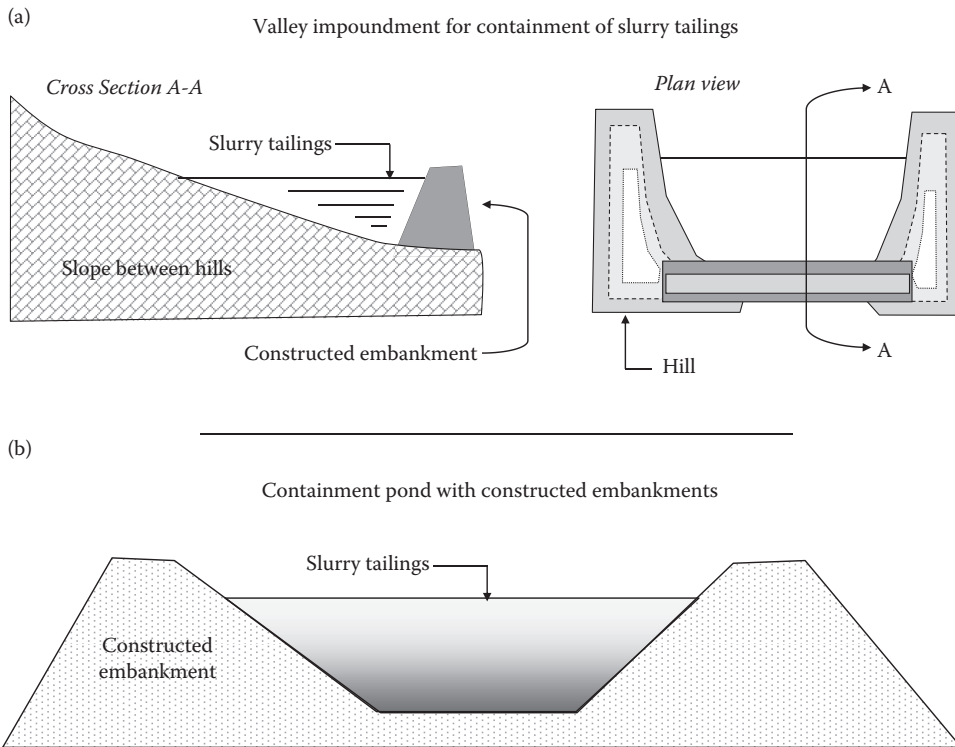
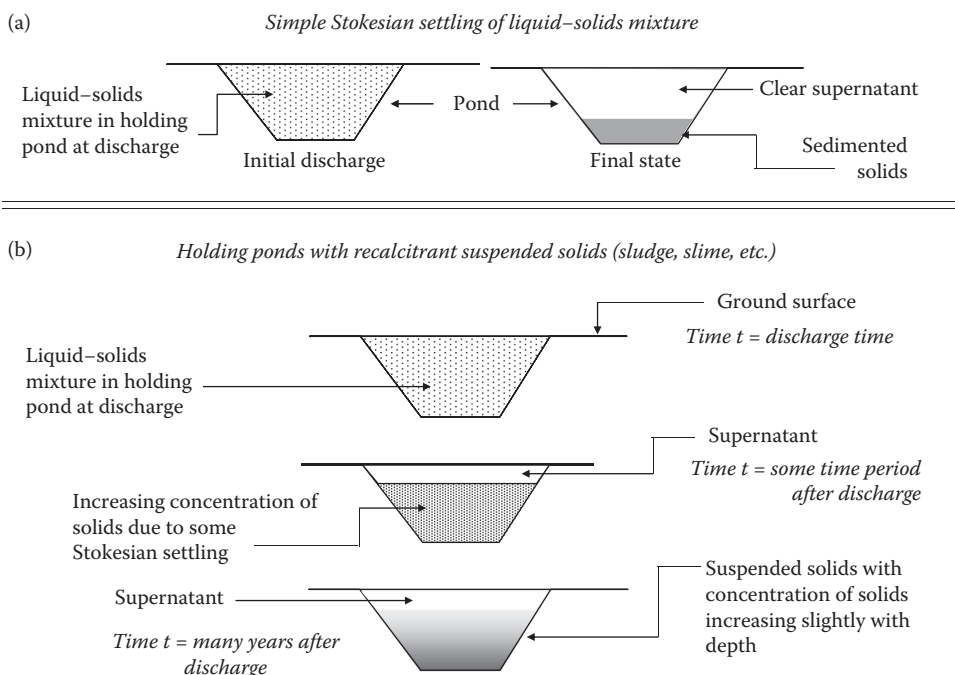
**FIGURE 5.8**

Illustration of valley impoundment for containment of slurry tailings (a) and constructed pond (b).

There are at least three basic types of slurry tailings impoundment facilities: (1) abandoned, used-up, fully exploited mine pits, (2) dammed-up valleys, as illustrated in Figure 5.8, and (3) constructed ponds with containment embankments (Figure 5.8). The choice of containment facility depends on many factors, not the least of which is site conditions and company mining strategy. These are not within the scope of this book and will not be addressed.

There are two distinct categories of slurry tailings contained in the containment facilities or structures:

1. Containment structures that contain sedimented solids and particulates discharged from mineral extraction processes. These structures will show a “solids-sedimented” layer overlain by water as illustrated by the containment pond shown in the top diagram in Figure 5.9. For such kinds of sediment slurries, treatment of the supernatant (liquid) may or may not be necessary—depending on the chemistry and/or toxicity of the supernatant. In some mining processes, such as aggregate harvesting from transported surface soils, since water is the only agent used in the beneficiation process, the supernatant obtained is considered to be nontoxic. As an example, tin mining of placer deposits using the gravel pump and dredging method will leave behind slime ponds with well-developed sediments and clear supernatants.

**FIGURE 5.9**

Two types of behavior of liquid–solid discharge in slurry tailings containment structures. The examples shown are containment ponds. (a) Simple Stokesian settling of the solids in the liquid–solids mixture. (b) Solids behavior over some period, ending up with recalcitrant performance of suspended solids.

2. Containment structures that contain solids' suspensions. The solids in these suspensions may or may not finally settle to the bottom of the containment structure to form sediments. Using containment ponds as an example, the bottom diagrams in Figure 5.9 show the characteristics of these kinds of ponds. The dispersion stability of these types of slurry tailings will be discussed in the next subsection.

For suspended fines in slurry tailings that do not exhibit liquid–solid separation behavior, some common features can be identified. If one determines the solids concentration with depth of the slurry tailings, one will obtain at least four distinct zones. These are (1) clear supernatant liquid, (2) a transition zone where the solids concentration begins to register some small value that increases as one progresses in depth, (3) a stagnant zone where the solids concentration remains relatively constant or increases imperceptibly with depth, and (4) a sediment zone that contains the solids that have finally settled to the bottom of the containment structure. Figure 5.10 shows a typical solids concentration (sc) profile in the four zones that are typical of various kinds of sludges, slimes, slurries, etc. The sc values refer to the weight ratio of the suspended solids to aqueous phase that constitutes the suspension fluid. Figure 5.11 shows the solids concentrations in the stagnant zones for various types of slurry tailings. Leaving the suspended fines in the containment structures is not an acceptable land-use option. Strategies have been developed to render the material in the containment structures to a state that would not pose a threat to the immediate environment and biota (Yong, 1983a, b).

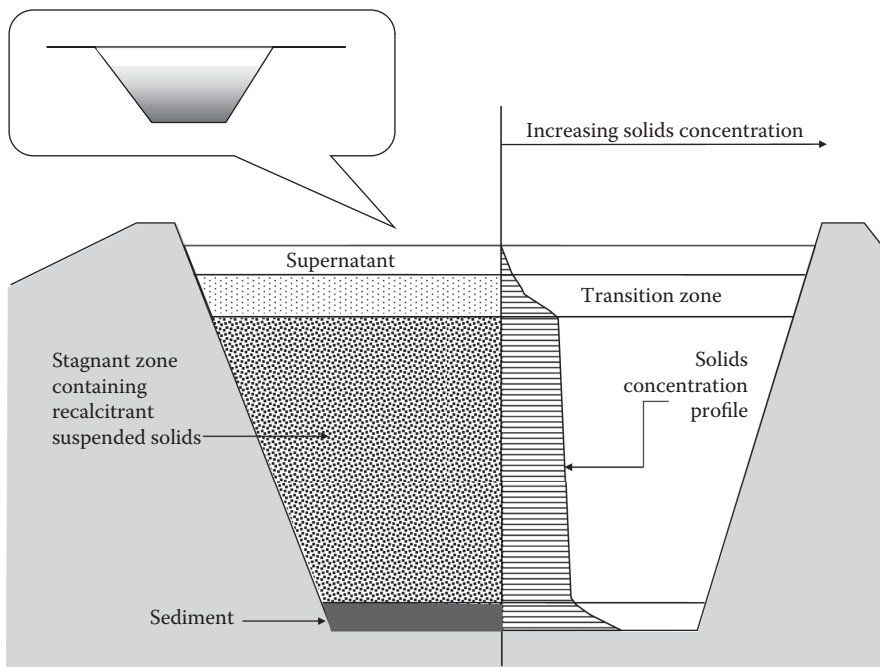
**FIGURE 5.10**

Illustration showing solids concentration profile for the recalcitrant suspended solids behavior pattern – typical of such sludges and slimes as red muds, tar sands sludges, phosphatic, and other clay slimes.

Soil-organic slime

sc \approx 2 to 20%

Wet milling of humate-cemented sand grains for extraction of heavy minerals.

Oil sands sludge

sc \approx 40 to 44%

Sludge from hot water extraction process for bitumen from oil sands.

Aggregate slime

sc \approx 12 to 18%

Wash-extraction of coarse aggregates from weathered granite.

Clay coating slurry

sc \approx 50 to 54%

Clay coating slurries in kaolin mineral processing for paper coating.

Phosphate slime

sc \approx 13 to 20%

Phosphate rock digestion, acidulation, and wet process phosphoric acid production, concentration, clarification and superphosphate production.

Bauxite red mud

sc \approx 20 to 40%

Bayer processing of bauxite for extraction of aluminium.

Beneficiation slurry

sc \approx 8 to 10%

Discharge wash from extraction of clay coated coal ore.

Tin mining slime

sc \approx 48 to 54%

Gravel-pump mining discharge from hydraulic mining of placer deposits.

[sc = solids concentration]

FIGURE 5.11

Some examples of slurries, slimes, and sludge found in holding ponds. The solids concentrations (sc) are obtained from results reported by Yong and his colleagues (see, for example, Yong, 1984). Details of the compositional features of the slurries, slimes, and sludge are given in Table 5.3.

5.4.2 Nature of Contained Slurry Tailings

Studies on the nature of the solids in suspensions in slurry tailings facilities (ponds, etc.) where solids remain in suspension for some considerable length of time show that the principal factors responsible for the dispersion stability of the suspended solids include (a) colloidal nature of the solid fines, (b) reactive surfaces on the fines, and (c) chemistry of the suspending fluid. The theoretical basis for the dispersion stability of the colloidal-type solid fines has been well developed and reported (Kruyt, 1952). The diffuse double layer (DDL) model is a good fit with the types of suspended fines (e.g., montmorillonite, kaolinite, amorphous materials) found in many slurry tailings. It essentially provides one with a basis for determining (theoretically) the maximum volume of water or fluid in the diffuse ion layer that surrounds individual reactive suspended particles.

The intensity of the interaction forces between the two particles resulting from the interpenetration (or overlapping) of the contiguous diffuse ion layers is a function of (a) the extent of the overlapping or interpenetration of the adjoining diffuse ion layers, (b) the nature of the reactive surfaces of the particles, and (c) the chemical composition of the suspending fluid. The electrostatic interactions of the ions in the diffuse ion layer and their relation to the surfaces of the reactive suspended particles are expressed as an electric potential ψ that decreases in an exponential manner as one departs further from a particle surface. The DDL model provides one with the basis for computing the average electric potential ψ as a function of distance from the surface of the particle as follows (Yong and Warkentin, 1975):

$$\psi = -\frac{2\kappa T}{e} \ln \coth \left(\frac{x}{2} \sqrt{\frac{8\pi z_i^2 e^2 n_i}{\epsilon \kappa T}} \right) \quad (5.5)$$

where the negative sign on the right-hand side indicates that the potential ψ decreases as one departs further away from each particle surface and where κ is the Boltzmann constant, T is the temperature, e is the electronic charge, n_i and z_i are the concentration and valence of the i th species of ions in the bulk solution, respectively, and ϵ is the dielectric constant. A detailed treatment of the DDL theory and models can be found in Kruyt (1952). The development and application of the DDL models to soil mineral particles such as those found in slurry tailings can be found in Yong and Warkentin (1975) and Yong (2001a).

Calculations of the volume of water associated with a gram of soil particle in equilibrium in an aqueous phase, based on type of soil fraction and DDL interactions, can be made using the DDL models. These can be compared with measurements of equilibrium solids concentrations obtained in soil suspension experiments. The results of solids suspension tests reported by Yong (1984) are shown in Table 5.3 for some typical soil solids found in slurry tailings. These results are expressed as the equilibrium volume of water per unit weight of suspended solids, and the units are given as cc/g of soil. The void ratios shown in the third column of 5.3 have been calculated from the measured equilibrium volumes.

Yong (1984) has shown good correlation between calculated and measured equilibrium solids concentration for the stagnant region of a slime pond using the equilibrium volumes shown in Table 5.3. In the actual cases examined, predicted solids concentrations were compared with actual solids concentrations obtained from samples in the stagnant zone (Figures 5.7 and 5.8) for phosphatic slimes, aggregate slimes, tin mining slimes, beneficiation slurry (slimes), tar sand sludges, etc. Table 5.4 shows that except for the aggregate

TABLE 5.3

Equilibrium Suspension Volumes Obtained from Soil Suspension Tests

Suspended Solids	Equilibrium Volume, cc/g	Void Ratio
Kaolinite	1.3	3.4
Illite	3.1	8.2
Montmorillonite	21.5	57
Amorphous Fe ₂ O ₃	20.5	82
Gibbsite	1.0	2.6
Mica	3.0	7.9
Quartz	0.14	1.12

Source: Adapted from Yong, R.N., Particle interaction and stability of suspended solids, in: *Sedimentation Consolidation Models: Predictions and Validations*, R.N. Yong and F.C. Townsend (eds.), American Society of Civil Engineers Publication, pp. 30–59, 1984.

TABLE 5.4

Composition of Slurry Tailings Solids and Suspension Fluid in Stagnant Zone of Slurry Tailings' Ponds

Type of Slurry Tailings	Suspended Solids Composition	Suspension Fluid, Dominant Ions	Measured sc (%)	Computed sc (%)
Phosphate slime (Florida)	Carbonate–flourapatite, quartz, montmorillonite, attapulgite, wavellite, feldspar, dolomite, kaolinite, illite, crandallite, heavy minerals	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , SO ₄ ²⁻ , HCO ₃ ⁻	14	13.4
Aggregate slime Southeast Asia	Kaolinite, montmorillonite, illite	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , SO ₄ ²⁻	14.3	10.5
Clay coating, Southeast USA	Illite, montmorillonite, mixed-layer minerals, chlorite, quartz	CO ₃ ²⁻ , HCO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , Na ⁺ , Mg ²⁺ , Ca ²⁺	52.7	51.8
Tin mining slime, Malaysia	Kaolinite, gibbsite, mica, quartz, “other”	Na ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺	52	50.8
Beneficiation slurry, Western Canada	Montmorillonite, illite, feldspar, kaolinite, chlorite	CO ₃ ²⁻ , HCO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , Na ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺	8.7	9.1
Tar sands sludge, Western Canada	Kaolinite, illite, chlorite, montmorillonite, mixed-layer minerals, feldspar, quartz, siderite, ankerite, pyrite, Fe ₂ O ₃	Not available	41.9	42.2

Source: Adapted from Yong, R.N., Particle interaction and stability of suspended solids, in: *Sedimentation Consolidation Models: Predictions and Validations*, R.N. Yong and F.C. Townsend (eds.), American Society of Civil Engineers Publication, pp. 30–59, 1984.

Note: sc, Solids concentration.

slimes obtained from aggregate recovery of aggregate loams, a comparison of the predicted solids concentration with actual measured values showed good accord. The ratio of predicted to measured solids concentration (predicted/measured) varied from 0.96 to 1.05. What this tells us is that colloidal dispersion of the suspended solids is responsible for the dispersion stability of the slurry tailings (Table 5.4).

5.5 Geoenvironment Impacts and Management

There are at least four significant kinds of geoenvironment impacts associated with resource mining and extraction operations: (1) mining excavations, pits, underground caverns, and debris piles, waste rock, rejects, overburden, etc., (2) acid generation and/or AMD from exposure of debris piles and exposed mine cavities, etc., (3) slurry tailings containment facilities, and (4) fate of contaminated fluids in underground in situ extraction of hydrocarbons. The second and third concerns can be seen in Figure 5.7. Mining excavations and underground mining create situations where the excavated (empty) volumes present challenges that are beyond the scope of the material discussed in this book. The impact from debris discharge and heaping into “tips” has been briefly mentioned at the beginning of this chapter (Section 5.3.1). In addition to the sterilization of the immediate landscape surrounding the tips as a result of the leachates emanating from the tips, possible instability of the tips is a question and problem that needs attention.

5.5.1 Geoenvironmental Inventory and Land Use

By and large, a major proportion of mining and on-site resource extraction operations are initially in regions situated some distance from urban centers. Original land use, prior to the time of mining exploration in such regions, would be characterized by the local physiographic features such as those discussed in Chapter 1. An environmental inventory and more specifically a geoenvironmental inventory prior to mining operations is needed to establish a base upon which decisions regarding impacts on land use, sustainability indicators, and restorative requirements can be sensibly made. The principal features of the geoenvironmental inventory, which is a baseline descriptor of the state of the various constituents of the local geoenvironment (*ab initio* condition), include

- a. Regional controls such as climate and meteorological factors
- b. Local terrain features including linear features, physical attributes, topography, watershed, local hydrology, surface layer quality, vegetative cover, receiving waters and water quality
- c. Subsurface features such as geological and hydrogeological settings, soil subsurface system, and groundwater–aquifer regimes

Decisions on sustainability of potential land uses or site functionality cannot be made without the inventory and without determination of the qualities of the attributes necessary for various land uses. These are highly dependent on whether (a) the mining and resource extraction operations remain isolated from urban communities or (b) small urban communities are located contiguous to the mining site. In the first instance, where mining operations remain isolated from habitable communities, the return of the exploited land to original natural conditions, are requirements to satisfy sustainable land use aims. These conditions entail restoring the original site functionality to protect human health and other biota. Specification of *ab initio* land environment sustainability indicators will be guided by the geoenvironmental inventory established before mining operations. Historically, geoenvironmental inventories have not been made prior to and even during mining operations. Nevertheless, a study of the natural geoenvironment system contiguous to the mining operations will serve to provide the basis for establishment of *ab initio* sustainability indicators. Although return of the land to its pristine original function, as a

sustainability objective, may not be absolutely possible, one can return the land to its natural state and natural site functionality. For example, one could seal shafts and openings, relevel and contour the landscape to conform to local topography, add organic fertilizers, and reseed with tolerant plant species (Davies, 1999). This procedure recognizes the fact that whereas the natural resource that has been harvested no longer exists, proper mine closure allows for recovery of the functionality of the affected ecosystem.

It is not uncommon for small urban communities to be developed within regions close to mining and resource extraction operations to service the mining operations. Land use and land restoration will depend on the requirements of the urban community and will undoubtedly be markedly different from *ab initio* land-use conditions. The general procedure is to perform an assessment of impacts on land use from the mining–extraction operations and to determine what reclamation and land restoration requirements are needed to meet the needs of the community. The basic steps shown in Figure 5.12 include

- a. Determination of impacts to geoenvironment and to land use. This requires information from *ab initio* geoenvironmental inventory.
- b. Compilation of community and/or regulatory land-use schemes or plans, e.g., return to *ab initio* conditions, housing estates, parklands, schools, recreation facilities, natural landscape, waste dumpsite, industrial estate, agriculture, etc.
- c. Determination of land quality requirements for land-use schemes and plans.

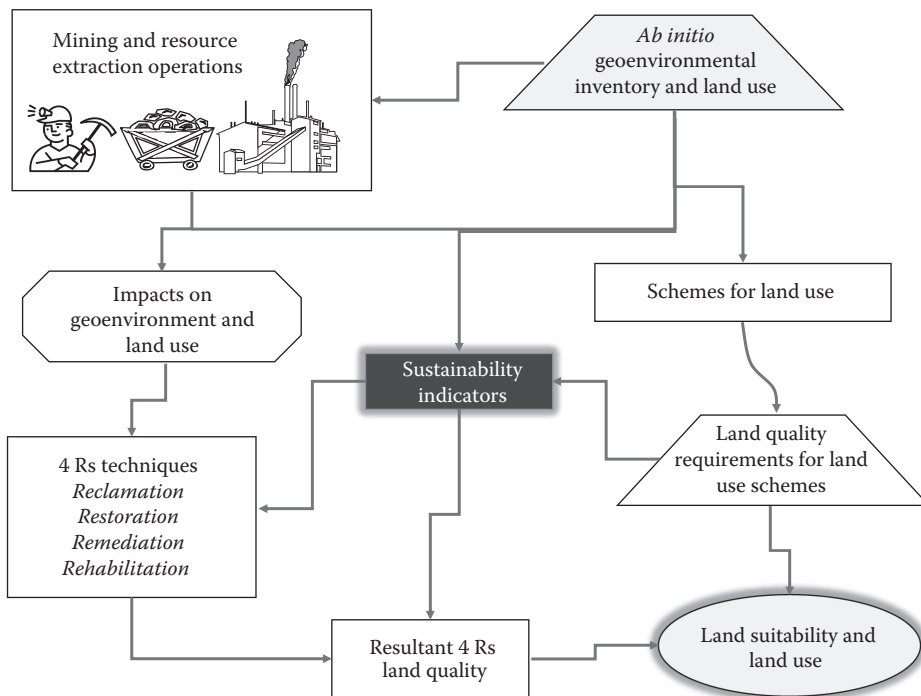


FIGURE 5.12

Basic steps for rehabilitation of lands affected by mining–extraction operations. Implementation of schemes for land use is dependent on the restored land quality. In the final analysis, land suitability is dependent on the quality of the rehabilitated land.

- d. Assessment of the required 4R technologies—remediation, reclamation, restoration, and rehabilitation requirements to meet the required land-use schemes or plans.
- e. Assessment of quality of rehabilitated lands.

Matching land quality, land suitability, and site functionality with community or regulatory land-use plans and requirements for rehabilitated land use that does not necessarily mean returning the land to initial conditions, for example, reclamation of land for housing developments.

5.5.2 Acid Mine Drainage Impact Mitigation

As mentioned previously, other than the presence of metal sulfide minerals, the two main elements in the production of acidic leachates are oxygen and water. These two constitute the sources for the acid (chemical) stressors. The impacts from these stressors are seen in the contamination of receiving waters and surface land soils. Although it may not be possible to totally eliminate or obviate these impacts, there are two clear paths where impact mitigation can be implemented. These are (1) source control and (2) leachate management. In the case of source control, the mitigating actions undertaken by the stakeholder include (a) control of quality of discharges by the stakeholder and (b) control of discharge by limiting and channelization of flow into treatment stations prior to discharge. These actions include technology and processes that are physical, chemical, geochemical, and biogeochemical—and various combinations of these. In the case of leachate management, the steps taken to mitigate impact of the acid leachates are essentially remediation efforts, i.e., remediation efforts undertaken “once the horse has left the barn.” These efforts have been called “passive control methods,” which are designed to minimize the deleterious effects of acid leachates on the environment by treating the leachates in transport through the geoenvironment. The industries involved in this type of problem, together with the pertinent governmental agencies have spent (and are still spending) some considerable effort in combating AMD. There are countless documents reporting on the various studies and efforts in “curing the problem,” and the reader is advised to consult these for detailed elaboration of the various research and case studies undertaken (and also presently underway). For the discussion that follows, only the basic elements of the mitigating efforts will be addressed.

The phenomenon of acid generation from heaps with trace amounts of sulfide minerals and from exposed sulfide minerals in mined-out caverns, pits, etc., has been discussed in Section 5.2. The magnitude of the sets of cascading problems attributed to the actions of acid leachate cannot be overstated. Cleanup of all the affected areas, mining sites, waterways, etc., is estimated in the billions of dollars in North America. Not only is the threat expressed in terms of acid leachates finding their way onto the land environment and into receiving waters, but also in terms of release of trace metals into the geoenvironment. The leachates and released metals will negatively affect the functionality of the various ecosystems that comprise the geoenvironment—causing them to be eventually unsustainable. In terms of sustainable land use, the obvious protection against such stressors (acid leachates) is to remove conditions and circumstances favorable for generation of acid leachates through source control. This means denying access to oxygen and water. The principle of “keep it dry” is a good principle to practice at mine sites. This is an easy statement to make, but is in reality a very difficult and an almost impossible principle to adhere to. Since water is an essential element in mining–extraction processes, “keeping it dry”

requires one to provide protective covers, isolation barriers, and pump–discharge operations. Implementation of these techniques is dependent on site- and operation-specific conditions. Adherence to the *keep it dry* principle is one of the basic requirements for minimization of impacts to land use, and to the 4Rs technique (Figure 5.12).

For conditions where acid generation has occurred and acid leachate has found its way to the land environment and its receiving waters, the two courses of required action are (1) protection of the affected land receptors and water bodies from accepting further acid leachates and (2) treatment of the affected land and water bodies. It has been suggested that once pollution of the receiving waters such as those described in Section 5.2 has occurred, destruction of aquatic habitat will render these waters to be bereft of aquatic life for a very long time. Nevertheless, treatment of these waters is necessary. Methods for treating polluted water were discussed in Chapter 3.

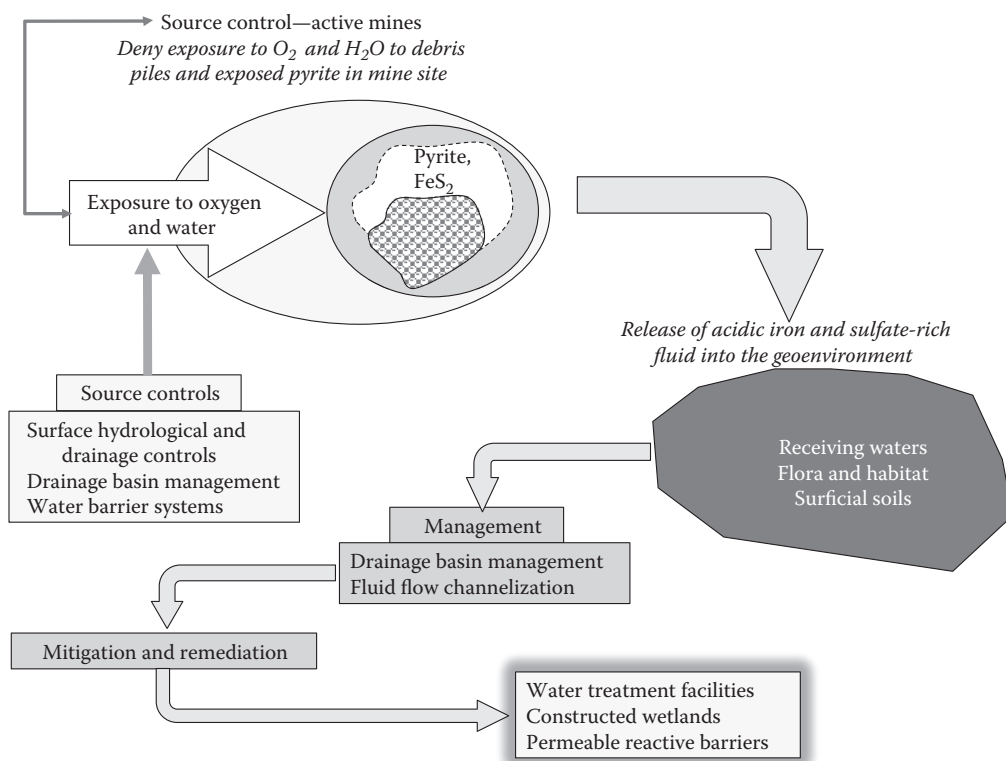
5.5.2.1 Acid Mine Drainage Management

AMD can also be managed. Active treatments that use wastewater treatment techniques are possible. They are expensive and must be maintained regularly such as the use of chemical or electrolytic treatments. The essential element here is the capture of leachate for treatment—an expense that will be ongoing for an interminable period since the source of acid generation will most likely be almost inexhaustible. Prevention of AMD is possible by addition of limestone or by sealing the area with fly ash grouts. For example, Bulusu et al. (2005) used a grout of coal combustion by-product to reduce AMD. The grout was durable and did not exhibit signs of weathering.

Alkaline agents (calcium oxide, calcium hydroxide) and wastes (cement kiln dust, acetylene gas sludge) can be added to pools of AMD for neutralization. Alkaline trenches with limestone or soda ash are used to neutralize runoff. Bacteriocides have to be used to inhibit bacterial growth and hence pyrite oxidation. Natural treatment through carbonate formations may also be possible as in the case of Cretaceous chalk underlying the coalfield slag heaps in the north of France (Chamley, 2003). PRBs may also be a solution. Constructed wetlands are a low-cost alternative for passive treatment as described in the next section. Anoxic limestone drains are being evaluated for use because of their ease in maintenance and operation. However, they require large areas for effective application.

The essential procedures for mitigating AMD stressors impacts include (a) diversion of waters around the mine sites as part of the *keep it dry* (*keep it as dry as possible?*) strategy, (b) channeling the generated leachates through constructed aerobic and anaerobic wetlands as a neutralization procedure and/or through permeable treatment walls (to be discussed in Chapter 10), (c) complete inundation of mined-out sites—to deny access to oxygen, and (d) capturing and channeling the generated leachates for active treatment before discharge (Figure 5.13).

There is also a significant capacity for natural attenuation at mining sites. A particular example of this is the Falun Copper Mine in Sweden. During its operation of more than a hundred odd years, it is estimated that a half to one megatonne of copper, lead, zinc, and cadmium were emitted into forest soils and streams in the area (Lindeström, 2003). Concentrations of 70 and 2000 µg/L were found in streams in the city of Falun after treatment of the mine water was initiated but decreased thereafter. Soils in the area, however, were able to recover substantially faster. Most of the metals concentrated in the sediments in two lakes. Copper was 120 to 130 times normal background levels, whereas lead and zinc levels were 30 to 40 times. Cadmium accumulation was much less. The aquatic ecosystem

**FIGURE 5.13**

Basic elements of source control and passive treatment procedures for AMD stressor mitigation.

was able to return due to the low bioavailability of the metals and possible interactions between the metals.

5.5.2.2 Wetlands

Natural wetlands are areas of land with the water level close to the land surface, thus maintaining saturated soil conditions and vegetation that includes plants, peat, wildlife, microbial cultures, cattails (*Typha* spp.), reeds (*Phragmites* spp.), sedges (*Carex* spp.), bulrushes (*Scirpus* spp.), rushes (*Juncus*, spp.), water hyacinthe (*Eichhornia crassipes*), duckweeds (*Lemna* spp.), grasses, and others (Mulligan, 2002). Algae and mosses, together with the wet areas can trap the heavy metals. Constructed wetlands have been specifically designed to include these species for the removal of BOD, suspended solids, nutrients, and heavy metals for optimal performance. It has been reported by Reed et al. (1995) that 1000 managed wetlands are in operation throughout the world. In 1988, 142 North American wetland systems were used for acid-mine drainage (Wieder, 1989).

Iron and manganese removal are often the key objectives in treatment of mine drainage. Because of possible clogging of subsurface systems due to precipitation of iron and manganese in subsurface systems, preference is usually given to surface systems since they can be aerated more efficiently. Since the pH typically decreases from 6 to 3 in AMD phenomena, the Tennessee Valley Authority (TVA) has developed an anoxic limestone drain (ALD) for use as a treatment tool. This consists of a high calcium limestone aggregate

TABLE 5.5

Monitoring Requirements for an AMD Drainage Remediation Process

Category	Parameter
Physicochemical	pH
	Redox potential
	Total dissolved solids
	Specific conductance
	Dissolved oxygen
Cationic and anionic species	Fe, Cu, Pb, Zn, Cd, Hg, As, SO_4^{2-}
Gases	O_2 , CO_2 , SO_2 , H_2S
Flow	AMD flow rate, hydrostatic pressure
Meteorological conditions	Precipitation, temperature, sunlight, wind speed

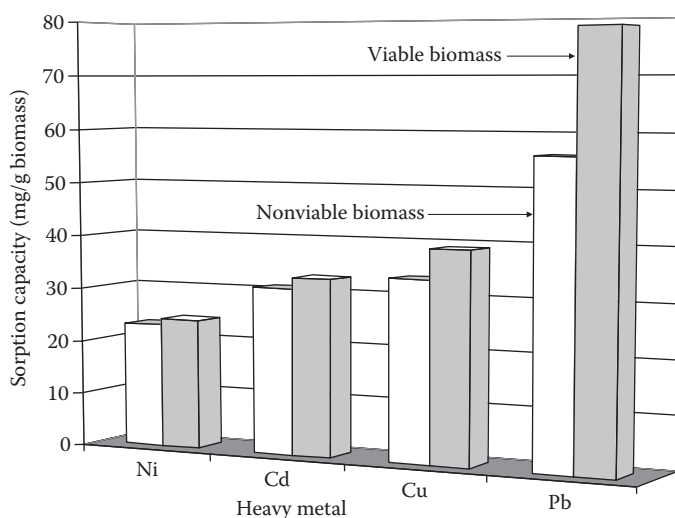
Source: Adapted from Fytas, K. and Hadjigeorgiou, J., *Environmental Geology*, 25, 36–42, 1995.

(20 to 40 mm) placed in a trench of 3–5 m wide and 0.6–1.5 m in depth (Brodie et al., 1993). The anoxic conditions in the trench are ensured by backfilling with clay. A plastic geotextile is placed between the clay and limestone. The inlet of the trench is placed at the source of the AMD. However, when oxygen content in the drainage is greater than 2 mg/L or the pH is greater than 6 and the redox potential is greater than 100 mV, use of the ALD is detrimental due to the formation of oxide coatings. Installation of a sedimentation pond before the wetland treatment with or without ALD is preferred since it is easier to remove iron precipitation from the pond than the wetlands. Sanders et al. (1999) have indicated that wetlands systems were used to remove Zn, Fe, Cu, Pb, and some other heavy metals from a moderate to severe acidic drainage from a mining complex in Montana. This treatment will be required for decades. Long-term monitoring will be needed as shown in Table 5.5.

5.5.2.3 Biosorption

Biosorption is a potentially attractive technology for treatment of water containing dilute concentrations of heavy metals. Activated carbon is the currently recognized adsorbent for removal of heavy metals from wastewater. However, the high cost of activated carbon limits its use in adsorption. A search for a low-cost and easily available and renewable adsorbent has led to the investigation of wastes of agricultural and biological origin as potential metal sorbents (Hammami et al., 1999). Biosorption is the ability of certain types of microbial biomass to accumulate heavy metals from aqueous solutions by mainly ion exchange mechanisms. A large number of microorganisms belonging to various groups, such as bacteria, fungi, yeasts, and algae have been reported to bind a variety of heavy metals to different extents (Volesky and Holan, 1995).

The main requirement of an industrial sorption system is that the sorbent can be utilized as a fixed or expanded bed for use in a continuous process. Immobilization techniques have been developed, but the employment of immobilization procedures is expensive and complex (Liu et al., 2003). Two attempts to market two different types of immobilized microbial biomass, one by BV SORBEX and the other by the U.S. Bureau of Mines were not commercially successful application (Tsezos, 2001). The feasibility of anaerobic granules for industrial wastewater reactors was investigated as a novel type of biosorbent for the removal of cadmium, copper, nickel, and lead from aqueous solution by Al Hawari and Mulligan (2006).

**FIGURE 5.14**

Comparison of a viable and nonviable anaerobic granulated biomass for the biosorption of heavy metals. (Adapted from Al Hawari, A. and Mulligan, C.N., *Bioresource Technology*, 97, 692–700, 2006.)

Results showed that a living biomass has a higher sorption capacity than a dried biomass but due to the difficulties in maintaining the biomass, the dried biomass would be more suitable for industrial applications (Figure 5.14). Unlike most forms of biomass, immobilization or stiffening was not necessary prior to using the biomaterial. Anaerobic granules possess compact porous structures, excellent settling ability and high mechanical strength. Even under aggressive chemical environments (acidic or basic conditions), the biomass demonstrated good stability with no visible structural damage—making this biomass more advantageous over other biosorbents. The biomass was also tested for arsenic sorption and was found to be favorable compared with other biosorbents (Chowdhury and Mulligan, 2011).

5.5.3 Slurry Tailings Ponds Impact Management

Slurry tailings ponds are by far the major type of containment facilities for slurry tailings. Their use has been discussed in the previous section. Their presence in the landscape degrades land quality and considerably reduces land-use capabilities. An illustration of such kinds of ponds is shown in Figure 5.15, for tin mining slurry ponds in Southeast Asia obtained as a result of alluvial tin mining hydraulic operations using the wash separation technique. Sand and debris are collected at the end of the sluice box—with the ponds serving as sedimentation facilities (Chow, 1998). It is not unusual for these ponds to develop a crust overlying a slime layer with solids concentration ranging from 50% to 60%. Encroachment of housing estates onto such kinds of ponds and debris, as seen, for example, in Figure 5.15, will pose limits on housing and introduce safety hazards. Reclamation of the ponds is necessary to allow for utilization of the reclaimed land for further urban development and other land uses consistent with an urban ecosystem.

Sustainable land use, in the context of slurry tailings ponds and their like, is not different in principle from the acid mine problem or mined-out caverns, pits, etc. We will consider sustainability of land use in the physical landscape sense, i.e., in respect to the physical features and properties of the land and its utility. Figure 5.16 gives a summary view of the various

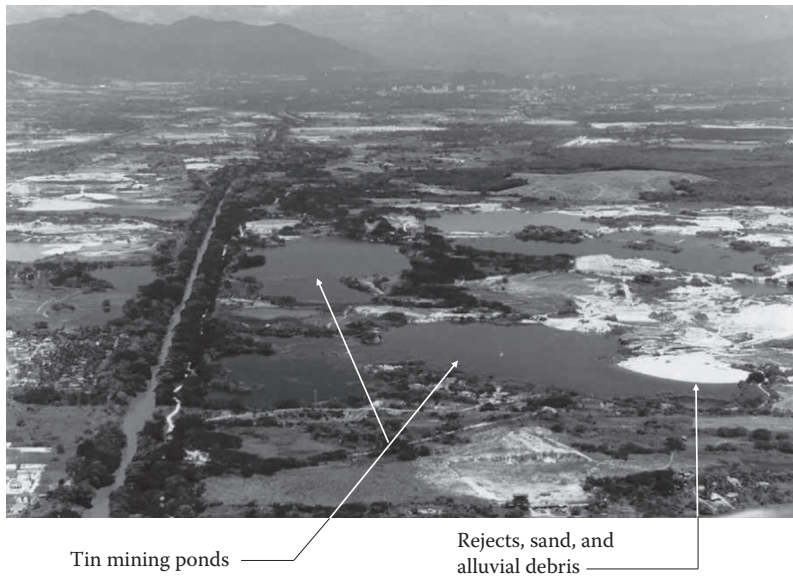


FIGURE 5.15
(See color insert.) Tin mining slurry ponds obtained as a result of hydraulic dredging and pumping. Reclamation of ponds is necessary to accommodate expansion of housing units seen at left of the picture (and left of the canal).

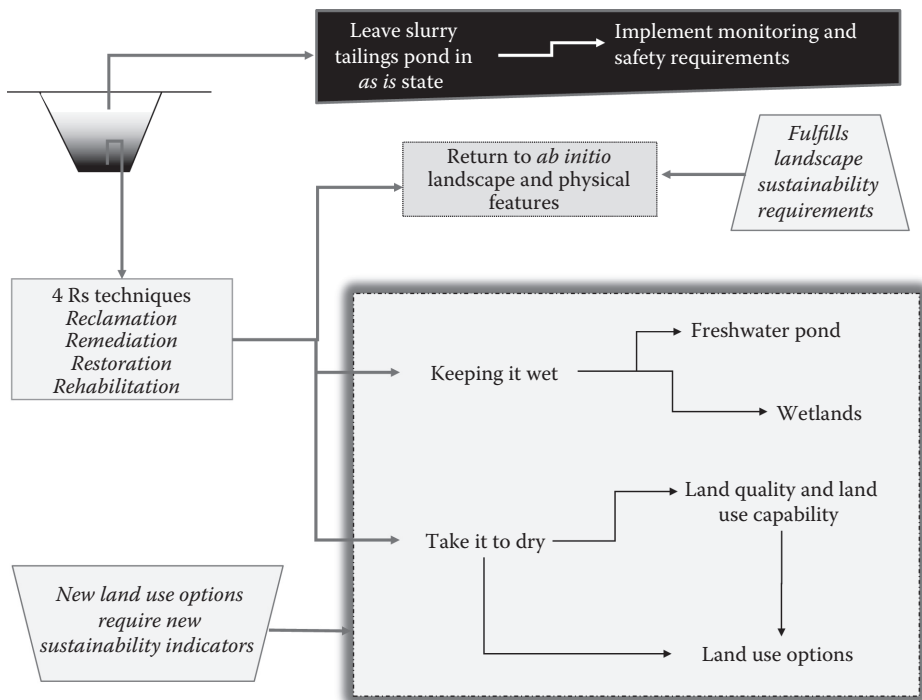


FIGURE 5.16
Sustainable land use in the context of slurry tailings pond. Options range from nonsustainable to enhanced land use and new sustainability scenarios.

options available for management of slurry tailings ponds. The first option is to leave the ponds in their disposal state. This is not a generally acceptable option, but nevertheless must be considered, in the event of negligent abandonment of such ponds. Health and safety concerns require implementation of (a) monitoring procedures for these ponds and (b) health and safety measures to protect human and wildlife population. Figure 5.16 also shows three distinct categories of sustainable land-use options for the slurry tailings ponds are available: (a) return of land to *ab initio* physical condition, (b) reclamation of the ponds in the *keep-it-wet* state, and (c) reclamation of the ponds in the *take-it-to-dry* state. Returning the land to its *ab initio* landscape condition fulfils the landscape portion of sustainability requirements.

Two basic options are available for the *keep-it-wet* state: (1) freshwater pond, and (2) wetlands. In the *take-it-to-dry* category, the options available depend to a large extent on (a) quality or competency of *dry* land obtained from the reclamation process and (b) regulatory and community requirements. The basic element of all the schemes for reclamation of slurry tailings ponds and other types of containment facilities must deal with the question of “what to do with the stagnant layer.” Liquid–solids separation and treatment of the released water are basic requirements for any of the pond reclamation options. Physical methods for liquid–solids separation include surcharging the top of the stagnant layer to achieve consolidation—a geotechnical process that provides compression of the solids skeletal matrix through the applied surcharge and drainage of the water in the skeletal structure. Other physical methods include removal of the stagnant layer for treatment, and filling of the emptied pond with new fill material.

Chemical and physicochemical methods for increasing the sedimentation rate of the suspended solids in the stagnant layer include the use of polyacrylamides and polyelectrolytes. The basic intent of these kinds of flocculants is to overcome the domination of interparticle forces typical of colloidal interaction. Various kinds of flocculants and flocculating agents have been developed for such types of slimes and sludges (Yong and Sethi, 1982, 1983, 1989). They all have the aim of promoting aggregation of the particles into flocs, thus increasing the mass of individual groups of particles and hence allowing for gravitational forces to dominate and sedimentation to occur. Calculations performed by Yong and Wagh (1985) using two-particle collision theory to study the stability of the suspended solids in the stagnant zone have shown the effect of aggregation on the settling velocities of the suspended solids. Confirmation of their calculations has been obtained from experiments on a pure clay mineral suspension (kaolinite) and the red mud discharge from bauxite processing (Figure 5.17). Aggregation of the red mud particles with increasing solids concentration caused the increase in settling velocity. For the kaolinite soil suspension, increasing solids concentration in the soil suspension served to decrease the settling velocity—probably due to the hindrance effect posed by the proximal particles.

Another method for increasing the settling velocity of the suspended particles is to increase the zeta potential (ξ) of the particles. This is the potential that represents the charge at the shear layer between the suspended particle surface and the suspending fluid. We recall from Equation 5.5 that the potential ψ provides us with a means for determining the electric charge distribution at a distance from the particle surface. This potential has two basic components: (1) the potential at the surface of the particle, represented by ψ_o , and (2) the potential ψ_s at the Stern layer boundary (double-layer boundary) where the shear action with the liquid medium occurs. This potential, which is commonly identified as the zeta potential (ξ) is a function of the nature of the surface charge possessed by the suspended particle, the ions in the suspending fluid, and the ions in the double layer. By changing the zeta potential, aggregation of the suspended particles in the stagnant zone can be obtained, with resultant increased settling velocities. Figure 5.18 shows the relationship between zeta potential (ξ) and the dispersion stability for clay soils reported by Yong (2001b).

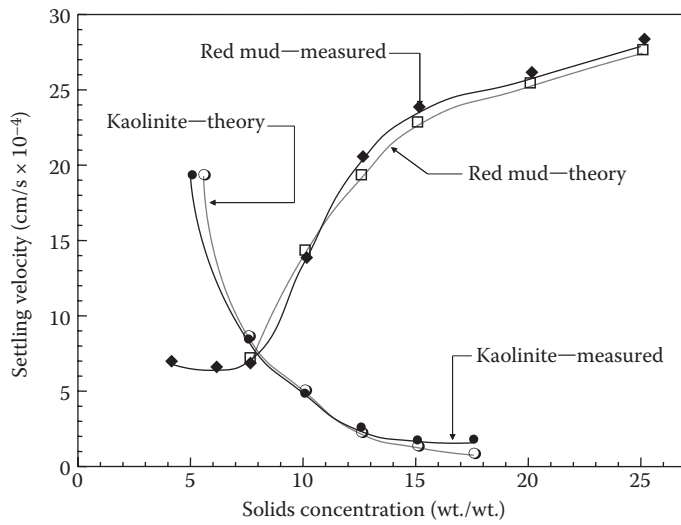


FIGURE 5.17
Calculated and measured settling velocities for a kaolinite soil suspension and bauxite red mud.

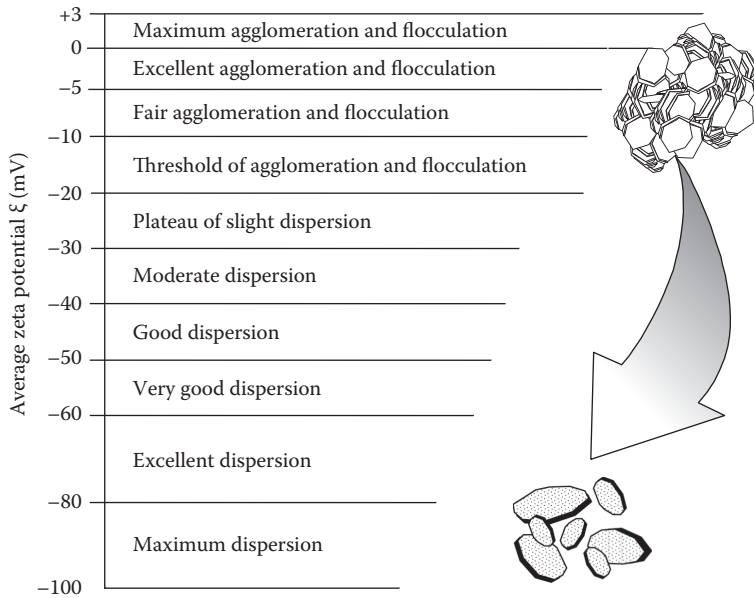


FIGURE 5.18
Relationship among zeta potential (ξ), soil microstructure (flocs and aggregations of particles), and dispersion stability for clay soils.

5.6 Concluding Remarks

5.6.1 Mining Activities

Harvesting of nonrenewable natural resources brings with it at least three major areas of geoenvironmental impacts: (1) depletion of the nonrenewable resource, (2) mining excavations on the surface and underground, and (3) discharges from processes associated with extraction of the natural resource. The biological components of the terrestrial ecosystem are not covered in the discussions in this book. We have focused specifically on the land-use aspect of the geoenvironment in mining operations as an upstream activity. The use of the raw materials obtained from such mining operations by downstream industries is covered in Chapter 7. From the viewpoint of geoenvironment sustainability, we accept that depletion of nonrenewable or depleting resources will not qualify for inclusion in any category of sustainable resources. This means that if one requires land use to be sustainable, one must deal with the physical landscape problems raised by above- and below-ground mining processes, together with operations and discharges from extraction and beneficiation processes.

Underground mining excavations pose problems in two categories: (1) the physical aspect of excavations as empty chambers, tunnels, etc., together with the heaping of debris and other spoils as heaps and tips and (2) the chemical problem represented by acid generation and the resultant AMD problem because of the interaction of the exposed sulfide minerals in the mined-out areas to oxygen and water. If sustainable land use requires one to return the land to its *ab initio* condition, this would mean filling the empty mined-out chambers and excavations. This would, or should, avoid or minimize the problem of acid generation. Since practical and economic considerations have so far militated against this course of action, attention has been directed toward mitigating AMD and ARD problems.

5.6.2 Contaminated Water Management

The problem of water usage and “what happens to the used water,” which most often is contaminated with products issuing from extraction/beneficiation and from usage in underground in situ extraction of hydrocarbons (SAGD, CSS, and fracking), is perhaps one of the most critical problems that requires considerable management to avoid and/or minimize chemical stressor impacts on the geoenvironment. Two particular issues or concerns need attention: (1) generation of acid leachates giving rise to the commonly identified problem of AMD and (2) contamination of shallow and deep-seated aquifers from “used waters” associated with underground in situ hydrocarbon extraction practices. Cleaning up contaminated aquifers is a task that is almost impossible, not without some considerable expenditure and time. To avoid contamination of groundwater and aquifers, it is essential to implement monitoring of water movement in the subsurface through the use of monitoring wells and through systematic evaluation of the hydrogeological settings and continuous hydrochemical analyses of abstracted samples from the monitoring wells. The use of appropriate and valid analytical transport and fate models that address site- and project-specific in situ hydrocarbon extraction process, whether it be the steam-assisted processes or the fracking process, would add considerable value to the monitoring schemes required to ensure that hydraulic stressors carrying contaminants are not delivered to receiving waters—above ground and groundwater and aquifers.

Measures undertaken by industry to better protect against acid generation in present mining and extraction operations, and in underground in situ hydrocarbon extraction

operations are continually being improved. However, for historic and abandoned mine sites, the problem of AMD remains. The direct impact on land use from acid generation problems is not only in the immediate sense of acid interactions with the land environment, but also in the ripple or cascading effect. Contamination of groundwater and receiving waters, together with contamination of shallow and deep-seated aquifers pose severe threats to native habitat and plant life and other receptors. The challenge for geoenvironmental engineering is to provide measures that will preserve and maintain the original functionality of the land component of the geoenvironment. The schematic diagrams of Figures 5.12, 5.13, and 5.16 provide a starting base for implementation of sustainable practices in geoenvironmental engineering.

5.6.3 Tailings Discharge and Mine Closure

In regard to tailings slurry discharges and containment facilities, sustainable land use is not different in principle from the acid mine problem or mined-out caverns and pits. Options for reclamation of the slurry tailings ponds and containment facilities have been summarized in Figure 5.16. Much depends on both regulatory and industry requirements.

Closure of mining sites requires site restoration procedures to ensure that the restored sites may be used for other purposes and to prevent risk to the environment and humans. The reuse of mining residues, stabilization of mine areas, and neutralization of pollutants are some of the challenges. Numerous techniques are being investigated such as replanting, wetland treatment, and biological treatments. As a more sustainable approach, waste products must be recycled as much as possible and should also be integrated into the treatment processes. An integrated approach for land, solids, and leachate management is highly desirable.

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6

Agricultural-Based Food Production Geoenvironment Stressors

6.1 Introduction

The discussion in this chapter is concerned with the geoenvironment stressors generated from the primary sets of activities associated with agricultural-based food production. These activities include the production and harvesting of farm products (including livestock) and the industries identified with these sets of activities. These industries are *upstream industries*. They fall under the classification of *agroindustry*. By definition, upstream industries deal with the production of raw materials that are later transformed to finished products by downstream industries. They are known generally as *agroprocessing industries*. They include industries producing food products for the consumer, textiles, forest products, etc. Agriculture (farming and food production) is a basic activity and an essential component in the life-support system of the human population. To obtain a sustainable society, the geoenvironment natural capital must be maintained at a sustainable level—meaning that harvesting and utilization of the resources represented by the natural capital must meet the requirements of replenishment and regrowth. In respect to the vital issue of food production to satisfy the needs of a sustainable society, this means that the activities associated with food production must be managed within the context of a sustainable agroecosystem.

Agroecosystems consist of two main components: (1) naturally occurring and (2) human-related components. The naturally occurring component consists of rivers, lakes, ponds, groundwater and aquifers, and flora and fauna. The human-related group consists of components that are the result of manipulation by humans to produce food, fibers, and other products such as cultivated pastureland, seasonal and permanent crops, cultivated forests, and livestock or animal farming. In the *seasonal crops* category, for example, the list of human-related actions include land clearing, soil tillage and planting of crops, addition of water and nutrients, weed and pest control by various mechanical and chemical aids, and harvesting when crops mature. The crops that are planted are *seasonal* in the sense that they (crops) are harvested in one seasonal growing cycle. Meanwhile, the permanent crops exist for much longer periods. They consist of orchards, cotton fields, tea plantations, etc.

6.1.1 Food Production

Hunger and nutrient deficiencies are experienced daily by more than a billion people. Nutrient deficiency is defined as insufficient levels of food proteins and caloric energy. As can be seen in the famines in many parts of the world, nutrient deficiency is a major

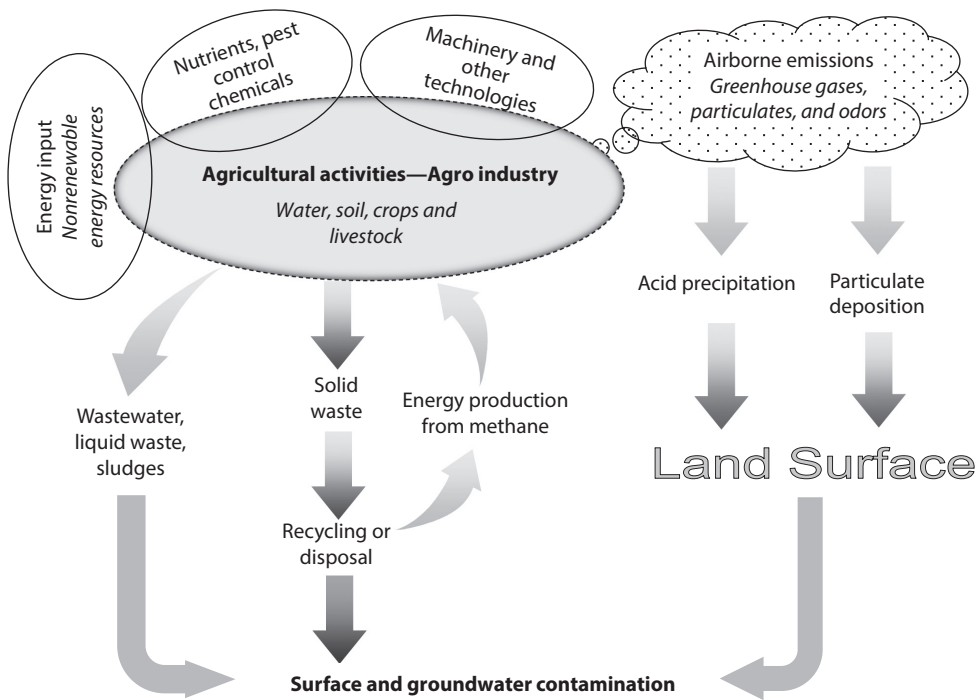
problem. The Food and Agriculture Organization (FAO) of the United Nations estimates that in the period of 2010 to 2012, approximately 870 million people, representing 12.5% of the global population, were chronically undernourished. Of these 870 million, it is estimated that about 850 million live in underdeveloped countries (FAO, WFP, and IFAD, 2012). The Rome Declaration on World Food Security called for a decrease of undernourished people from the present amount to 400 million by the year 2015. If one factors in the increase in population up until that time, this would mean a rate reduction of undernourished people of more than 50% (WFS, 1996).

The demands for food are immense and as we have discussed previously in Chapter 1, according to the Malthusian model, food availability is linked with population growth (Malthus, 1798). It has been estimated (Daily et al., 1998) that by 2050, food demand (a) could double in response to population growth, (b) would increase in relation to per capita income, and (c) would increase in response to measures to reverse the undernutrition of the poor. Increased urbanization has decreased available agricultural land. To increase yields, the use of fertilizer and pest control chemicals has increased. Irrigated areas have expanded and high-yield crops have been developed. Some of these agricultural activities designed to enhance crop yields have led to decreases in soil fertility and increases in soil and water contamination. Subsequent depletion of the soil resource and the presence of these contaminants could lead to a decline in per capita food production according to Meadows et al. (1992), which could be a threat to human survival (Commoner, 1971). More than 75% of the arable land in North and Latin America, 25% in Europe and 16% in Oceania can be considered damaged. This threatens future food supplies (Fischer Taschenbuch, 1996). North America's breadbasket (the U.S. Midwest to the Great Plains in Canada) is particularly at risk due to wind and soil erosion and fertility loss. Loss of native habitat in Canada due to farming has been significant. The Canadian Biodiversity Information Network (CBIN) reports that more than 85% of shortgrass prairie, 80% of mixed-grass prairie, 85% of aspen parkland, and almost all the native tallgrass prairie have been lost (CBIN, 1998).

Food production must be increased without increasing the impact on the geoenvironment. Improper irrigation can lead to waterlogging and soil salinity problems. Use of pest control chemicals has increased pest resistance and destroyed natural species (NRC, 1991). The many aspects of agricultural engineering and soil management practices are subjects that are well studied in soil science and agronomy. Their attention to efficient food and crop production, together with research into the various issues of soil management and soil quality have the aim of providing agricultural productivity without compromising the objectives of sustainable agriculture.

6.1.2 Geoenvironment Engineering: Sustainable Issues

There are many stressor impact issues associated with agricultural-based production of food. Most, if not all, of them are issues that fall under the purview of agricultural engineering and soil science. That being said, there are some impact issues that are common to geoenvironmental engineering land management. These issues—i.e., the stressors and their impacts—constitute the focus of this chapter. The discussion in this chapter is directed toward the likely geoenvironmental impacts due to food production activities such as pesticide use, nutrient addition, and waste management as depicted in Figure 6.1. The geoenvironment-associated problems resulting from these activities are common to those found in land disposal of wastes and other soil contamination problems encountered in geoenvironmental engineering. Discussion on management, alleviation, and mitigation of the impacts due to

**FIGURE 6.1**

A summary of some of the major inputs and outputs related to agricultural activities.

stressors originating from these activities will be addressed in the latter part of this book in the chapters dealing with the subject of soil contamination, management, and remediation.

The impacts from the agricultural activities depicted in Figure 6.1 that can be mitigated and alleviated fall into the category of *surface and subsoil contamination*. The stressors responsible for contamination of the surface and subsoil are (a) the various waste discharges into or onto the land surface environment, (b) the various kinds of chemicals used in pest controls (herbicides, pesticides, etc.) and as fertilizers, (c) airborne emissions from the operation of machinery and other devices in the various operations and activities, and (d) deposition of noxious airborne particulates onto the land surface.

6.2 Land Use for Food Production

Soil is a natural resource material and is considered a geoenvironment natural capital. Agricultural soil has a balance of inorganic and organic components. Both climate and the environment control the value of the soil. Factors such as water content, soil type (composition), soil thickness, salt content, and other physical, chemical, and biological properties are important determinants of soil quality. In regions where winters and cold temperatures are factors, the presence or absence of permafrost will also contribute to soil value. The combination of physical, chemical, and biological agro-aids, climate, soil management, and technology has rendered the soils in Europe and North and Central America favorable

for agriculture. In contrast, the lack of many of the agro-aids, inadequate technology, poor soil management, and unfavorable climate have combined to produce nutrient-depleted soils in regions of Africa and Asia.

The requirement for sufficient food to sustain life has led humans to require substantial use of grasslands, forests, and freshwater. Factors such as excess or lack of water, drainage, soil quality and thickness, salinity, annual mean temperatures, and in cold regions, the freezing index and the presence or lack of a permafrost area determine the appropriateness of the soil for agriculture. Richards (1990) reports that there has been a five-fold increase in agricultural lands in the last 300 years. This needs to be balanced with the large quantities of land lost from production due to erosion, salinization from irrigation, desertification, and conversion to roads and urban uses. The capillary rise of salts (chlorides, sulfates, and carbonates) due to groundwater extraction and irrigation is threatening the U.S. High Plains, Canadian prairies, and Australian soils. This rate of loss has increased to 79,000 km²/year according to FAOSTAT (FAO, 2006a). With the exception of a few high value crops, the market value of the land for nonagricultural purposes is much higher—a factor that appears to drive conversion of these lands to urban uses. The other consideration that is significant is the increasing productivity of agriculture in the last century—a factor that has decreased famine rates significantly (Pinstrip-Anderson et al., 1997). Innovations including high-yield crop varieties, application of fertilizers and pest control, and utilization of mechanized equipment in both developed and developing countries have substantially increased agricultural productivity.

More than 50% of the land's surface is involved in one way or another with forestry, agriculture, or animal husbandry. Pastures alone make up 6% to 8% of the land. This does not include land for grazing. Agriculture, in combination with urban areas occupy up to 10% to 15% of the land (Vitousek and Mooney, 1997). More than 130,000 km²/year of forests were eliminated for the period 1990–2005, and of this, 98,000 km²/year were converted to agricultural crop use (FAO, 2006b). This has substantial implications in global warming since forest soils and removed trees account for recycling of much larger amounts of carbon dioxide from the atmosphere than agricultural lands. Deforestation also leads to increased risk of soil and wind erosion because of exposure to the elements. Although some forests have been allowed to regrow upon depletion of agricultural lands, reforestation rates are much smaller than deforestation rates.

Ploughing disrupts (a) soil horizons, (b) chemical weathering, and (c) soil horizon interchanges. Ploughing compacts soil and decreases soil permeability. This inhibits evaporation processes and plant germination. Cattle and sheep herds also compact the soil. In arid climates, the soil is particularly vulnerable to erosion due to mechanization of ploughing. Overgrazing and slash-and-burn cultivation also reduces soil cohesion leaving many areas affected by soil degradation and loss of vegetation. More than 35% of all degraded land is due to overgrazing (Quendler and Reichert, 2002). Arid and semiarid lands are particularly susceptible in Oceania and Africa.

From the geoenvironmental perspective, one could ask “how sustainable is agriculture?” Although most agree that agriculture is not sustainable under present practices, there is considerable debate concerning the means for measuring sustainability (FAO, 1995, 1996). Although full consensus is not available, it is agreed that the factors that need consideration are the use of genetically identical plants, irrigation water, fertilizers and pesticides, and the assortment of wastes produced. Intensive agricultural practices utilizing high levels of technology and mechanization are generally not kind to the soil environment. A simple summary of the major inputs and outputs of agricultural activities is depicted in Figure 6.1. The impact of agricultural activities on the land environment will be discussed in more detail in the next section.

6.3 Stressor Impacts on Water and Soil

Two of the most important ingredients in agricultural-based food production, other than climatic conditions, are *water* and *soil*—more specifically, adequate water supply and soil quality.

6.3.1 Water Utilization

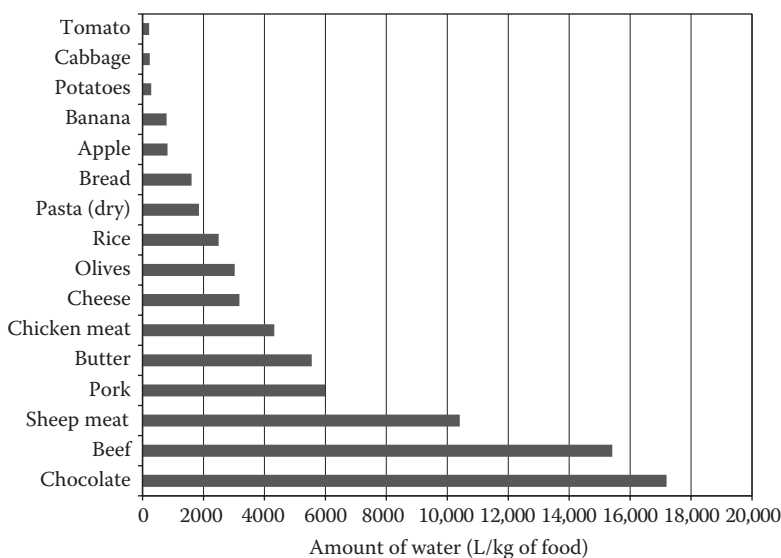
The availability and quality of water are two important water factors that impact significantly on the health and welfare of a growing population, particularly in developing countries. Freshwater is a precious resource because of the limited amounts directly available for use. More than half of runoff water is used by humans, and 70% of this is for agriculture (Postel et al., 1996). Rivers are diverted to serve the needs of humans. Only 2% of the rivers in the United States have not been manipulated. As an example of the impact of excessive use of water for agricultural purposes, it is reported that the water levels of the Aral Sea, located in Central Asia in the lowlands of Turan, have been substantially reduced by agricultural practices. The result of this has been (a) loss of native fish and biota, (b) creation of a source of windblown dust from the exposed salty sea bottom, (c) increase in the frequency of human diseases, and (d) creation of a drier local climate (Micklin, 1988).

The cost of energy influences one's ability to extract, pump, and irrigate abstracted groundwater. Increasing agricultural yields coupled with increasing land for agriculture result in corresponding increases in water demand. About 33% of the world's food is produced by irrigation (Postel, 1992). Management for salinity and drainage is required to avoid decreases in agricultural yields. Falling water tables increase the costs of abstraction of groundwater—a factor that needs to be incorporated into management of irrigation.

Irrigation involves exploitation of rivers, aquifers, or other freshwater sources, causing a disruption of the natural hydrological cycle. If irrigation is poorly controlled, desiccation can occur between watering periods. This can lead to increasing rates of aridification and wind erosion. Over-irrigation can deplete freshwater sources, and the soil can become salinated due to increased evaporation at the surface horizons. Substantial amounts of water are required for production of various crops. As shown in Figure 6.2, the growing of corn, rice, and soybeans require substantially more water than wheat. Livestock requires 100 times more water than 1 kg of vegetable protein. Overall, in 2005, less than 1% of the total amount of water was used to raise livestock (Kenny et al., 2009). It has been estimated that up to 20,000 L of water are required to produce 1 kg of beef on a range, approximately 100 times the amount to produce 1 kg of tomatoes (214 L/kg) (Institution of Mechanical Engineers [IME], 2013). Increase in livestock and crop production required to satisfy the needs of a growing population will continue to stress water resources (Giampietro and Pimentel, 1995)—in addition to extensive food wastage (30% to 50% of all food produced) due to inadequate harvesting, storage, and transportation procedures (IME, 2013).

Mining of groundwater is necessary because of demand for freshwater by the increasing population and subsequent use of irrigated agricultural practices (Falkenmark, 1989). Up to 68% of the groundwater withdrawn in the United States is for agriculture (USGS, 2014). Water tables have fallen at the rates of 3 to 120 cm/year in the United States in some areas (Sloggett and Dickason, 1986), and in China, at rates of 1 to 2 m/year (Postel, 1992). Some groundwaters cannot reach the ocean in the dry season.

Conflicts over water use due to irrigation have occurred in various parts of the world. The Egyptians have used the Nile for more than 5000 years while the other nations in the upper

**FIGURE 6.2**

Amount of water required to produce one kg of food.

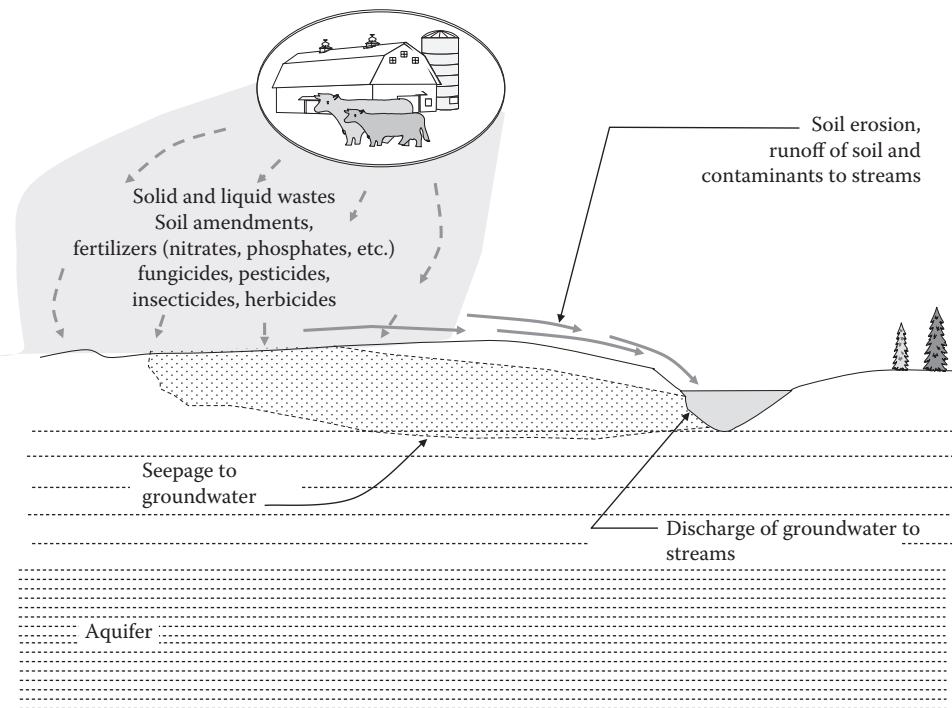
drainage basin have not (McCaffrey, 1993). Recently, however, lack of water and increasing populations have made the other nations more dependent on the Nile. Construction of a dam on the Ganges River by India has led to riots and protests in Bangladesh, as the water needed for irrigation is now diverted (Kattlemann, 1990).

6.3.2 Soil and Water Quality Stressors

6.3.2.1 Chemical Soil Nutrients

Agricultural practices can have a significant impact on groundwater and receiving waters—as summarized in Figure 6.3. Chemicals such as nitrogen (N), potassium (K), phosphorus (P), sulfur (S), and magnesium (Mg), introduced as plant nutrients, can have significant impact on water quality and can affect human health and other biotic receptors—if and when they become non-point source contaminants for receiving waters and aquifers. Other sources of nutrients in the farming industry include inorganic fertilizers, animal manure, biosolids, septic tanks, and municipal sewages. In Canada, in 2011/2012, an average of 2,160,000 tonnes of nitrogen and 733,000 tonnes of phosphorus were purchased for agricultural lands in the form of fertilizers (IFA Short-Term Prospects for World Agriculture and Fertilizer Demand 2010/11–2012/13; IFA Fertilizer Consumption 2011/12–2016/17 Country Reports). In 2000/2001, almost 400,000 tonnes of commercial fertilizer were applied to crops in the province. In 2000 in Quebec, 3850 tonnes of pesticides were sold, which is a decrease of 3.4% since 1992 (MDDEP, 2013).

The U.S. Environmental Protection Agency (USEPA) has established 10 mg/L of nitrate N as the maximum contaminant level in groundwater and a goal of 0.05 mg/L. It has also set a maximum of 0.1 mg/L for phosphate effluents that will enter a lake or reservoirs (USEPA, 1987). Nash (1993) determined that 25% of the U.S. drinking wells had above 3-ppm levels of nitrate and other wells have nitrate levels that have reached as high as 100 ppm.

**FIGURE 6.3**

Schematic of contaminant transfer from agricultural activities to surface and groundwater: geoenvironmental perspective.

According to the U.S. Geological Survey report of 1999 (USGS, 1999), nitrate concentrations exceeded the USEPA drinking water standard in 15% of samples collected in shallow groundwater near urban and agricultural lands. Amounts were measured in agricultural streams and found to be less than 20% of the phosphorus and less than 50% of the nitrogen applied annually to the land. This is due to the greater tendency of phosphorus to attach to soil particles and move with runoff to surface water compared with nitrogen. Extensive herbicide use is in agricultural areas. Approximately 70% of the total national use of pesticides is in agricultural areas, and thus, there is widespread occurrence in agricultural streams and shallow groundwater. The highest rates of detection were found for herbicides, atrazine, metolachlor, alachlor, and cyanazine. Insecticides were more frequently found in some streams draining watersheds with high insecticide use than in shallow groundwater as they also tend to sorb onto soil or degrade quickly after application. As there are no USEPA aquatic-life criteria for the major herbicides, Canadian guidelines were employed and concentrations were found to be elevated, particularly for atrazine or cyanazine in 17 of the 40 agricultural streams studied. Also, in the case of currently used insecticides, the major organochlorine insecticides (e.g., DDT, dieldrin, and chlordane), exceeded guidelines for aquatic life in at least one water sample from 18 of the 40 agricultural streams and recommended sediment-quality guidelines for protection of aquatic life at about 15% of agricultural sites.

Soybeans, alfalfa, and other legumes fix more than 40 Tg/year of nitrogen fertilizer (Galloway et al., 1994). Depletion in nitrogen levels can impact soil fertility. Nitrate runoff from agricultural fields can decrease water quality. The nitrogen cycle can subsequently

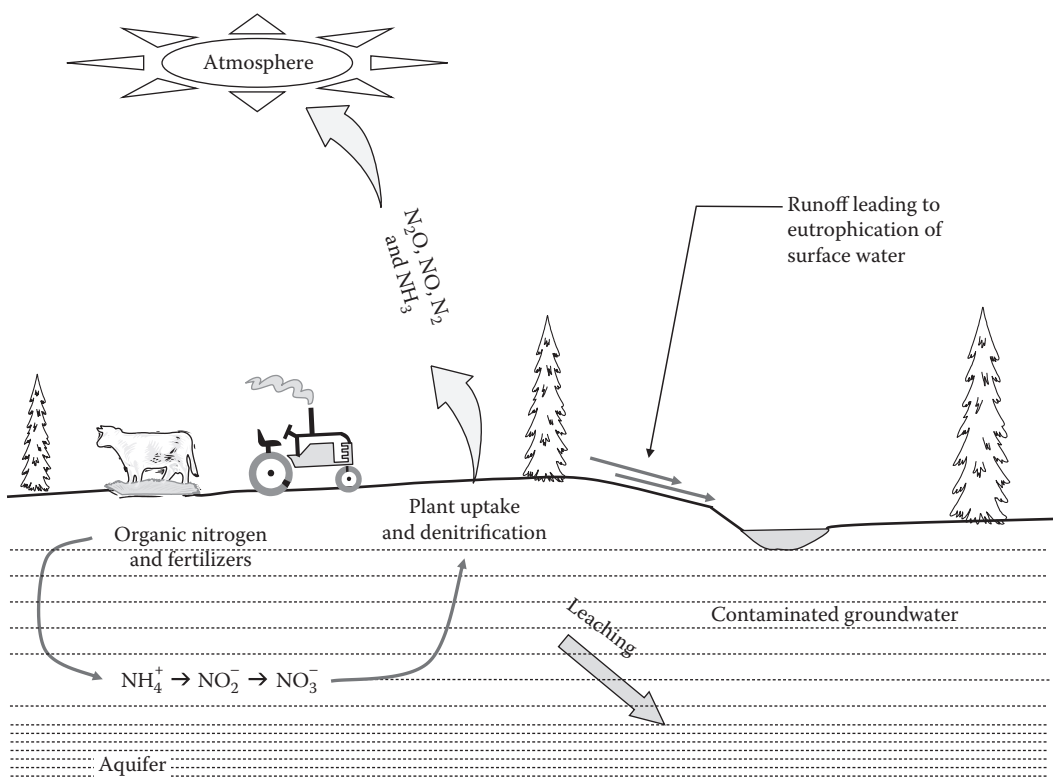
**FIGURE 6.4**

Illustration of the nitrogen cycle as it relates to the geoenvironment and farming practices.

be altered through production of nitrogen oxides, which can impact human and ecosystem health (Figure 6.4). The nitrogen can travel from agricultural fields, to the rivers, streams, groundwater, and finally to the oceans. The diffusion processes for fertilizers (1 m/year) are slow. Consequently, groundwater contamination may not be seen until a decade after a large amount of fertilizer is spread (Chamley, 2003).

Nitrogen from fertilizers can be converted to nitrate before uptake by plants. When this happens, contamination of rivers, lakes, estuarine, deltaic, or coastal waters can occur, as shown, for example, in Figure 6.4. Toxic algal blooms (by the dinoflagellate *Pfisteria*) can result from the eutrophication of estuaries and kill fish via their toxins. Eutrophication processes also deplete the oxygen in the water, destroying aquatic ecosystems. These phenomena affect the sustainability of fisheries. In the United Kingdom, eutrophication decreased tourism and the values of waterfront properties by \$105 to \$160 million/year in the 1990s and has led to expenditures of \$77 million/year to fix the damage (Millenium Ecosystem Assessment, 2005). Humans can also be affected by shellfish poisoning. High nitrate levels (above 10 ppm) can also lead to methemoglobinemia (also known as blue-baby syndrome), abortions, and increased rates of non-Hodgkin lymphoma. Levels above 5 ppm can affect young animals (Pimentel, 1989). Algal blooms initiated by the elevated nutrient levels lead to (a) disruption of the ecology through oxygen consumption, (b) accumulation of organic content, (c) reduction of water and sediments, (d) asphyxia, and (e) biota mortality such as plankton and benthos (Chamley, 2003). Inorganic nitrogen levels in coastal areas have increased by a factor of 2.5 and phosphorus levels by 2, particularly

in Western Europe. Dating of ^{210}Pb in Tahiti has allowed the determination of the accumulation of phosphorus in the sediments. The steps included exchangeable, iron-sorbed, carbonate, marine organic, and terrigenous phosphorus forms. In the 1950s, terrestrial phosphorus increased significantly due to both soil erosion and waste discharges.

The conversion of ammonia to nitrate lowers soil pH, particularly in northeastern Canada and Scandinavia (Chamley, 2003), where the bedrock formations are siliceous. The acidity increases the mobility of the toxic components, aluminum and manganese. This can diminish vegetation and plant growth and increase soil erosion.

Due to its charge, phosphorus binds to soils but will leach from sandy soils with low levels of clay, oxides, and organic matter. Surface runoff will most likely cause contamination of streams and lakes, whereas groundwater contamination by nitrates is more likely since these anions are held more weakly by negatively charged clayey soils than phosphorus. Nitrate diffusion in the groundwater is very slow, in the order of 1 m/year. Thus, the impact from excessive fertilization of the soil may only be seen in the groundwater a decade later.

Inorganic fertilizers and other soil amendments such as animal manure and biosolids contribute to elevated levels of N and P in the environment. Inorganic fertilizer use increased by 20- and 4-fold from 1945 to 1980. Their use has since leveled off. Animal manure contributes 6.3 million tonnes of N and 1.8 million tonnes of P compared with 10.8 million tonnes of N and 1.8 million tonnes of P from inorganic fertilizers (USGS, Circular 1225, 1999). About 15% of shallow groundwaters sampled beneath agricultural areas were above the acceptable levels for nitrates.

In the Australian government-funded project to study the movement of phosphorus in soils supplemented with piggery effluents (Redding, 2005), soil samples were taken down to 5 cm in areas with and without the effluent amendment. Leaching was not significant if correct management procedures were used, but it did occur if application rates were excessive. Significant adsorption of the phosphorus occurred in the top 5 cm and phosphorus runoff readily occurred from surface soil.

6.3.2.2 Pesticides

Pesticides are chemicals that have the purpose of eliminating (controlling) “pests” and are classed as *biocides*. Most of these are considered as toxic chemicals that are injurious to human health and other biotic receptors. There are several types of pesticides such as herbicides, insecticides, fungicides, rodenticides, verucides, etc., each of which is used directly for control of specific “pests.” Herbicides are used for controlling unwanted plants, insecticides are used to control insects etc. They have been used since the nineteenth century in the form of lead, arsenic, copper, zinc salts, and nicotine for insect and disease control. Since the 1930s and 1940s, with the introduction of 2,4-D and DDT, agricultural use has increased substantially. It has been reported that worldwide use of pesticides is approximately 2.4 billion kg (USEPA, 2006, 2007). The *Database on Pesticides Consumption* called FAOSTAT (United Nations Food and Agriculture Organization, 2003) which is maintained by the United Nations’ FAO provides information on the use of specific pesticides within each country.

Although pesticides have enhanced crop yields, concerns are increasing regarding their effects on the health of humans and animals and their transport in the environment. Levels of contamination of surface streams and groundwater increase with increased nutrient and pesticide use (USGS, 1999). Agricultural streams show the highest concentrations of pesticides. Herbicides are the most frequent pesticides found in agricultural streams and groundwater. Atrazine ($\text{C}_8\text{H}_{14}\text{ClN}_5$), deethylatrazine ($\text{C}_6\text{H}_{10}\text{ClN}_5$),

metolachlor ($C_{15}H_{22}ClNO_2$), cyanazine ($C_9H_{13}ClN_6$), alachlor ($C_{14}H_{20}ClNO_2$), and EPTC (*S*-ethyl dipropylthiocarbamate, C_9H_9NOS), are the most commonly detected chemicals—correlating well with their usage (USGS, 1999). Frequent pesticide and fertilizer use can alter the natural resistance of the plants and may also increase their resistance to parasites. This will make some soils unusable for agricultural purposes. Levels of contaminants typically found in agricultural areas are shown in Tables 6.1 and 6.2. From 2000 to 2007, the application of pesticides has decreased from 0.54. to 0.5 billion pkg (USEPA, 2006, 2007), and 80% is used for agriculture. Overall, more than 2.3 million tonnes of pesticides (22% of the world use) are applied—resulting in the pollution of more than 10% of

TABLE 6.1

Levels of Contaminants in Agricultural Areas

Contaminant	Streams	Shallow Groundwater
Nitrogen	Medium to high	High
Phosphorus	Medium to high	Low
Herbicides	Low to high	Medium to high
Currently used insecticides	Low to medium	Low to medium
Insecticides used in the past	Low to high	Low to high

Source: Adapted from USGS, *The Quality of Our Nation's Waters—Nutrients and Pesticides*. U.S. Geological Circular 1225, 1999. Available at <http://water.usgs.gov>.

TABLE 6.2

Frequency of Detection of Herbicides and Insecticides in Streams and Groundwater in Agricultural Lands as a Percentage of Samples

Pesticide	Streams	Groundwater
<i>Agricultural</i>		
Atrazine	65	30
Deethylatrazine	35	29
Metolachlor	53	8
Cyanazine	25	2
Alachlor	28	2
EPTC	12	1
<i>Urban herbicides</i>		
Simazine	44	12
Prometon	26	10
2,4-D	11	1
Diruron	7	2
Tebuthiuron	7	1
<i>Insecticides</i>		
Diazinon	10	1
Carbaryl	6	<1
Malathion	4	<1
Chlorophirofos	10	<1

Source: Adapted from USGS, *The Quality of Our Nation's Waters—Nutrients and Pesticides*. U.S. Geological Circular 1225, 1999. Available at <http://water.usgs.gov>.

the rivers and 5% of the lakes in the United States. Groundwater quality is also impacted with pesticide use.

Estimated mass balances of pesticides have been used to evaluate the fate and transport of the pesticides in the environment, as illustrated in Figure 6.5. These estimates exhibit substantial variation in some cases, due to, for example, atmospheric drift because of weather conditions, application method, and properties of the pesticide. Unaccounted-for pesticides can be due to the formation of covalent bonds with plant material or organic matter of soils (Xu et al., 2003) or biodegradation.

The interactions of organic chemicals with soil organic matter (SOM) have been briefly discussed in Section 2.5 in Chapter 2 and is further discussed in detail in Chapter 9. These discussions show that the association of pesticides with the organic matter of soil can be described by the relationship: $C_{oc} = k_{oc} C_{aq}$, where C_{oc} is the concentration of solute contaminant sorbed onto the soil organic carbon, k_{oc} is the organic carbon–water partition coefficient, and C_{aq} is the dissolved concentration of the contaminant. The Freundlich adsorption isotherm for many pesticides can be described by the following relationship $C_{oc} = k_f C_{aq}^{1/n}$, where k_f and $1/n$ are Freundlich parameters. These parameters are known for more than 60 pesticides (Barbash, 2005).

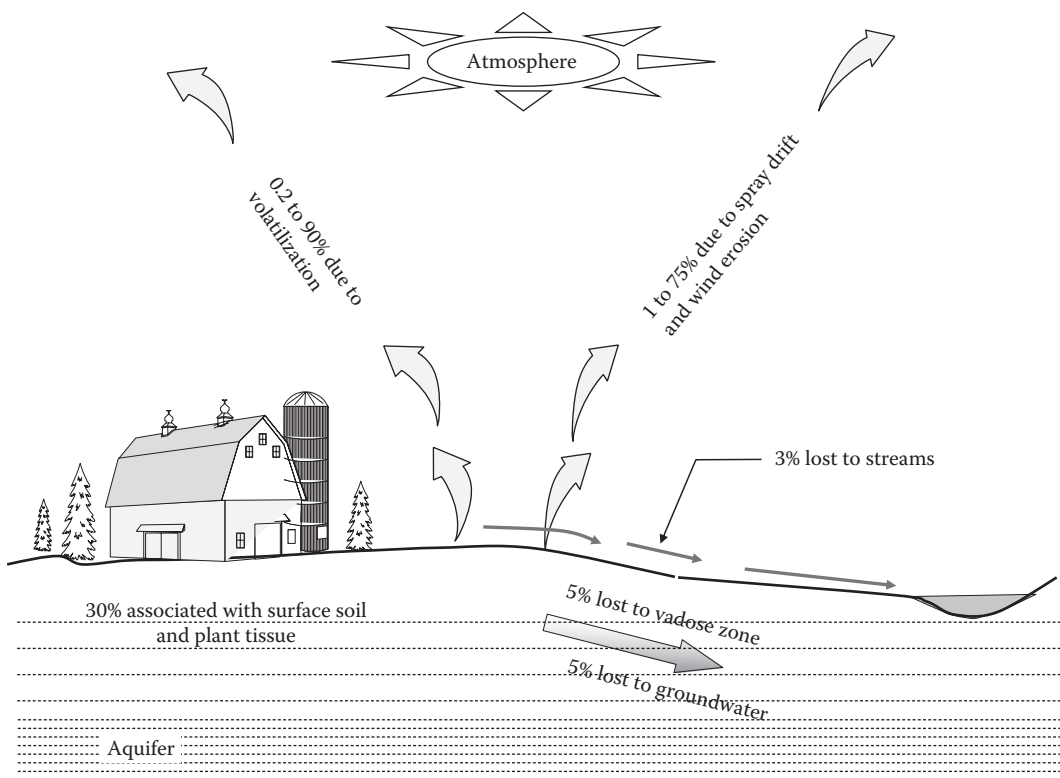


FIGURE 6.5

Estimates of the fate of pesticides after application to the soil for agricultural use (data from Barbash, 2005). Percentages of pesticide associated with plants and other and lost to various to atmosphere, vadose zone, and streams are dependent on highly climatic factors, soil management practice, type of pesticides used and manner of application, etc.

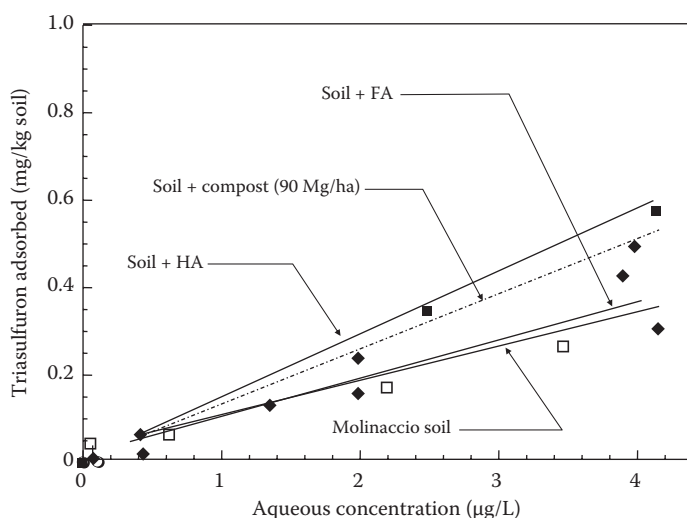


FIGURE 6.6

Adsorption of triasulfuron ($C_{14}H_{16}ClN_5O_5S$) on a Molinaccio soil. HA and FA are humic acid and fulvic acid, respectively. (Adapted from information reported by Said-Pullicino, D. et al., *J. Environ. Qual.*, 33, 1743–1751, 2004.)

The sorption of a herbicide, triasulfuron ($C_{14}H_{16}ClN_5O_5S$), in Molinaccio clay loam, with and without humic and fulvic acids as organic materials, determined by Said-Pullicino et al. (2004) are shown in Figure 6.6. The Freundlich isotherm values, k_f ($\mu g^{(1-1/n)} mL^{1/n} g^{-1}$) were 0.14 for the soil, 0.18 (with the compost), 0.20 with the humic acid, and 0.15 with hydrophobic dissolved organic matter. The $1/n$ values were all less than 1. The high concentration of compost from municipal waste led to an increase in sorption. However, in all cases, saturation was not reached, and the herbicide preferred to remain in solution and thus was highly likely to leach. The humic acids and the hydrophobic dissolved organic matter in the compost were responsible for the sorption characteristics of the compost.

6.4 Food Production Stressor Impacts

In addition to the chemical stressors in the form of fertilizers, pesticides, and wastes from livestock, trace elements in the form of trace metals, heavy metals, metalloids, micronutrients, and trace inorganics are also found in soils and surface and groundwater. These have been traced to application of commercial fertilizers, liming materials, irrigation waters, and biosolids. Their presence in soils and groundwater serves to reduce the quality and functionality of soils—in addition to their potential to cause injury to human health and other biotic receptors—as shown in Figure 2.2 in Chapter 2. The discussion in Chapter 10 pays special attention to the presence of these kinds of contaminants in soils and groundwater and the ways and means to minimize the adverse impacts created by these stressors.

6.4.1 Impact on Health

The impact on public health due to activities associated with food production has been studied by many international organizations. Although agricultural yields have increased, irrigation, land conversion, and disturbances of the ecosystems have increased the rates of even older diseases such as malaria. Irrigation has increased the number of diseases, up to 30 diseases, including mosquito-borne diseases in Central and South America (WHO, 1996), malaria, and Japanese encephalitis due to rice paddy irrigation. Irrigation systems in hot climates are directly linked to schistosomiasis incidences.

Deforestation and increasing cultivation decreases the soil's ability to retain contaminants and nutrients. Chemicals such as mercury, which are normally stabilized by iron oxyhydroxide adsorption, can bioaccumulate in fish. Erosion destabilizes mercury, thus increasing the release of mercury into the water supply. Freshwater fish can contain an average of 48 µg/L of mercury, a potential health hazard (Richard et al., 2000).

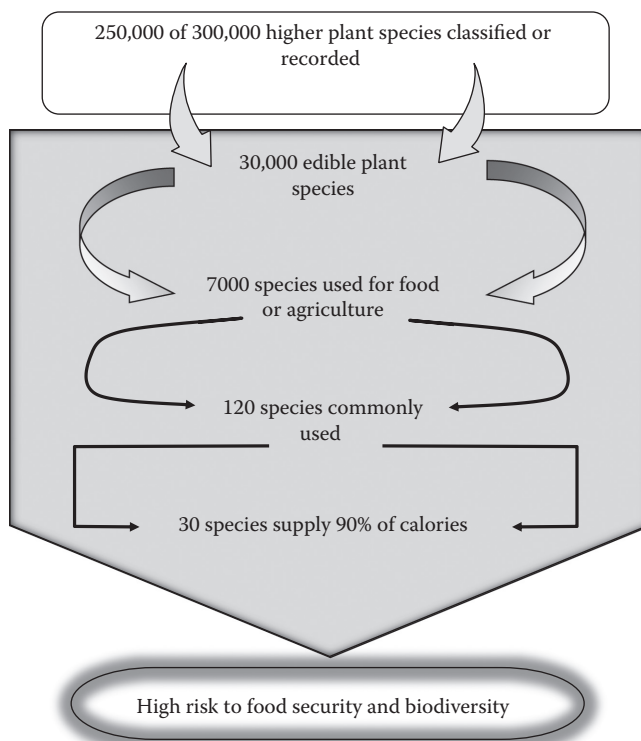
The decrease in water quality due to pollution from a variety of urban and industrial sources also can contaminate crops and lead to the poor health of farm workers and consumers of the contaminated crops. Agriculture cannot be viewed in isolation to the other sectors. It has been called both a cause and victim of water pollution (Ogaji, 2005).

6.4.2 Impact on Biodiversity

One of the major impacts of land transformation for food production and other uses has been the extensive loss of biodiversity. Food production activities in the agricultural sector has led to the extinction of more species than any other sector. The rates of extinction have increased from 100 to 10,000 times the level prior to the industrial revolution. Decreases in the amounts of pollinating insects have negatively impacted yields of particular crops (Nabhan and Buchmann, 1997). The diversity of soil organisms has also decreased due to the decreased opportunity for organic decomposition and increased nutrient content. As a result, specialized predators and weeds will also develop due to the low diversity of species in agricultural lands. Changes in land use has affected the various cycles within the global system including the carbon, water, biogeochemical and biotic, to name a few. For example, lack of SOM and soil organisms will impact the carbon cycle.

Biological diversity is the highest in forested areas. For example, although inter-tropical forests make up only about 6% of the surface area, they nevertheless make up half of all plant and animal species. Thus, conversion of these forested areas to agriculture can be highly detrimental to biodiversity. Modifying rivers and lakes for irrigation purposes can lead to extinction of the fauna, flora, and terrestrial organisms due to variations in water composition, temperature, and flow. Water pollution from runoff of pesticides, fertilizers, and salinization can influence biodiversity. Salinity levels in the Aral Sea have tripled due to cotton irrigation (WRI, 1992). This has led to extinction of 24 species of fish (Postel, 1992). In addition, erosion can be detrimental to fish and other aquatic organisms due to siltation of breeding grounds. Mulholland and Lenat (1992) estimated that there has been a decrease of up to 50% of the species in streams affected by agriculture. Increasing the use of surface water for agriculture can also damage ecosystems in lakes and watersheds. The biodiversity losses or changes may not be evident initially but in the long term can have significant impacts on the sustainability of agricultural practices.

New breeding methods have caused a significant loss of agricultural biodiversity. Some of these impacts are shown in Figure 6.7. The schematic diagram shows that although there is a large number of species available, only a small portion is utilized for food production.

**FIGURE 6.7**

Risk to food security due to loss of agricultural biodiversity. (From El Bassam, N., Fundamentals of sustainability in agricultural production systems, and global food security. In *Proceedings of the International Conference on Sustainable Agriculture for Food, Energy and Industry*, joint conference of Food and Agriculture Organization [FAO], Society of Sustainable Agriculture and Resource Management [SSARM], and Federal Agriculture Research Centre [FAC], Braunschweig, Germany, June 1997, James & James, London, 1998.)

Uniformity and standardization of farming practices has led to this restricted biodiversity—a clear demonstration of the effect of human activities on biological diversity. The genetic base of crops needs to be widened to avoid dependence on a restricted genetic base that renders the world's food supply at risk to diseases, pests, and other dangers. New crops will also ease the demand for food in areas where it is scarce, and new management techniques will be required to incorporate new or underdeveloped crops to broaden the genetic base. Insofar as biodiversity is concerned, minimization of the negative impacts on natural biodiversity is paramount, together with conservation of the available genetic resources—to obtain a measure of sustainability in agricultural food production. It is useful to bear in mind that agricultural fields are not isolated from the surrounding natural environment. Current agricultural policies concentrate on product yields, demographic changes, and land ownership (Fischer Taschenbuch, 1999). Genetic erosion will lead to increased risks to food security as plants will be less able to adapt to changes in the environment. Agrobiodiversity is a vital factor in agricultural management practices.

Other impacts on biodiversity have been studied in the United Kingdom. Hedgerows were used extensively in the past as field boundary markers (Nature Conservancy Council, 1986). However, more than 16,000 km of hedgerows have been removed annually in the

1960s, and it has been estimated that the 20 species of mammals, 37 species of birds, and 17 species of butterflies that live in the boundaries could be threatened by the loss of the hedgerows. Biodiversity has been severely impacted due to removal of the hedgerows and other intensified agricultural production processes. Other species such as brown hares, arthropods, insects, bees, flowers, and bats are also threatened.

6.5 Managing Geoenvironment Stressor Impacts

As in the previous sections, the discussion in this section concerning agricultural practices and farm-related stressors and impacts on the geoenvironment are all structured from the geoenvironmental perspective, i.e., impacts to the geoenvironment. It is accepted that geoenvironment stressors will be generated by activities associated with agricultural food production. The section title “Managing Geoenvironment Stressor Impacts” is used to mean “implementation of measures” (a) to prevent, where possible, the various stressors from impacting on the geoenvironment and/or (b) where it is not possible to prevent stressors from impacting on the geoenvironment, to mitigate the adverse stressor impacts on the geoenvironment. The preceding discussions have shown what the major geoenvironment stressors are and how they come about. We have seen how they impact on the geoenvironment, human health and biodiversity. Insofar as geoenvironment sustainability is concerned, agricultural-related food production activities need to (a) eliminate (if possible) or mitigate stressor impacts on the geoenvironment and (b) implement procedures and technology that will manage geoenvironment stressor impacts to achieve and maintain soil, surface, and groundwater quality. The measures (procedure and technology) taken to manage the geoenvironment impacts can be implemented at the source, as *source management control*, and/or impact remediation and rehabilitation procedures, i.e., procedures implemented on impacted site.

It can be argued that many of the measures for mitigating, minimizing, and even preventing impacts from contaminant loading and soil quality impairment run counter to intensive agricultural practices. From the perspective of the agroindustry, there is validity to this set of arguments. However, as has been realized for countless years, conflicts between agricultural productivity and protection of the geoenvironment have always existed. With better awareness of the sources of geoenvironment stressors, and with better tools for management of stressor impacts on the geoenvironment, these conflicts will continue to lessen as one strives toward obtaining sustainability for both agricultural-based food production and the geoenvironment.

6.5.1 Examples of Practices to Reduce Stressor Impacts

6.5.1.1 Soil Degradation

Changes in agricultural practices can lead to reduction in soil degradation rates. Most of these practices are well known in the industry and are now routinely applied in everyday agricultural engineering and farming practices. These include rotation of crops, protection of soils from erosion, increase of organic matter and nutrient contents, and restructuring of the soil. It is common practice to alternate between high-yield cereal or tuber plant with leguminous or fallow land planting. Adding mulches, composts, or manures can also

increase the organic content. Mechanical measures including contouring, terrace cultivation, and contour hedges can reduce erosion and increase yields. In the following sections, we will look at some measures to reduce impact. They are by no means an exhaustive list but serve as examples of more sustainable practices farmers today.

6.5.1.2 Soil Erosion

In respect to the impact of farming practices on soil erosion, the Franklin Sustainability Project in New Zealand evaluated different methods, including raised access ways, benched headlands, silt fins and traps and contour drains for erosion minimization (Hicks and Anthony, 2001). It had been estimated that 98 mm of top soil has been lost since 1952. Grasses and sedges were effective as sediment filters and in combination with benched headlands can be very effective for trapping sediment but do not prevent erosion. Appropriate water management techniques are required to avoid subsidence and groundwater depletion. Cattle herds and flocks should be limited to avoid excessive trampling and overpasturing. Waterlogging should be avoided to prevent loss of the land to salinization. Adequate drainage is required to leach out the salts and remove the excess water from the soil.

6.5.1.3 Integrated Crop Management

The British Agrochemical Association has developed an approach called *Integrated Crop Management* to “avoid waste, enhance energy efficiency and minimize pollution” (ECIFM, 2014). This approach advocates (a) crop rotation, (b) selection of appropriate cultivation techniques and seed varieties, (c) minimization of fertilizers, pesticides, and fossil fuels, (d) landscape maintenance, and (e) encouragement of wildlife habitats. Use of farm-produced inputs for fuels, pesticides, and fertilizers is encouraged. Soils are protected to (a) minimize energy use, (b) reduce erosion, and (c) reverse adverse effects on beetles, spiders, and earthworms. Crop production that is appropriate for the climate, soil type, and topography are maintained. Trials have shown that with such practices, (a) costs are reduced by 20% to 30%, (b) pesticide use is reduced by 30% to 70%, and (c) there is a reduction in requirement for nitrogen by 16% to 25%. The results also show that biodiversity was increased and nitrate leaching and soil erosion were reduced.

Livestock generate significant stressor impacts on the geoenvironment, such as overgrazing, erosion of the soil, river and lake pollution, desertification, and deforestation (Regenstein, 1991). Their numbers have increased substantially to the point where they now outnumber humans 3:1 (Goodland, 1998). Incentives and taxes could be used to promote good environmental practice in food and agriculture. Reduction in water use and recycling of manure can be practiced. Cattle feedlots provide the most significant impact. Sheep generate lesser impact since they graze on more natural grassland.

Biotechnology has been employed to increase food quality and production through the availability of transgenic plants. The main objectives are to develop plants that are resistant to bacteria, fungus, viruses, and environmental stress. At this point, conventional crop breeding is commanding more attention, due in part to the need to broaden capabilities and alternatives to the production of genetically altered plants.

Optimized uses of both fertile and fragile soils together with measures to rejuvenate production on degraded lands are procedures that can be pursued. Lower quality soils could support more species than high-yield agricultural lands (Dobson et al., 1997). Planting

trees for shelter can also help to (a) reduce evaporation and transpiration by 13% to 25% (Mari et al., 1985), (b) reduce wind erosion, and (c) increase crop yields such as corn by 10% to 74% (Gregersen et al., 1989).

6.5.1.4 Water Quality

The Farm Waste Management Plan of the United Kingdom (Saha, 2001) has listed the following items for pollution control:

- Delay ploughing in of crop residues
- Reducing the use of fertilizers, manure, and sewage sludge
- Sowing autumn crops early
- Managing farm waste carefully

With regard to water quality, Sagardoy (1993) listed the following items to avoid water pollution:

- Development of water quality monitoring schemes
- Optimization of the use of farm inputs and other agricultural activities that impact wetlands
- Establishment of water quality criteria for agriculture
- Prevent soil runoff and sedimentation
- Proper disposal of animal and human wastes
- Ionization of agricultural chemicals for pest management
- Education of the community to minimize impact on water quality and ensure food safety

The capability of soils for retention of contaminants is a good means for reducing the threat or impact of contamination of groundwater. A case in point could be the cereal cultivation in northeastern France that has led to pollution of the Rhine Valley groundwater by nitrates (Bernard et al., 1992). These agricultural soils contained much lower organic contents than forest soils. Considering that forest soils with their higher organic contents will show greater capability in retaining the contaminants and converting the nitrates to N_2O through denitrification, it would appear that conversion of these agricultural lands through reforestation can significantly reduce groundwater pollution.

Although attention is normally given to soil permeability in consideration of transport of fertilizers in the ground, the attention received by the underlying geology has not been as significant. This oversight can lead to serious consequences. The example of Brittany, France, with underlying densely fractured and weathered granite rocks is a good demonstration. These densely fractured weathered rocks allow infiltration of contaminated water, in contrast to metamorphic schists that prevent seepage into the underlying rock (Chamley, 2003). Nitrates and phosphates from farms are retained by the granite that can then contaminate areas downstream. Geological maps and corresponding laboratory data on the rock properties are useful tools in predicting the impact of pollution from farm fertilizers. Réunion, a sloped territory with increasing agricultural activities, urban and tourist areas produced a map in the year 2000 for such purposes.

The U.S. Soil Conservation Service (1993) developed a wetland process for treatment of agricultural runoff consisting of a wet meadow, followed by a marsh and pond with an optional vegetated polishing area. It is applicable for the removal of sediments and nutrients such as phosphorus. The wet meadow with a slope of 0.5% to 5% consists of permeable soils with cool-season grasses. The depth of the marsh with cattails varies from zero at the surface of the meadow to 0.46 m at the deep pond. The deep pond performs as a biological filter for the removal of nutrients and sediments. Fish, such as common or golden shiners, should be included in the pond to feed on the plankton. Average sediment and phosphorus removal in a system for potato growing in northern Maine over two seasons were determined to be 96% and 87%, respectively (Higgins et al., 1993).

Losses to the environment of pesticides and herbicides through volatilization and runoff must also be minimized. Large quantities of agrochemicals have been found in various water bodies such as the Great Lakes in North America. Application of these chemicals during calm conditions can minimize losses due to drift. Biological methods can be used to control weeds and insects.

It has been proposed that an “integrated pest management” (Janzen, 1998) strategy be utilized through chemical, biological, and cultural methods to optimize the use of pesticides. The EPA (2012) indicates that four steps are included: (1) action thresholds are set, (2) pests are monitored and identified, (3) pests are prevented from becoming a threat, and finally, (4) pests are controlled when other means fail.

6.5.1.5 Source Control

A major element in *source control* is reduction in use of various mineral and organic fertilizers and pesticides. These are sources for non-point contaminant stressors when they are transported in the ground. Other source control measures that can be exercised include

- Strict standards and monitoring to maintain ground and surface water quality, and storage systems commonly used in industrial processes—to reduce source contaminants
- Optimization of natural pollinators and predators to conserve species and ecosystems by maintaining natural vegetation near agricultural lands (Thies and Tschardtke, 1999)
- Optimization of the water supply and quantity by correct use of water and chemicals to protect human health and ecosystems (Matson et al., 1997)
- Use of technologies that reduce erosion, salinization, water consumption, chemical pollution, and other environmental effects
- Minimization of tillage to prevent runoff
- Use of intercropping and ground cover as, for example, inter-planting with red clover to reduce water runoff, Wall et al. (1991)—with resultant benefits of (a) reducing water and soil loss, (b) conservation of water, (c) decreasing non-point sources of pollution, and (d) increasing water availability for plants (NGS, 1995)
- Minimization of water use through precise applications, e.g., through night application, use of surge-flow irrigation, low-pressure sprinklers, and drip irrigation (Verplancke, 1992; Goldhamer and Snyder, 1989)

6.5.2 Impact of Soil Additives

Various agricultural and industrial wastes are utilized as amendments for agricultural soils. The addition of these amendments as aids to plant growth by and large generates chemical stressors that impact on the applied soil in a way that can threaten human health and other biotic receptors because of contamination of groundwater and receiving waters and uptake by plants. Irrigation with reclaimed sewage water is practiced in arid and semiarid areas. In Israel, irrigation for 28 years with sewage effluents has led to the accumulation of cadmium, copper, nickel, and lead in the top soil layer in coastal plain soils (Banin et al., 1981). Significant amounts of these metals accumulated in the oxide fraction of the soils. The amounts recorded show that (a) for Cd the percentages retained varied from 9% to 20%, (b) for Cr, this varied from 5% to 11%, (c) for Cu, the variation was from 16% to 23%, (d) for Ni, this was from 10% to 14%, and (e) for Pb, the variation was from 1% to 3.9%. Approximately 20% to 45% of produced sewage sludge is added for agricultural use in the United Kingdom, Germany, and United States, among other countries (Mullins, 1990). These sludges can contain high levels of heavy metals, in addition to N, P, K, and other micronutrients. Although extensive data are available on the distribution of copper and zinc in sludge-amended soils, the same cannot be said for such heavy metals as cadmium, chromium, nickel, and lead. After more than 10 years of application, copper, chromium, cadmium, and zinc have moved to the soil layer below the layer of application and zinc has been found below the plough layer (Han et al., 2001). Zinc has been shown to be bio-available and has been taken up by wheat, rice soybean, and maize plants. The degree of uptake depends on the conditions of pH, soil type, and *Eh*. Heavy metals added via wastes can runoff or seep into the soil, potentially contaminating groundwater or impacting the quality of the food and animals within the food chain. The heavy metals may also impact the soil microorganisms.

Heavy metals are major concerns in poultry and swine manure used as amendment to soils. Heavy metals in poultry litter, in particular, include As, Co, Cu, Fe, Mn, Se, and Zn (Sims and Wolf, 1994). The accumulation of heavy metals from manure amendment can occur over the long term. Extractable Cu and Zn concentrations increase over time, in addition to the heavy metal concentrations in runoff after amendment with poultry waste. Cu concentrations have also increased in soil and plants such as grass and corn after the addition of swine waste amendment (Kornegay et al., 1976; Sutton et al., 1983; Mullins et al., 1982; Payne et al., 1988).

Although beneficial, the practice of spreading of manure can negatively impact air, soil, and water quality. Besides providing nutrients, manure addition can reduce soil erosion and improve soil water holding capacity (U.S. Department of Agriculture [USDA], 1992). However, excessive levels of nitrogen, phosphorus, and organic matter can accumulate in the soil if the manure is not spread properly (Figure 6.8).

Heavy metals such as copper and zinc may also accumulate in manure and subsequently in the soil due to their use as food additives. In countries such as the Netherlands, Belgium, and Germany, 15%, 20%, and 50%, respectively, of the groundwater have nitrate levels higher than 50 mg/L, due most likely to manure loading on the land according to the European Commission report on the Nitrates Directive. However, EU-27 exhibited 62.5% of groundwater stations with nitrate levels less than 10 mg/L, 2.5% between 40 and 50 mg/L and 3% exceeded 50 mg/L (ec.europa.eu/environment/water/water-nitrates/index_en.html). Large facilities, in particular, do not have sufficient land to apply the manure as a fertilizer. In the United States, it has been reported that 350 million tonnes of manure are produced each year and that only 18% of hog farms and 23% of dairy farms

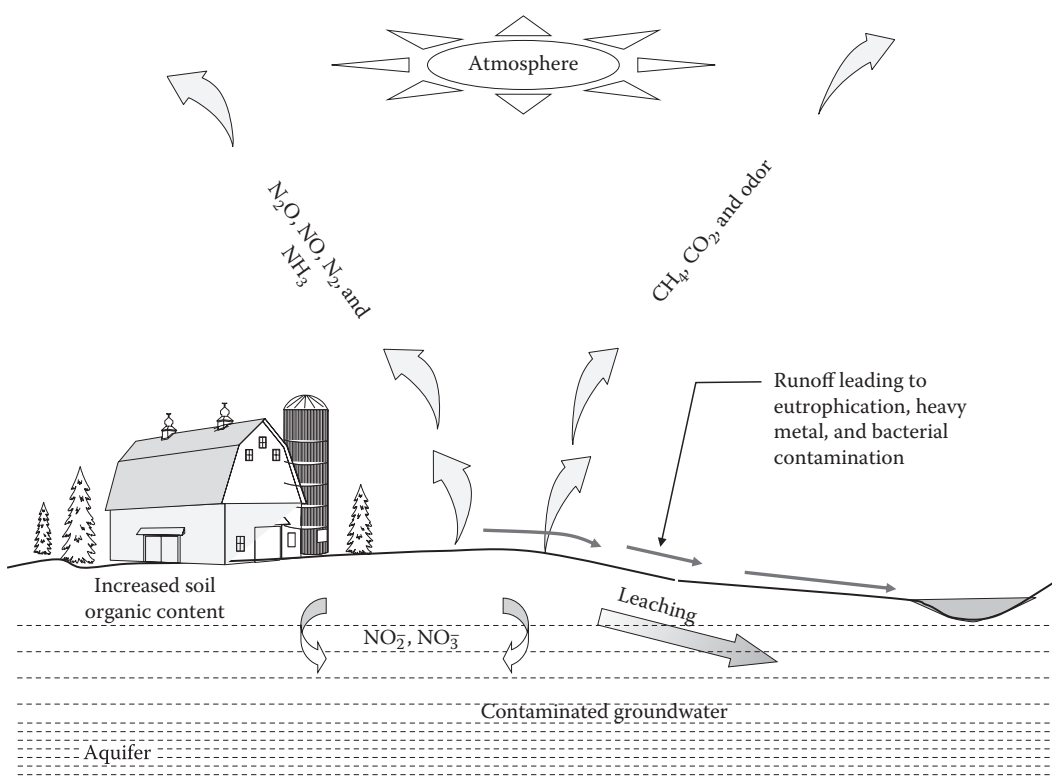
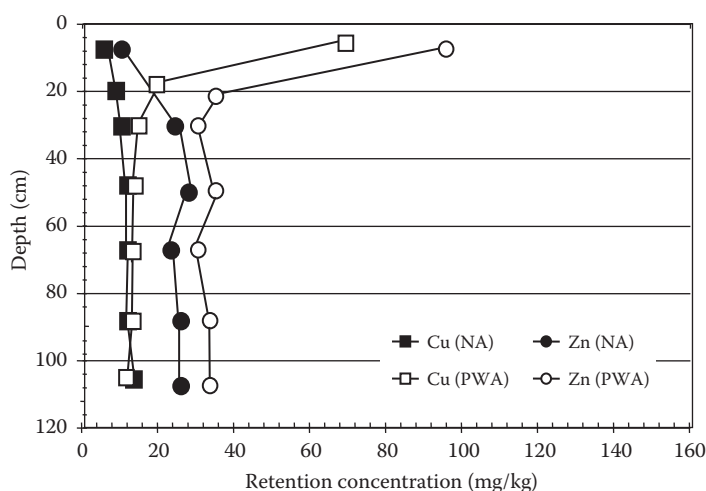
**FIGURE 6.8**

Illustration of the emissions and leachates due to manure spreading practices.

spread the manure on enough land surface so that nitrogen levels in the drinking water are maintained within water quality guidelines. About 5% of all cropland is fertilized by manure according to the USDA Report to Congress (USDA, 2009). Approximately, 50% of lake water and 27% of river water in the United States are also contaminated with nutrients (Gleick, 1993). Runoff of the manure during rain events causes high BOD levels in surface waters. Non-point sources pollution of surface waters (rivers, lakes, and oceans) and groundwater are considered to be the major source of water pollution.

Coarse-textured soils are particularly susceptible to (a) increased movement of nitrate below the surface and (b) increased salinity levels and groundwater nitrate concentrations as manure application rates increases. More effective means of spreading fertilizers by correlating with plant needs are required. Plant uptake capacities should not be exceeded.

Han et al. (2001) reviewed the accumulation and distribution of heavy metals in soils amended with animal wastes, sewage sludges, and other wastes (Figure 6.9). For poultry litter amended soil, copper, and zinc concentrations increased at a rate of 2 mg/kg-year. Most of the copper was present in the organic (46%) and residual fractions (52%), whereas most of the zinc was found in the easily oxidizable (48%) and organic (23%) fractions. Mobility studies indicated that there was slight movement of zinc downward in the soil, and copper moved to the 40-cm depth. Zinc was particularly mobile. At depths of 60 cm, iron oxide and residual fractions were twice that of the non-amended soils.

**FIGURE 6.9**

Retention profiles for total Cu and Zn for non-amended (NA) and poultry-waste-amended (PWA). (Data from Han, F.X. et al., Accumulation, redistribution, transport, and bioavailability of heavy metals in waste-amended soils. In I.K. Iskandar and M.B. Kirkham, (eds.), *Trace Elements in Soil, Bioavailability, Flux and Transfer*, Lewis Publishers, Boca Raton, pp. 145–174, 2001.)

6.5.3 Mitigating Manure Treatment Stressors' Impacts

6.5.3.1 Aerobic Composting

Composting can be used to stabilize manure, particularly storage. This method is preferable over other aerobic treatments that are subject to high operation costs and sludge production. It is, however, labor intensive and costly due to the requirement for aeration. The thermophilic conditions of 54°C to 71°C destroy most pathogens. Most of the ammonia is volatilized early in the process. Losses of nitrogen during the composting process, however, can be as high as 50% (Thomsen, 2000). Mixing with other substrates such as the bedding is usually required for bulking. Normally, straw or wood shavings are used as bulking agents with adjustments for nitrogen content to be about 1:20 or 1:40. Compared with untreated manure, volatilization and leaching of nitrogen, the risk of pathogen spreading and odor release are reduced. Yang et al. (2003) reported that (a) greenhouse gas (GHG) emissions of compost were 1.9 times less than slurry manure and 1.5 less than stockpiled manure for dairy manure (Table 6.3), (b) composted liquid pig manure, in comparison to liquid pig manure was more stabilized in terms of manure carbon, and (c) composted liquid pig manure produced reduced emissions of carbon dioxide and N₂O. Vervoort et al. (1998) determined that composting of poultry litter stabilizes phosphorus and reduced

TABLE 6.3

Comparison of Anaerobic Digestion Residue and Compost for Nitrogen Emissions

Treatment for Waste	Global Warming (tonnes CO ₂ equiv/year)	Acidification (tonnes SO ₂ equiv/year)	Eutrophication (tonnes O ₂ equiv/year)
Anaerobic digestion	654	43	688
Composting by reactor	2618	20	991

Source: Adapted from Dalemo, M. et al., *Resources, Conservation and Recycling* 24, 363–381, 1998.

losses by runoff. Others such as Delschen (1999), however, found that although the addition of 2.6 tonnes of composted manure led to higher accumulation rates of SOM than untreated manure, the amounts were approximately the same if the 40% to 60% carbon loss during composting is taken into account.

Various composting systems have been described by Mulligan (2002). Production of compost for soil conditioning leads to a more stable product with practically no odor. The more simple processes may also lead to increased ammonia emissions. The selected bulking material can influence ammonia emissions. Emissions of methane and nitrous oxide depend on the aeration rates. The benefits of compost for soil conditioning are well known.

6.5.3.2 Anaerobic Digestion

The organic content of manures can be treated by anaerobic digestion. The methane produced can be used for fuel or electricity production. Treatment of the manure by anaerobic digestion can significantly reduce the impact on water resources. Greenhouse gas (carbon dioxide, in particular) emissions are reduced and the products have improved fertilizer capability. Nitrogen and phosphorus availability for crops are increased, reducing chemical fertilizer requirements. A comparison of the mineralization of N of anaerobically stored manure with composted ruminant manure showed that anaerobic manure loses less nitrogen than during composting and therefore is a better source of inorganic N for fertilizer (Thomsen and Olesen, 2000). Only some of the nitrogen in anaerobic residues is organically bound, whereas most of the nitrogen in compost is in this form. It has been estimated that digestion can reduce greenhouse emissions by 1.4 kg of carbon dioxide per kg of volatile solids (VS) in manure. It has been reported that anaerobic treatment reduces N₂O emissions by more than 50% due to VS reduction after spring application onto soil, in comparison to untreated manure (Sommer et al., 2004). Although pathogens are reduced, the inactivation may only be about 1 to 2 log at 30°C (Burton and Turner, 2003).

In 2010 in Germany, there were approximately 1000 anaerobic plants using agricultural substrates (Biogas an all-rounder, 2013). The combination of government and environmental factors has led to the substantial growth in the numbers used on animal farms. The EU Waste Framework Directive requires that all member states recycle 50% of their municipal waste by 2020. Although all types of manure are digestible, cow manure is more difficult to digest because of the higher fiber content, as opposed to pig and poultry manures. Typically, yields of methane are in the order of 290 L/kg of volatile solids (VS) for pig manure and 210 L of methane per kg of cattle manure (Burton and Turner, 2003). Co-substrates are often used to enhance the carbon and nutrient contents. These substrates include fodder beet and other green wastes. Cow manure in particular is well suited to co-digestion as it already contains high fiber content. The nitrogen content of the manure serves as pH buffering and as a continuous inoculum. The co-substrates also increase methane yields (Mulligan, 2002).

Lagoons have lower capital and operating costs than digestors. Organic matter is reduced while nitrogen and phosphorus remain in the end product. The use of lagoons is more frequent in warmer climates. Proper sizing and management of lagoons are required to ensure odor control. Loading rates of 60 to 90 g of VS/m³ of lagoon/day have been suggested by the Natural Resources Conservations Service in the North East of the United States. Since methane is a greenhouse gas, gas collection should be practiced to avoid release into the atmosphere. Odors may also be a problem. Floating covers are becoming more popular. Temperatures of 35°C are required to maintain optimal biogas production. Heating systems may be required, particularly in the winter. Pathogen reduction in lagoons is also minimal (Burton and Turner, 2003).

6.5.3.3 Wetlands

The liquid portion of effluents from farm operations must usually be treated because of their high nutrient and organic contents. Since the wastewater contains a higher concentration of soluble ammonia than the initial feed, land spreading is a viable option since this allows for easier uptake by plants. Algal ponds or constructed wetlands may also be used to improve water quality to allow water reuse. Constructed wetlands are operated as subsurface flow or free surface flow (Mulligan, 2002). Nutrients are removed by the plants growing in the wetlands. Subsurface systems are not as efficient for nutrient removal. Hammer et al. (1993) has reported on a two-cell surface system used for a 500-swine operation to reduce 90 to 36 kg BOD/day in a 3600-m² wetland. Nitrogen loading rates should be from 3 to 10 kg/ha-day, and ammonia concentrations in the influents should not be higher than 100 to 200 mg/L. In general, N, P, and solids reductions should be greater than 50% and BOD greater than 60% if the wetlands are not overloaded. Wetlands offer a method of enhancing biodiversity while treating liquid effluent discharges.

6.5.3.4 Integrated Manure Treatment

A comparison of manure management methods is shown in Table 6.4. The choice of the most appropriate method for management of manure must include minimization of emissions and other impacts on the environment such as decreased water, groundwater, and soil quality. Dalemo et al. (1998) utilized a simulation model (ORWARE) for the calculation of energy and nutrient flows from soil and liquid organic wastes from restaurants. Composting and anaerobic digestion were compared. A life cycle approach was used that included the processes and soil emissions from the product. Soil emissions were in the form of N₂O production. Since the content of ammonia is lower in the compost, emissions of ammonia in the soil are also lower in comparison to anaerobic digestion residues where the organic nitrogen is mineralized. In respect to concerns for eutrophication, (a) emissions are mainly in the form of nitrate leaching from the soil, (b) ammonia is released during composting, and (c) NO_x is released during combustion of biogas for electricity generation. In short, composting produces ammonia emissions during the composting process, in addition to NO_x and SO_x.

In the various models compared by Hansen et al. (2006), such as DST (Decision Support Tool, USA), IWM (Integrated Waste Management Tool, United Kingdom), IFEU (Germany),

TABLE 6.4

Comparison of the Sustainability of Manure Treatment Methods

Treatment	Energy	Emissions	Products	Costs
Land spreading	None produced, energy for spreading	Ammonia, methane, N ₂ O, odor, leaching of N, P, bacteria	Fertilizer	Low
Composting	Energy for mixing and mechanical separation, heat generation	Carbon dioxide, ammonia losses higher than anaerobic	Compost for soil improvement	Depends on sophistication
Anaerobic digester	Energy produced in form of methane, heat required for the digester	High BOD liquid effluent	Methane for electricity or energy	Depends on sophistication
Anaerobic lagoon	Energy produced in form of methane	Odors, N ₂ O, and methane, if not covered well	Methane for electricity or energy	Low

Source: Adapted from Dalemo, M. et al., *Resources, Conservation and Recycling* 24, 363–381, 1998.

ORWARE (Sweden), and EASEWASTE (Environmental Assessment of Solid Waste Systems and Technologies (Denmark), the last three are life cycle assessment models, whereas DST considers water BOD and IWM includes reduced air emissions only. Their case study comparison indicated that different assumptions, wastes, and local conditions can greatly affect the obtained results. In addition, DST and IWM did not provide sufficient information to allow decision support for organic waste land application (Hansen et al., 2006).

The integrated manure management system shown in Figure 6.10 takes advantage of the less severe impact of the anaerobic digestion process for primary treatment and subsequent composting for final treatment and disposal. As shown in the diagram, combined wastes (green and manure) are sent to the anaerobic digestion system for treatment. This reduces the VS content. The digestate is then removed from the digestors for solid/liquid separation by screw press or other means. The solids are sent for composting, whereas the liquid is sent for wastewater treatment. After biological treatment (wetlands or a reactor if space is limited), the water can be stored and reused as required or spread on the land surface. The remaining solids content is ideal for composting. The requirements for oxygen will be decreased due to the previous anaerobic digestion step. This step also requires energy that can be produced by the anaerobic digestion process. The resulting compost would be high grade compost full of nutrients with adequate pathogen reduction. The application rates to the soil would need to be based on N and P crop requirements to avoid excess soil nutrients (Cooperbrand et al., 2002).

Land spreading of manure creates numerous environmental problems in the agroecosystem. Manure treatment by anaerobic digestion is a step in the direction toward sustainable agricultural practice since it is a renewable source of energy. The main benefits are shown in schematic form in Figure 6.11. Manure treatment enables farmers to reduce (a) pathogens, odor, N_2O , and carbon dioxide emissions and (b) air, soil, and groundwater pollution caused by manure spreading. As anaerobic digestion is not a complete solution, an integrated one including composting to produce a soil conditioner will be required to ensure complete management of all aspects of manure treatment, as shown in Figure 6.12.

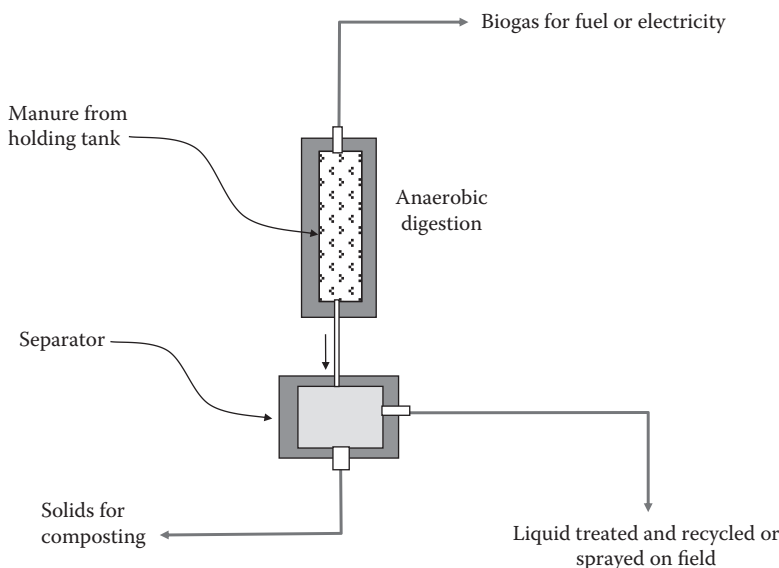
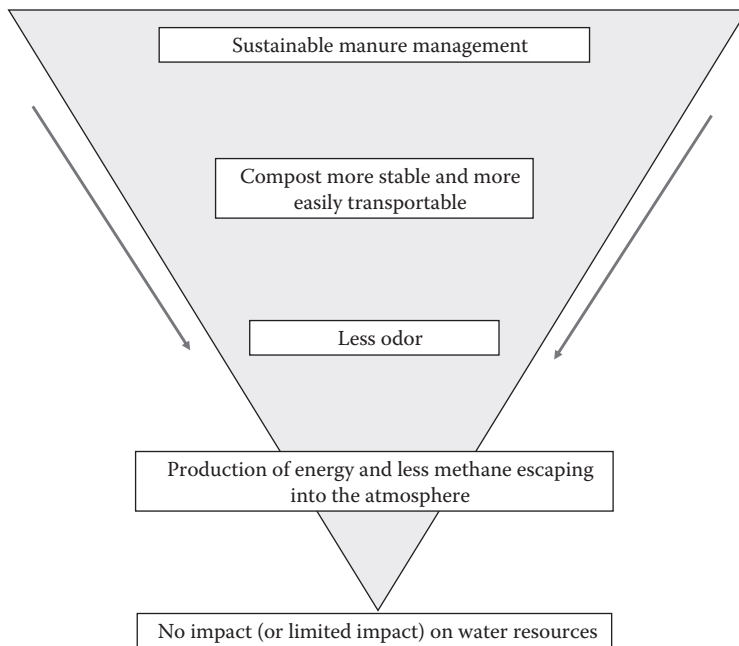
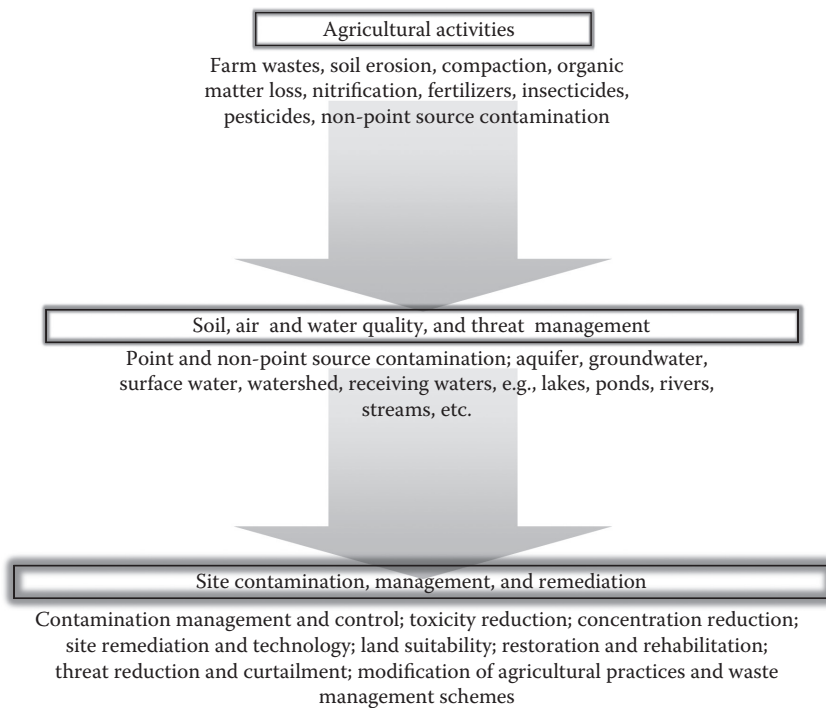


FIGURE 6.10

Schematic diagram showing flow sequence for sustainable management of manure.

**FIGURE 6.11**

Impact of a sustainable manure management process on the geoenvironment.

**FIGURE 6.12**

Summary of agricultural activities, their impacts, and minimization of the impacts.

Modeling of the emissions based on C, N, and P mass balances is an effective method to compare manure management methods. However, soil conditions, climate, and other factors can significantly influence the results of the comparison. This approach is a clear example of minimization of the impact of agricultural practices shown in Figure 6.12.

6.6 Tools for Evaluation of Geoenvironment Impacts from Farming Stressor Sources

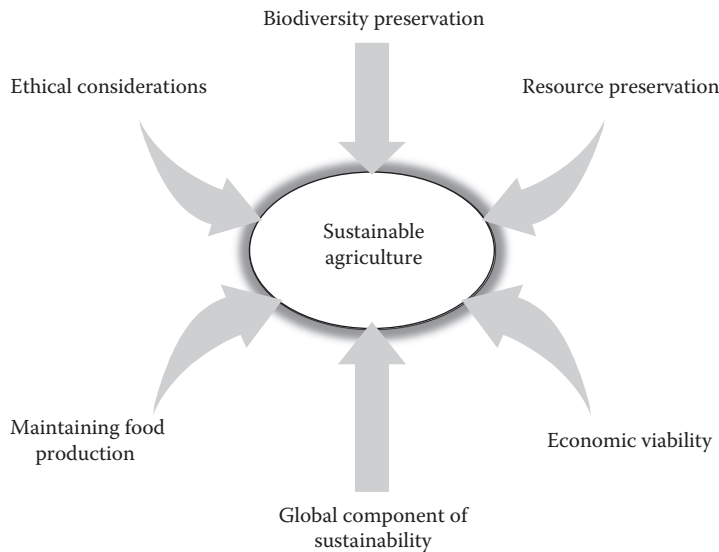
6.6.1 Agricultural Sustainability

To avoid and/or mitigate risks and protect soil quality and geoenvironmental quality as a whole, we need to develop a methodology for evaluation of potential and existing risks to agricultural and geoenvironment sustainability as a result of agricultural activities. It has been estimated that 28% of soil degradation is due to faulty agricultural practices (Quendler and Reichert, 2002). There appears to be some significant room for improvement. One needs to (a) examine the impact of the farming practices on the quality of groundwater and other receiving waters, soil quality, and biodiversity; (b) seek methods to quantify the various kinds of emissions that take the form of stressors to the geoenvironment; and (c) determine the fate and transport pathways of the harmful emissions (stressors). By including air, water, soil, and vegetation as part of the agroecosystem, one could seek measures in an integrated approach to (a) limit the harmful discharges and (b) curtail inefficient practices or emissions—as the first major step toward generation of sustainability. Some of these measures include (a) ecological footprint, (b) sustainable processing index (SPI), and (c) material intensity per service unit (MIPS) or land intensity per service unit (LIPS) (Quendler et al., 2002). Models and sustainability indicators are also tools that can be used to evaluate sustainability. The analysis of sustainability thus will rely on sustainability indicators, reference values, and an established evaluation method. A listing of some indicator systems has been reported by the OECD (1996).

Attempts have been made to define the components of agricultural sustainability. One of the most inclusive was formulated by Christen (1996) as depicted schematically in Figure 6.13. Ethical considerations include fairness between generations. Resources and biodiversity need to be preserved without reducing production but by minimizing environmental impact. Economic viability must also be ensured both for small and large enterprise farming units. Since soil will always be used for agricultural purposes, the impact of pollution and erosion must be determined through research and field studies.

Some authors have argued that the definitions of organic farming (Quendler and Schuh, 2002) should follow the same principles as those used to establish sustainable agriculture. These principles include

- Working with a closed system to draw on local resources
- Maintaining the fertility of the soil over the long term
- Avoiding all forms of pollution
- Producing high nutritional quality food in sufficient quantities
- Reducing the use of fossil fuels to a minimum
- Giving livestock humane conditions

**FIGURE 6.13**

Components of sustainability for agriculture. (Information from Christen, P., Konzept des Sustainable Development bzw. Für den landwirtschaftlichen Bereich sustainable agriculture (gemäß dem erichtöur common future/bzw dem Brundtland—Report), *Berichte über Landwirtschaft, Landwirtschaftsverlag, Münster-Hiltrup, Germany*, 74, 66–86, 1996.)

- Making it possible to allow agricultural producers to earn a proper living
- Using appropriate technologies for biological systems and decentralized systems for product processing, distribution, and marketing
- Creating aesthetically pleasing systems to all
- Preserving and maintaining wildlife and their habitats

The Food, Agriculture, Conservation, and U.S. Trade Act of 1990 established that practice of sustainable agriculture is to

Satisfy human food and fiber needs; enhance environmental quality and the natural resource based upon which the agricultural economy depends; make the most efficient use of non-renewable resources and on-farm resources and integrate where appropriate natural biological cycles and controls; sustain the economic viability of farm operations and the quality of life for farmers and society as a whole.

Canada's International Institute for Sustainable Development agrees with this but says that organic farming is not the only way to achieve sustainable agriculture (University of Reading, Sustainable Agriculture, 2014). Technology needed to achieve sustainability is minimized in organic farming.

Various other organizations have also provided inputs into defining sustainable agriculture as there is no commonly accepted definition. The following quote gives the United Kingdom DEFRA definition that includes

- Ensuring the continuing availability to the consumer of adequate supplies of, wholesome, varied and reasonably priced food, produced within accordance with generally accepted environmental and social standards

- Maintaining a flexible and competitive industry which contributes to an economically viable rural society
- Ensuring effective protection of the environment and prudent use of natural resources
- Conserving and enhancing the landscape, wildlife, cultural and archaeological value of agricultural land
- Respecting a high level of animal welfare

The U.S. Sustainable Agriculture Network defines sustainable agriculture as “agricultural production and distribution system” that

- Achieves the integration of natural biological cycles and controls
- Protects and renews soil fertility and the natural resource base
- Optimises the management and use of on-farm resources
- Reduces the use of non-renewable resources and purchased production inputs
- Provides an adequate and dependable farm income
- Promotes opportunity in family farming and farm communities
- Minimizes adverse impacts on health, safety, wildlife, water quality, and the environment

6.6.2 Development of Analytical Tools

A pertinent question that can be posed is:

What methods can we use to determine the impact of the practices on the geoenvironment, and how can we measure and optimize the improvements of these practices so as not to adversely impact the geoenvironment?

The development of predictive models and sustainability indicators to measure sustainability progress is an ongoing process to accomplish the task needed to answer the question posed.

We have seen in Chapter 2 that soil can provide means to retain contaminants by natural attenuation of both organic and inorganic contaminants. This subject is discussed in greater detail in Chapter 10. For example, in Germany, levels of nitrate as high as 250 mg/L, aluminum as high as 0.64 mg/L and potassium up to 60 mg/L have been found in the groundwater in agricultural areas (Houben, 2002). Acid rain has decreased the pH of the soil to 2.75 and that of the groundwater to 3.4, and soil buffering capacity had also been diminished. Cation exchange, autotrophic denitrification (reaction of nitrate with FeS_2) and other natural attenuation mechanisms have restricted the movement of the contaminants. Modeling, in Houben's (2002) study, together with determination of the age of the groundwater, mass balances, and reactive transport were undertaken using hydrochemical and geochemical data. The PHREEQC-2 geochemical model was used for the hydrochemical equilibrium modeling. Sorption and desorption column experiments with undisturbed samples of sandy sediments for magnesium, sodium, potassium, and aluminum ions were performed. Modeling was accurate for most ions with the exception of potassium. Competition cannot be accounted for in the mass balance approach. Due to the high velocity of fluid flow in the columns, there was insufficient time for the nitrate to react with the pyrite. The models indicated that the contaminants move a few centimeters per year. A newer version PHREEQC-3 is now available (USGA, 2014). New features were

added from experimental results of laboratory and field studies. The code also now can be used by other software programs for calculation of chemical reactions or distributions.

A number of models have been developed to integrate scientific information to enable policy development and future management practices. Integrated assessment modeling in particular has been applied to determine the impacts and to predict climate change. The California Agricultural Land Evaluation and Site Assessment (LESA) Model is used to evaluate soil resource quality, using the indicators of the project's size, water resource availability, surrounding agricultural lands, and surrounding protected resource lands. For a given project, the factors are rated, weighted, and combined, resulting in a score that determines project's potential significance.

The Global Change Assessment Model is an integrated assessment model linking energy, agriculture, and land use with a climate model (JGCRI, 2014). In 5-year time steps from 1990 to 2095, the model can assess various climate change policies and technology strategies for the globe over long time scales in 14 geographic regions. Emissions and atmospheric concentrations of greenhouse gases (CO_2 and non- CO_2), carbonaceous aerosols, sulfur dioxide, and reactive gases are estimated with the associated climate impacts, such as global mean temperature rise and sea level rise.

Other models focus on predicting contaminant transport and leaching in the soil. According to the USDA, Agricultural Research Service (ARS), Great Plains Systems Research (Fort Collins, Colorado), the Nitrate Leaching and Economic Analysis Package (NLEAP) is a field-scale computer model developed to provide a rapid and efficient method of determining potential nitrate leaching associated with agricultural practices. It combines basic information concerning on-farm management practices, soils, and climate and then translates the results into projected N budgets and nitrate leaching below the root zone and to groundwater supplies and estimates the potential off-site effects of leaching. The NLEAP model was designed to predict leaching of nitrate. The processes modeled include movement of water and nitrate, crop uptake, denitrification, ammonia volatilization, mineralization of SOM, nitrification, and mineralization-immobilization associated with crop residue, manure, and other organic wastes. It can be used with various GIS systems. An example is NLEAP GIS 4.2, Nitrogen Loss and Environmental Assessment Package with GIS capabilities and a Nitrogen Trading Tool (NTT) application, which has several components programmed in different computer languages. An interface for running the program in a Microsoft Excel® environment was developed (Delgado and Shaffer, 2008). NLEAP GIS 4.2 with NTT application can be used to assess how one can reduce the losses of reactive nitrogen, and also assess nitrogen dynamics and pools across various landscapes to increase nitrogen use efficiency.

The Soil and Water Assessment Tool (SWAT) has been developed to model changing land-use patterns and practices on nitrogen and phosphorus movement to surface and groundwaters. It is a public domain model jointly developed by USDA-ARS and Texas A&M AgriLife Research of the Texas A&M University System. SWAT is applicable for small watersheds to river basin-scale models for the simulation of the quality and quantity of surface and groundwater and predict the environmental impact of land use, land management practices, and climate change, for assessing soil erosion prevention and controlling non-point source pollution control and regional management in watersheds. Sediment transport, crop growth, and nutrient cycling are simulated. It has also been used for pesticide transport (Rekolainen et al., 2000). It is integrated into ArcView geographic information systems (GIS) software and was developed by the USDA-ARS.

Developed by the USEPA, the USDA-ARS, and the University of Arizona, the Automated Geospatial Watershed Assessment (AGWA) tool is a GIS interface used with the SWAT and

KINematic Runoff and EROsion (KINEROS2) hydrological models that frequently require significant data preparation. Using the two models with AGWA, hydrological modeling and watershed assessments at various temporal and spatial scales can be performed. For large river basins, usually SWAT is used. AGWA can provide outputs of runoff (volumes and peaks) and sediment yield, plus nitrogen and phosphorus with the SWAT model (USEPA, 2011).

Various simulation models were examined by NIFA-CEAP (Arabi et al., 2012) used for agricultural watershed projects. It was found that SWAT was used the most. Other models included Agricultural Non-Point Source (AnnAGNPS), Water Erosion Prediction Project (WEPP) and GWLF. Various lessons learned regarding the use of these tools for watershed conservation projects are elucidated, in addition to the relationship between monitoring data and modeling in conservation practice evaluation.

It is a combination of EPIC and Groundwater Loading Effects of Agricultural Management Systems (GLEAMS). GLEAMS was developed to determine the effect of various management practices on pesticide and nutrient leaching at, through, and below the root zone. The model simulates the downwater movement of pesticides via percolated water, runoff, and sediment or upward movement of pesticides via plant uptake by evaporation and transpiration. More pesticides have been incorporated in to the database and other updates have been performed.

CREAMS (Knisel, 1980) is a field scale model for prediction of runoff, erosion, and chemical transport from agricultural management systems. It is suitable for application to individual storms or long-term averages over a period of 2 to 50 years. It is able to estimate runoff, percolation, erosion, adsorption of plant nutrients, and pesticides. CREAMS (Knisel and Davis, 1999) is a forerunner of SWAT and was also the basis for GLEAMS. The model has shown promise for the development of best management practices in reducing non-point source pollution in watersheds (USEPA, 1997). SWAT has been used by decision makers and could be used to protect water quality, if it is adequately tested.

PRZM3 is the most recent version (version 3.12.3 was released June 2006) of a modeling system developed by the EPA that includes PRZM and VADOFT to predict pesticide transport and transformation down through the crop root and unsaturated zone (Suárez, 2005). PRZM is a one-dimensional, finite-difference model that predicts the fate of pesticides and nitrogen in the root zone of crops. It can also predict pesticide concentration in runoff water and solid particles. The latest version (PRZM3) includes the capability to simulate soil temperature, volatilization and vapor phase transport in soils, irrigation simulation, and microbial transformation, in addition to the transport and transformation of the parent compound and up to two daughter species. The input parameters include the characteristics of the pesticide, the application of the pesticide, crop, climatic, and site information (soil and hydrological properties, agricultural practices, topography, etc.). VADOFT is a one-dimensional, finite-element code that solves the Richard's equation for flow in the unsaturated zone. Several versions of the PRZM system are available from the EPA web site (USEPA, 2014). PRZM can also be used with the EXAMS model to simulate the fate and transport of the pesticide in water. Volatilization, sorption, hydrolysis, biotransformation, and photolysis are processes that are included in the model structure. An aseptis system module is available for evaluating nitrogen fate and transport.

LEACHM is a suite of models for simulating the leaching and fate of water and chemicals within the soil (Hutson and Wagenet, 1989). Input data are similar to the PRZM-EXAMS model. One or more growing seasons can be simulated. Output includes a profile of the pesticide concentration throughout the soil and water and pesticides fluxes in the groundwater (Ecobas, 2007).

The computer model Holos has been developed by Agriculture and AgriFood Canada. It is used to estimate the greenhouse gas (GHG) emissions of carbon dioxide, nitrous oxide, and methane emissions. The emissions can originate from enteric fermentation and manure management, cropping systems and energy use. Carbon storage and loss from lineal tree plantings and changes in land use and management can also be estimated so that the user on the farm can identify ways to reduce farm emissions. The Holos software is continually being updated with new data and improved features. Holos 2.0, released in March 2013, includes updated Canadian data based on new beef and dairy research. Other features are more detailed user inputs on monthly herd size adjustments and estimates of production.

6.6.3 Indicators of Agroecosystem Sustainability

Although crop yields are a measure of sustainability, they do not provide any indication of the impact on the ecosystem and the geoenvironment or land environment in particular. Monitoring of ecosystem damage must be determined, particularly to differentiate natural changes with that due to human activity. GIS, remote sensing, and landscape ecology are new measuring approaches to indicate land-use changes. Indicator organisms can be monitored for changes in the ecosystem. Various organizations such as the Organization for Economic Co-operation and Development, FAO, the World Bank, and the Commission of Sustainable Development have published various indicators for agriculture related to the economic, social, environmental processes, farming practices, and environmental impacts.

For example, the UK Sustainable Development Strategy articulated by the U.K. Local Government Management Board and Touche Ross Management Consultants (1994) provides a list of indicators to determine if development is improving in sustainability. The indicators are grouped in 21 families. Those related to agriculture are shown in Table 6.5. Soil quality is included as it is deemed vital for food production and an ecosystem for vital organisms. Concentrations of organic matter, acidity, nutrient concentration (P and K), and heavy metals are the parameters included. This varies somewhat from the indicators in Canada that were initially developed by McRae et al. (2000) and are now modified and expanded to include new indicators that are shown in Table 6.6 (Eilers et al., 2010). The data show some of the environmental factors impacting agriculture and how they change over time. Some improvements such as soil quality are noted over time but others such as water quality are of concern due to intensification of cropping and livestock production.

Other groups such as Sustainable Measures (West Hartford, California) have developed a searchable database for evaluating sustainability in various sectors including agriculture. Some of the indicators for soil include soil erosion per acre of cropland, average soil erosion, area affected by soil erosion and SOM. Surface water indicators included phosphorus concentration and BOD in county streams. Numerous other indicators are also included in environmental parameters.

Pesticide indicators have also been developed by the OECD (2002). Pesticide use and pesticide risks are the two indicators. Most countries have decreased the use of pesticides. Reduction in risks to human health and the environment can be achieved by reducing particular pesticides. For water use, the three indicators developed include (1) intensity of water use, (2) water volume consumed, and (3) economic value of water use. Water use is very high for many OECD countries. Technical and economic efficiency information are difficult to obtain, as well as information on water stress caused by diversion of water from rivers for agricultural use. The impacts on the geoenvironment from agricultural practices

TABLE 6.5

Sustainability Indicators Developed by the United Kingdom

Area	Indicator
<i>Agriculture, rural economy, society</i>	
Structure of the agriculture industry	Agricultural assets and liabilities Age of farmers Percentages of holdings that are tenanted
Farm financial resources	EU Producer Support Estimate (PSE) Agri-environment payments to farmers Total income from farming Average earnings of agricultural workers
Agricultural productivity	Agricultural productivity
Agricultural employment	Agricultural employment
<i>Farm management systems</i>	
Management	Adoption of farm management systems
Organic farming	Area converted to organic farming
Codes of practice	Knowledge of codes of agricultural practices
<i>Inputs</i>	
Pesticide use	Pesticides in rivers and groundwater Quantity of pesticide active ingredients used Area treated with pesticides Pesticide residues in food
Nutrients	N and P losses from agriculture P levels due to agriculture in soil Manure management Ammonia emissions
Greenhouse gas emissions	Emissions of methane and NO _x from agriculture
Energy	Direct consumption by farms Trends in energy inputs to agriculture
<i>Resource use</i>	
Water	Use of water for irrigation
Soil	Organic matter in soil Heavy metals in top soils
Agricultural land	Area of agricultural land Change in land use from agriculture to herd development
Nonfood crops	Planting of nonfood crops
<i>Conservation value of agricultural land</i>	
Environmental conservation	Area of agricultural land committed to environmental conservation
Landscape	Characteristic features of farmland
Habitats	Areas of cereal field margins under environmental management
Biodiversity	Area of semi-natural grassland Populations of key farmland birds

Source: Adapted from MAFF, *Towards Sustainable Agriculture: A Pilot Set of Indicators*, Ministry of Agriculture, Fisheries and Food, MAFF Publications, London, February, 74 pp., 2000.

TABLE 6.6

Canadian Agro-Environmental Indicators

Indicator Group	Subgroup	Brief Description
Farm management	Agricultural land use	Land-use practices
	Soil cover by crops	Number of days per year soil is covered by crops
	Farm environment management	Management practices for fertilizer, manure, pesticides
	Wild life habitat capacity	Water used for irrigation
	Water use efficiency	Wildlife capacity on farmland
	Risk of wildlife damage	Driving forces for wildlife damage
	Risk of invasive species	Population distribution and numbers on agriculture land of invasive species
Soil quality	Water erosion	Soil loss due to water runoff
	Wind erosion	Soil loss due to wind and landscape conditions
	Soil organic carbon	Change in soil organic content
	Tillage erosion risk	Soil redistribution due to tilling and cropping
	Soil compaction risk	Degree of soil compaction due to cropping
	Soil salinization risk	Increases in soil salinity due to land use, hydrological, climate, and soil conditions
Water quality	Trace elements	Contamination by trace elements
	Nitrogen contamination risk	Increase in nitrogen levels in water leaving farm
	Phosphorus contamination risk	Increase in phosphorus levels in water leaving farm
	Coliforms	Increase in coliform levels in water leaving farm
Air quality	Pesticides	Increase in pesticide levels in water leaving farm
	Agricultural greenhouse gas budget	Estimates of N ₂ O, CH ₄ , CO ₂ due to agriculture in CO ₂ equivalents, ammonia emissions, and particulate matter in air
	Ammonia	
Food and beverage industry	Particulate matter	
	Energy use and GHG emissions	Energy content of agricultural input and output
	Water use	Water intake and discharge intensity
	Packaging	

Source: Adapted from Eilers, W., MacKay, R., Graham, L. and Lefebvre (eds.), *Environmental Sustainability of Canadian Agriculture. Agri-Environmental Indicator Report Series*, Report 3, Agriculture and Agri-Food Canada, Ottawa, Canada, 2010. Available at http://www.agr.gc.ca/env/naharp-pnarsa/index_e.php.

relate to (a) soil and water quality, (b) land conservation, (c) production of greenhouse gases, (d) biodiversity, (e) wildlife habitats, and (f) landscape. Soil quality was evaluated based on risk of water and wind erosion. These were considered of higher concern than soil compaction or salinization. Overall, about 10% of agricultural land is at risk to erosion. Conservation or no tillage of land, less intense crop production, and retiring lands can reduce the effects of soil degradation.

In 2013/2014, the OECD is reviewing all indicators worldwide and will decide future requirements. They have issued a compendium of indicators OECD (2013) that indicates there is evidence that OECD countries from 1990 to 2010 have shown positive signs regarding nutrient, pesticide, energy, and water management in terms of inputs per unit volume

of output. Environmentally beneficial practices are being utilized more by farmers, such as conservation tillage, improved manure storage, soil nutrient testing, and drip irrigation.

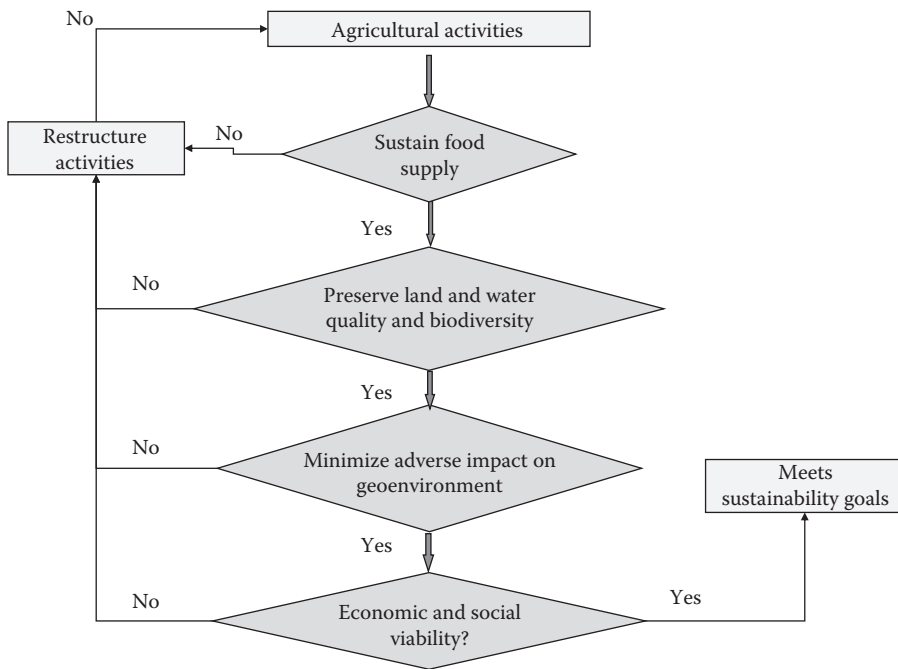
6.7 Concluding Remarks

The geoenvironment associated with agriculture plays a very important role in such activities and events as carbon and nutrient cycling, climate change, maintaining ecosystem biodiversity and water–groundwater quality, and pollution management. As has been stressed previously, the discussion concerning the impacts from agricultural practices in production of food are motivated primarily in respect to concerns for protection of the geoenvironment. Accordingly, the impacts and the means to mitigate impacts are all viewed from a geoenvironmental perspective. Many of these impacts and the means to alleviate and eliminate them are well known to the agricultural/farming community and that they share the same concern as those involved with geoenvironmental management. There is validity to the thesis that many of the measures for mitigating, minimizing, and even eliminating impacts from contaminant loading and soil quality impairment run counter to intensive agricultural practices. Conflicts between agricultural productivity and protection of the geoenvironment have always existed. However, if sustainability and/or preservation of the quality of the geoenvironment are goals that have merit, it is necessary to seek sustainable practices for both agricultural production and the geoenvironment.

Although soils have been exploited for agricultural and livestock purposes, they are very vulnerable to environmental stresses and are renewable at very slow rates (over centuries). They are at the interface of the lithosphere, hydrosphere, atmosphere, and biosphere. Aquifers are subjected to overpumping, subsidence, and contamination. Excessive extraction leads to subsidence, erosion, aridification, and salination. Contamination from farm wastes and other activities reduces the use of the water and can cause health problems. Lack of water will have a significant impact on agriculture. Conservation of water, energy, and soil resources are required, and new technologies for agricultural practices such as irrigation are needed. Recycling of crop residues and other wastes is another area where considerable development is required.

Agricultural reshaping of the land leads to erosion and other soil displacements. It changes the landscape and causes disruptions to the ecosystems and the environment overall. More than 99% of the world's food comes from the land ecosystems and more than 70% of the freshwater is used for agriculture. Lack of available and good quality water and soil limit food production today and will be even more strained as the population increases.

Many contaminants are discharged by diffused means from farming activities and are difficult to control. Water runoff and infiltration transports the contaminants to groundwater, lakes, rivers, and marine areas. The sediments are subsequently responsible for trapping many of these contaminants. Further investigations are required to better understand the retention of the contaminants by plants and soil and the chemical and microbial reactions governing the fate of the contaminants. Long-term monitoring is needed to develop databases for predictive modeling and to evaluate the sustainability of the various agricultural practices. An integrated approach of mitigation methods and reduction of the contaminants at the source are required to reduce the impact on the surface and groundwater. Multidisciplinary efforts and those involving the public are required to increase

**FIGURE 6.14**

Evaluation of the geoenvironmental sustainability of agricultural activities.

public knowledge and responsibility. To evaluate the sustainability of agricultural activities, a process as illustrated in Figure 6.14 will need to be followed.

If total costs involved in the production of food are to be determined, one would need to include not only the cost of physical operations in tilling and reaping the harvest, but also the cost of all the items needed to mount the effort in production. This would include the costs for production of the fuel needed to operate the machinery, production costs for the fertilizer and pesticides, etc. Expressing these all in terms of calories of energy, Pimentel and Wen (1990) calculated that more than 10 million kcal of energy are required for the operation of agricultural machines, production of fuel, fertilizer, and pesticide, and for irrigation and other inputs for 1 ha of U.S. corn. Approximately 3%–5% of total energy is used for the agricultural sector for OECD countries according to the FAO (2000). This is a useful basis for determining efficiency of operation and production of food. Government and nongovernmental organizations, the scientific community, and farmers must all work together as outputs in the order of two or three times present levels must be achieved by 2050 (NRC, 1999).

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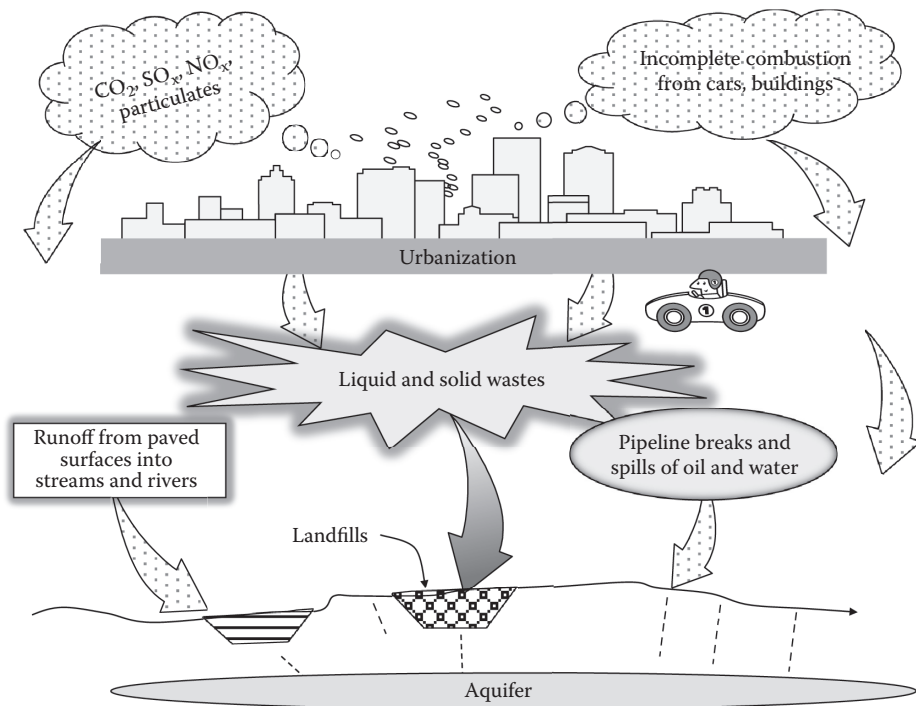
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Urbanization and the Geoenvironment

7.1 Introduction

In 2010, 50% of the world's population lived in cities, as compared with 20%, 10 years before (WHO, 2014). More than 60% of the population will live in urban areas by the year 2030, making this an increasingly significant component in the global environment. Cities account for 70% of the world's energy consumption and greenhouse gas emissions. Urban centers, together with their suburbs, constitute what is now called the *built environment*. This built environment includes (a) the various physical structures that serve the community; (b) the resultant products and discharges associated with the various industrial, municipal, and domestic activities such as wastepiles, dumps, aeration ponds, gravel pits; (c) the infrastructure, such as pipelines, transmission towers, roads, runways, bridges; (d) the various utilities necessary to service the community, such as power plants, gas plants, wastewater treatment plants, reservoirs; (e) the other kinds of resources associated with, and necessary to sustain the urban population and the welfare of the community (e.g., parks, lakes, forests, recreational and sporting facilities). By its very nature, the man-made environment that defines the built environment is often in conflict with the natural environment and in particular with the goals of sustainability of the land environment and its natural resources. The general perception is that urban centers consume significant resources and pollute the air, land, and water. Populations within the cities require clean air, clean water, sewage and waste management systems, adequate food supply, housing, and transportation. It is estimated that more than 200 million people live in cities that do not have access to clean drinking water and that more than 400 million people live in cities that do not have access to solid waste collection services and facilities. It is often argued that these demands are currently not well met, and that the demand deficit will continue to escalate with time. For example, in Accra, Ghana, only 5% of the inhabitants have access to a sanitation network, whereas 50% do not have a septic tank or access to public lavatories (Fauchon, 2012). In Lima, Peru, 90% of the sewage (more than 16 m³/s), is discharged directly into the sea. Some typical types of urban problems are summarized in the illustration shown in Figure 7.1.

A recent definition of urban sustainability offered at the Sustainable City Conference in Rio (2000) stated: "The concept of sustainability as applied to a city is the ability of the urban area and its region to function at levels of quality of life desired by the community, without restricting the option available to the present and future generations and without causing adverse impacts inside and outside the urban boundary."

**FIGURE 7.1**

Urban sources of contamination and their effect on the geoenvironment.

7.2 Land Uses by Urbanization

Urban development is a major consumer of land. Natural landscape areas around the cities are converted into housing estates, industrial parks, and other kinds of facilities designed to serve the community. Land is typically used for housing, businesses, industry, surface and subsurface infrastructures such as roads, wastewater supply, sewers, and power lines, and for recreational purposes such as parks and playgrounds. In the United States, it is estimated that about 100 m² of land per second is lost to urban uses; Germany loses about 14 m²/s, and Switzerland, a more environmentally aware country, loses about 1 m²/s (RSU, 2000). Abandoned industrial lands are not included in the estimates.

In the urban context, surface and subsurface soils may be contaminated and degraded. They serve a variety of functions, including (a) foundation base for buildings, (b) medium for plant growth, (c) open spaces, (d) park space, (e) urban gardens, (f) bases for roads, ponds, and reservoirs, and (g) sources and sinks of contaminants. Soils in urban areas tend to be more diverse because of the introduction of additives such as buried waste, debris, fuel ash, and other residues. Assessment of soil impairment requires specification of intended use of the soil. Particle size distribution, porosity, erodability, structural stability, hydraulic conductivity, and rootability are some properties that need to be assessed to determine the degree of impairment of the soil. For example, if playing fields, under repeated use in wet conditions are no longer usable for playing, the situation will need to be remediated

TABLE 7.1

Soil Physical Properties for Various Urban Uses

Requirement	Soil Properties	Application
Drainage	Hydrology, hydraulic conductivity (soil structure), porosity	Playing fields, effluent disposal
Load-bearing capacity	Bulk density, compactability, water content/potential, penetration resistance, shear strength, compressibility, consolidation	Playing fields, foot paths, load bearing support for surface infrastructures, and spread footings for light structures
Plant growth medium	Drainage, air capacity, water capacity, bulk density, structure, penetration resistance	Playing fields, gardens, parks or sports fields
Prevention of erosion and runoff	Infiltration, drainage, structural stability	Foot paths, effluent disposal, parks, or sports fields

Source: Adapted from Mullins, C.E., Physical properties of soils in urban areas. In P. Bullick and P.J. Gregory (eds.), *Soils in the Urban Environment*, Blackwell Scientific Publications, Oxford, pp. 87–118, 1990.

to return the land to its intended land use (Mullins, 1990). Signs of deterioration could include ponding, runoff, soil erosion, or poor grass growth. Soil properties relevant for use, soil type, and sensitivity of the properties to changes in soil use are important factors in mitigating soil damage. Some of the properties required for various uses are summarized in Table 7.1.

Derelict sites pose some unique problems. In general, these sites have become by default disposal sites with unauthorized disposed goods and substances that include urban garden wastes and other kinds of household wastes. Perhaps, the more dominant kinds of debris found in derelict sites are those items that are the result of demolished buildings or buildings in considerable distress. The debris generally found includes building materials such as pipes, pieces of foundations, tiles, wood, plaster, rusting steel, and broken concrete slabs and structures.

7.3 Impact of Urbanization on WEHAB

7.3.1 Impact on Water

In urban and suburban areas, more and more land surfaces are covered by buildings, roads, and constructed parking areas using concrete, bituminous concrete, asphalt, or other impervious coverings. Because these covered surfaces prevent infiltration of rainwater and ponded water into the subsurface, replenishment of the underlying groundwater is denied, and groundwater levels may consequently be lowered. Another effect of such covered surfaces is to allow surface flow (i.e., streaming) of rainwater into collecting areas. It is not uncommon to find contaminants in the surface flow water or streaming water because of noxious substances deposited onto the covered surfaces. Since these waters will eventually find their way into the receiving waters, they can be considered to be a non-point source contamination of lakes and rivers.

An extensive underground system of parking areas, sewers, pipes, deep building foundations, and tunnels to depths of 100 m can also significantly affect the underground terrain. Water leakage from buried and degrading water supply pipes leads to excessive

water accumulation. In some cities, due to a lack of maintenance, more than 40% of the water supply is lost due to leaking pipes.

In many cities, groundwater abstraction for consumption can be excessive, particularly in regions where available surface water is difficult to access and transport, in arid regions, and in regions where the quality of surface water supply is deemed unsafe for consumption. Examples cited by Fauchon (2012) show that the water table in Greater Beijing, China, is falling between 4 and 8 m each year and that in Chennai, India, 300,000 m³ more water per day are consumed than available. This will lead to severe problems of ground subsidence, soil erosion, aridification, and salinization. In coastal regions particularly, high rates of groundwater abstraction can lead to land subsidence and flooding during high rainfall periods. Seawater intrusion into the aquifers can also occur as a result of groundwater abstraction from the aquifers, resulting in contamination of shallow aquifers. If vertical communication exists between shallow and deeper aquifers, contamination of the deeper aquifers will eventually occur (Yong et al., 1994, 1995). Land subsidence will also result in damage to structures with foundations affected by differential settlement (Figure 7.2). This problem has been discussed in detail in the previous chapter in respect to the impact of high rates of groundwater abstraction in regions where cities are founded on Quaternary sediments.

Urban discharges can substantially degrade groundwater quality. For example, in China, phenols, cyanides, mercury, chromium, and arsenides and fluorine have been found in more than 50 urban regions. Urban effluent infiltration can also increase levels of nitrates, sulfates, and chlorine up to 90 m in depth (Chamley, 2003). Groundwater contamination causes many health problems and restricts human use.

Salinity is also increasing in the urban environment from discharges of domestic wastewater, seawater intrusion into aquifers, and contamination from road salt. Detergents,

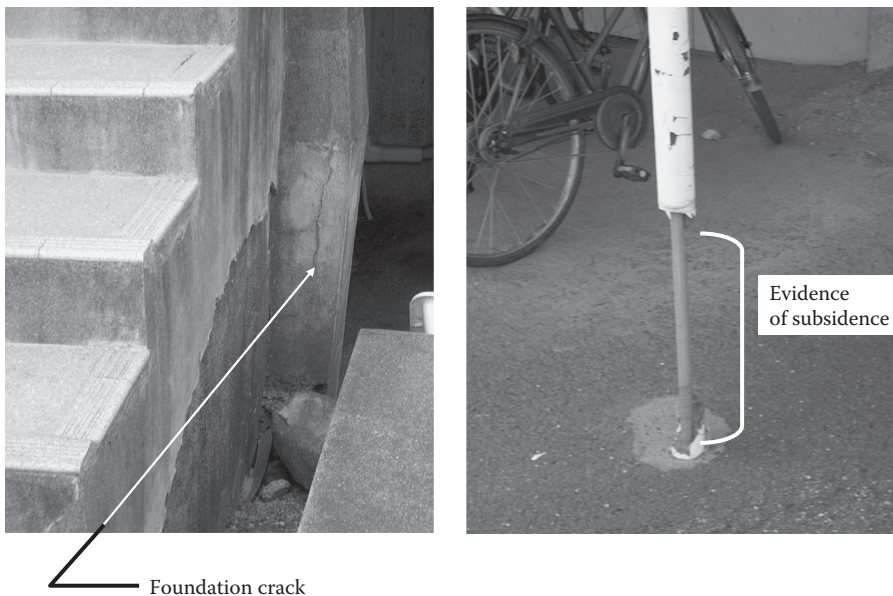
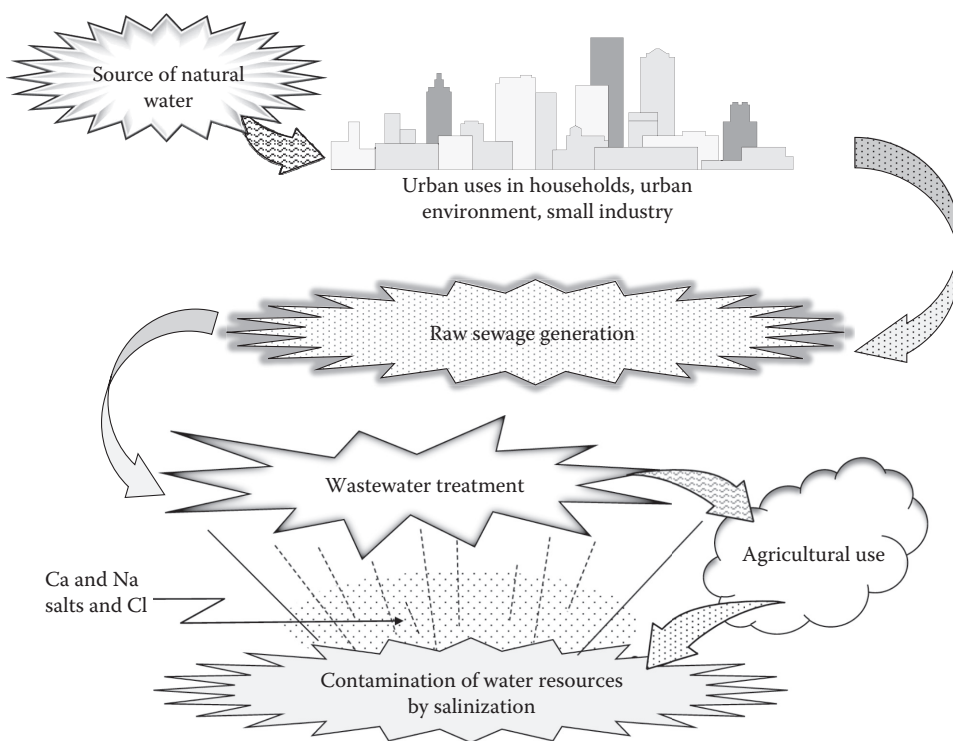


FIGURE 7.2

Subsidence and foundation impairment resulting from excessive groundwater abstraction.

**FIGURE 7.3**

Cycle of salinization of water due to urban use. (Reprinted from *Environmental Geochemistry*, Vol. 9, Vengosh, A., Salinization and saline environments, pp. 333–366, Copyright 2005, with permission from Elsevier.)

soaps, and salts are added to domestic wastewater, which is subsequently sent to wastewater treatment plants. The salts, sodium and chloride, however, are not removed in treatment process resulting therefore in increasing salinity of the water, as schematically illustrated in Figure 7.3. If the treated water is used for irrigation for agriculture, for example, in areas of the United States, Israel, and Jordan (Vengosh, 2005), groundwater and soil quality may be impaired. The addition of road salt for deicing also contributes to the salinization of groundwater. Powdered road salt used for deicing may be subject to wind dispersion, resulting in contamination of the surrounding area. Although calcium chloride can be used as a deicing salt, it is more expensive and is not as effective as sodium chloride. The combination of sodium chloride with calcium chloride can reduce the sodium-to-chloride ratio. To reduce the stress on the land and water resources, processes such as reverse osmosis and nanofiltration will be required for desalination.

7.3.2 Effect of Traffic and Energy Use

The impacts on the environment from traffic in urban areas are in the form of airborne, land, and water contamination. Understanding these problems and finding solutions for reduction of emissions are of paramount importance for the health and welfare of society and the geoenvironment. The occurrence of air contaminants from vehicular emissions at elevated levels can lead to serious health problems for the population living in high

traffic areas. Pedestrians or passengers in vehicles that do not stay in the area long will not be affected but there could be significant impacts for those that live in the area. Carbon monoxide is a major contaminant from vehicles. In particular, intersections where vehicles are stationary for a period can substantially increase the level of carbon monoxide (CO) released into the air. In general, although in the streets of large European cities, 8-h average carbon monoxide concentrations are lower than 20 mg/m^3 (17 ppm) with brief increases to around 60 mg/m^3 (53 ppm) (WHO Regional Office for Europe, Copenhagen, Denmark, 2000). The most prevalent air contaminants from vehicular emissions are nitrogen oxides (NO_x), hydrocarbons, and CO.

In the past, lead in gasoline led to accumulation of lead on surface soils for many years. Page and Ganje (1970) showed that 15 to $36 \text{ }\mu\text{g/g}$ over a period of 40 years accumulated in high traffic areas compared with negligible amounts in low traffic areas. Although lead in gasoline has been eliminated in many countries, the low mobility of lead ensures that the lead remains in the ground as a contaminant for many years.

In terms of grams of emissions per mile, for the period from 1996 to 2003, emissions of (a) hydrocarbons were 0.25 g/mile , (b) CO, 3.4 g/mile , and (c) nitrogen oxides, 0.4 g/mile (USEPA, 1993). Although emissions have decreased substantially over the years, the combination of poorly maintained cars together with more cars and other types of heavy duty vehicles that consume more gasoline and emit higher emissions (such as sports utility vehicles, light trucks, vans, and pickup trucks) ensure that reduction in noxious emission will not be readily accomplished. Not only do vehicles emit various contaminants, they also contribute over 20% of the carbon dioxide emissions from gasoline. Other petroleum fuels add another 12%. Reduction in vehicle use or the use of alternate fuels or other means will be required to substantially reduce the emission of this greenhouse gas. Without entering into the lively debate on global warming and climate change and (a) human factors causing such changes, (b) reliability of available data, (c) how far back in time one needs for data scrutiny, and (d) viability and applicability of climate change models, it is pertinent to note that the accumulation of greenhouse gases will contribute to other factors that are responsible for climate change.

Paved road surfaces share the same problems as covered impervious areas in cities; rain water cannot infiltrate into the soil but will accumulate on roads and will wash away the contaminants on the streets. This can include motor oil, grease, antifreeze, metals, phosphorus, and other contaminants that classify as pollutants. These are then washed into local waterways and rivers by streaming flows, resulting in oxygen depletion and contamination of the waters, killing fish, plants, and other aquatic life. Public health is threatened when the contaminated water and contaminated fish are ingested.

Soil quality is another issue of importance. Air particulates (contaminants) are deposited on the ground from precipitation passing through the airborne particulates. These will find their way onto surface soils and into the subsoil and also into rivers and groundwater. Human exposure with the particulates can be through inhalation, contact with the soil, ingestion of water and crops grown in contaminated soil. Ingestion of vegetables grown in urban gardens and children playing in exposed sand boxes and bare soil landscape are good examples of human exposure to deposited air particulates that classify as contaminants/pollutants. Although awareness of the potential hazards of such a form of water and soil contamination exists, the same cannot be said for information and data on contaminant concentrations and distributions from such types of deposited airborne particulates.

Soils and sediments contiguous to roads can exhibit high levels of contamination. In Germany, levels of lead, cadmium, chromium, nickel, vanadium, and zinc in soils near

roads have been found to be up to 5 times higher than in soils located some distance from roads. In the case of PAHs, these were found to be up to 100 times higher than in soils distant from the roads. The source for these contaminants can be traced to vehicular exhausts (Münch, 1993). Cuny et al. (2001) reports that elimination of lead in gasoline has substantially reduced lead levels in parking and rest areas near the motorways in France.

Acid rain is a direct result of precipitation through sulfur and nitrogen oxides emitted from fossil fuel combustion in coal thermal power plants. Sulfuric and nitric acids are deposited on (a) the soil surface and into the underlying soil and perhaps into the groundwater, (b) surface water courses, and (c) other surfaces. Northeastern United States and eastern Canada have experienced rain with pH values ranging from 4 to 5. Deforestation by acid rain has been significant in the nineteenth and early twentieth centuries in North America and Europe. Forests affected by acid rain, in particular, have less ability to retain water and protect against wind erosion. Heavy metals in contaminated soils may also be released by the acid rain. Fish and other aquatic organisms are susceptible to many metabolic disorders when the pH of lakes and other water bodies drops to 5 and below. Although not directly a geoenvironmental land problem, it is pertinent to note that respiratory problems in smog events are significant human health problems.

7.3.3 Implications on Health

The pathways of exposure of urban soils include inhalation and ingestion of soil, and dusts through respiration, and consumption of home-grown foods and contact with the soil. Urban gardening is widely practiced. Thorton and Jones (1984) have reported on various tests conducted in the United Kingdom regarding radish and lettuces grown in typical urban gardens with soils containing different concentrations of zinc, copper, and lead. Measurable values of lead in the radish and lettuce were obtained, and it was concluded that both soil splash and foliar uptake contributed to the measured lead levels.

7.3.4 Impact of Land Use

Urban land can become degraded chemically and physically. As noted previously, contaminants degrade soil quality through release into the soil via spills, runoff, and other additives. Roads, sidewalk, parking lots, and other structures seal the land and reduce water infiltration into the groundwater. The installation of cables, sewers, foundation, and other underground structures disrupts the physical structure of the soil. Introduction of softer soils or wastes into the natural soil changes its characteristics.

Greenfields are lands that have not been disturbed. They have the capacity to maintain their biodiversity, ecological functions, soil quality, and can renew their groundwater resources. Brownfields, meanwhile, have been degraded by contamination from various sources—primarily industrial and manufacturing facilities such as refineries, rail yards, gas stations, warehouses, dry cleaners, and other commercial enterprises using or storing hazardous chemicals. Table 7.2 provides a list of the various industries, activities, and contaminants that lead to land contamination, mainly in urban areas. Abandoned urban lands (brownfields) are clear indications of failure in complying with the principles of sustainable development as envisaged in the Brundtland Report (World Commission on Environment and Development, 1987) as well as that of the Club of Rome.

TABLE 7.2

Urban Land Uses and Activities Leading to Contaminated Land

Industry	Activity Leading to Soil Contamination	Type of Contaminant
Airports	Deicing and fire control runoff, servicing, fueling	Acids/alkalis, asbestos, solvents, herbicides, PCBs, fuels, deicing agents, fire-fighting chemicals
Animal slaughterhouses	Leaking tanks, pipework, spillages	Acids/alkalis, organic compounds, pathogens, metals, metalloids
Auto repair and refinishing	Leaking tanks, spills, sprays, solid wastes	Metals, dust, VOCs, solvent, paints and paint sludges, scrap metal, waste oils
Battery recycling and disposal	Discarded batteries	Pb, Cd, Ni, Cu, Zn, As, Cr
Incinerators	Solid wastes, gaseous emissions	Dioxin, ash, metals, wastes
Laundries and dry-cleaning	Spillage of solvents and other contaminants	Organic compounds including solvents (chloroform, TCE), PCE, PCBs, fuels, asbestos
Landfills (municipal and industrial)	Leachates and gaseous emissions	Metals, VOCs, PCBs, ammonia, methane, household products and cleaners, pesticides, wastes, hydrogen sulfide
Paper and printing works	Leakage from drums and other contaminants, may be buried on site, spillages of solvents and other materials	Metals, inorganic compounds, acids, alkalis, solvents, inks, degreasing solvents, fuels, oils, PCBs, inorganic ions
Railway yards and tracks	Maintenance and repair of tracks, engines, coal storage	Fuel oils, lubricating oils, PCBs, PAHs, solvents, ethylene glycol, creosote, herbicides, metal fines, asbestos, ash, sulfate
Sewage treatment	Disposal of sludges, stones and solid matter in landfill and other places	Metals, PCBs, PAHs, solvents, pathogens, acids/alkalis, inorganic compounds
Transport depots	Fuelling, vehicle washing and maintenance, storage of tires and wastes, leaks from split drums	Metals such as Pb, Cr, Zn, Cu, vanadium, Acids/alkalis, solvents, PAHs, asbestos
Waste disposal	Landfill leachates, waste transfer station spills	Inorganic chemicals, oils, metals, PCBs, PAHs, solvents, acids/alkalis, inorganic compounds, detergents, asbestos

Sources: Adapted from Syms, P., *Previously Developed Land, Industrial Activities and Contamination*, 2nd ed., Blackwell Publishing, Oxford, 2004; USEPA, *Road Map to Understanding Innovative Technology Options for Brownfields Investigation and Cleanup*, 2nd ed., U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, EPA, 542 B-99-009, 1999b.

7.3.5 Impact of Urban Waste Disposal

Improper waste disposal has a major negative impact on the land. Wastes can be in solid forms as municipal solid waste (MSW), in liquid forms as sewage and wastewater, or in gaseous forms from vehicular emissions. Solid wastes can originate from (a) households as food and yard wastes, paper, chemicals, wood, and so on, (b) urban businesses that generate wastes similar to household wastes, (c) industrial wastes, and (d) construction wastes. Hospital wastes have been discussed in Chapter 4. As there are many factors that influence production of wastes, computer models have been developed to estimate waste production rates and contaminant transport through the waste.

Various hydraulic computer models have been developed to calculate contaminant infiltration rates. Some of these models include (a) hydraulic evaluation of landfill

performance (HELP) model (Schroeder et al., 1994), (b) HYDRUS (2D/3D) based on the early work of Neuman (1972) who developed their UNSAT model, and (c) unsaturated soil and heat flow model (UNSAT-H) (Fayer, 2000). HELP has been the most frequently used model for final cover and leachate collection system design and is particularly useful for humid and semihumid areas (Environmental Laboratory, 2014). Version 3.07 is now available at <http://el.erdc.usace.army.mil/products.cfm?Topic=model&Type=landfill>.

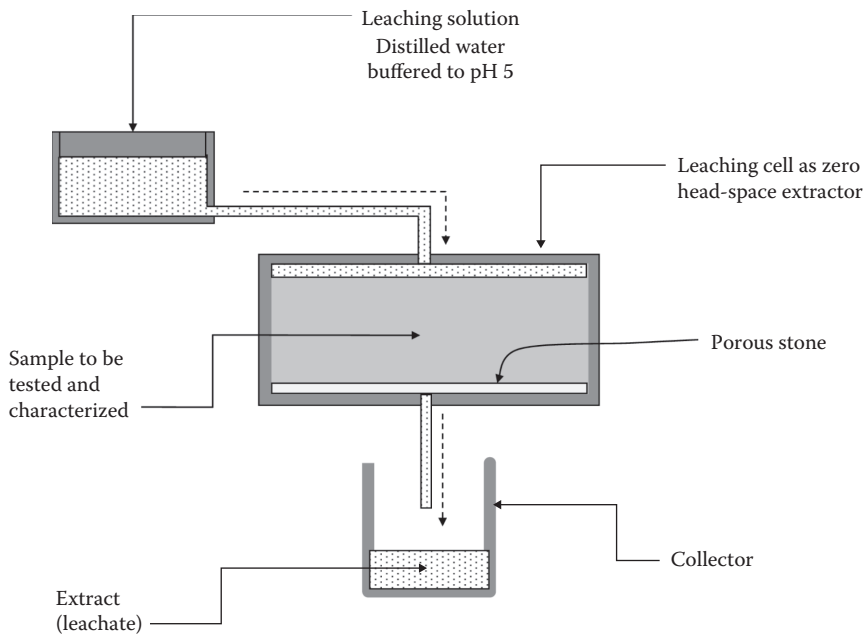
The HELP model does not simulate geocomposite lateral drainage layers well. UNSAT-H is more appropriate for arid and semiarid regions for landfill cover design. MIGRATEv9 (Scientific Software group, 1998) can be used for sorption, radioactive and biological decay, and transport through fractures, in landfills, buried waste deposits, spills, or disposal ponds. POLLUTE does not utilize a contaminant migration analysis program and thus requires little computational effort for landfill designs, from simple systems to those with composite liners and multiple barriers and aquifers. The WHI UnSat Suite combines SESOIL, VLEACH, PESTAN, VS2DT, and HELP in a revolutionary graphical environment specifically designed for simulating one-dimensional groundwater flow and contaminant transport through the unsaturated zone such as a landfill.

Wastes can also be classified as demolition, nonhazardous (municipal) and hazardous wastes. Inert or nonleachable wastes include many types of construction wastes such as soil, bricks, concrete, tiles, and gypsum board. As long as they are not contaminated, these materials can be reused as backfill material, subgrade and road materials, and even as building materials. Organic and inorganic wastes have been discussed previously in Section 2.3 in Chapter 2.

Wastes can be classified according to the physical state, origin, degree of hazard, or ability to be recycled or transformed. Wastes are classified as *hazardous* if they have any of the following characteristics:

- *Ignitability*: potential for fire hazard during storage, transport, or disposal under standard temperatures and pressures
- *Corrosivity*: potential for corrosion of materials in contact with candidate waste, resulting in environmental and health threats due to a pH less than 2.0 or greater than 12.5
- *Reactivity*: potential for adverse chemical reactions when in contact with water, air, or other wastes
- *Toxicity*: per the toxicity characteristics leaching procedure (TCLP). The leaching test system for application of the TCLP procedure is shown in Figure 7.4 and the regulatory levels of the compounds in the leachate are given in Table 7.3

In common with wastes generated from the various industries and manufacturing facilities, MSWs also will ultimately find their way into one or all of three disposal media: (1) receiving waters, (2) atmosphere, and (3) land. Land disposal of waste products and waste streams appears to be the most popular method for waste containment and management. The various impacts arising from this mode of disposal and containment include degradation of land surface environment and ground contamination by pollutants. Because of the inhomogeneous nature of wastes, stability problems on the surface of the landfill, slope stability, and settling of the landfill can occur. Chemical and biochemical reactions within the landfill and water infiltration will inevitably change the mechanical properties of the landfill.

**FIGURE 7.4**

Typical leaching cell used as a zero-head extractor for application of TCLP procedure. The results of chemical analysis of the extract (leachate) should be compared with the regulatory values shown in Table 7.3. (Adapted from Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, 307 pp., 2001.)

TABLE 7.3

TCLP Compounds and Regulatory Levels in Extract

Compound	Level (mg/L)	Compound	Level (mg/L)
Arsenic	5.0	Hexachloro-1,3-butadiene	0.5
Barium	100.0	Hexachloroethane	3.0
Benzene	0.5	Lead	5.0
Cadmium	1.0	Lindane	0.4
Carbon tetrachloride	0.5	Mercury	0.2
Chlordane	0.03	Methoxychlor	10.0
Chlorobenzene	100.0	Methyl ethyl ketone	200
Chloroform	6.0	Nitrobenzene	2.0
Chromium	5.0	Pentachlorophenol	100.0
<i>o</i> -Cresol	200.0	Pyridine	5.0
<i>m</i> -Cresol	200.0	Selenium	1.0
<i>p</i> -Cresol	200.0	Silver	5.0
1,4-Dichlorobenzene	7.5	Tetchloroethylene	0.7
1,2-Dichloroethane	0.5	Toxaphene	0.5
1,1-Dichloroethylene	0.7	Trichloroethylene	0.5
2,4-Dinitrotoluene	0.13	2,4,5-Trichlorophenol	400.0
Endrin	0.2	2,4,6-Trichlorophenol	2.0
Heptachlor	0.008	2,4,5-TP (silvex)	1.0
Hexachlorobenzene	0.13	Vinyl chloride	0.2

Both the wastes themselves and the products they produce (such as leachates and emissions) are health and geoenvironmental threats. Disposal of wastes in the ground, illicit dumping, leaking underground storage tanks and others are all causes for concern. A sampling of backyards in the Montreal area where wastes had been previously dumped indicated elevated levels of the heavy metals lead and zinc (Figure 7.5).

Water entry into wastepiles in landfills, together with dissolution processes result in the generation of waste leachates. A liner and leachate collection system such as that shown in Figures 1.11 and 3.12 in Chapters 1 and 3, respectively, is required to protect the groundwater from fugitive leachates. A cap system is required also to prevent rain from entering the wastepile and producing leachates. Typical leachates from landfills include organic chemicals (e.g., BTEX, PAHs, phthalates, ketones, dioxins, phenols, pesticides, solvents) and inorganic components (e.g., mercury, cadmium, chromium, copper, zinc, lead, nickel). The composition of leachates varies significantly depending on the age and type of waste and landfill technology used to contain the waste. The groundwater level and the nature of the soil under the landfill are important factors in managing leachate contamination risks to the groundwater. Concentrations of both organic and inorganic components can be high as shown in Figure 7.6.

In the past, quarries and other pits without proper barrier and liner systems were used for waste disposal, for example, the Gloucester landfill in Canada (Lesage et al., 1990). From 1969 to 1980, hazardous wastes, including laboratory organic chemicals, were disposed in this landfill, which is situated on glacial outwash deposits with a semiconfined aquifer. The chemicals reacted with the explosive charges that were also in the waste pile, and the leachate plume of more than 300 m in the aquifer in 1990 was found to contain the unaltered and transformed chemicals from the wastepile.

Gaseous emissions from biodegradation of organic materials in landfills also occur. These gases generally contain both carbon dioxide and methane. More than 350 m³ of

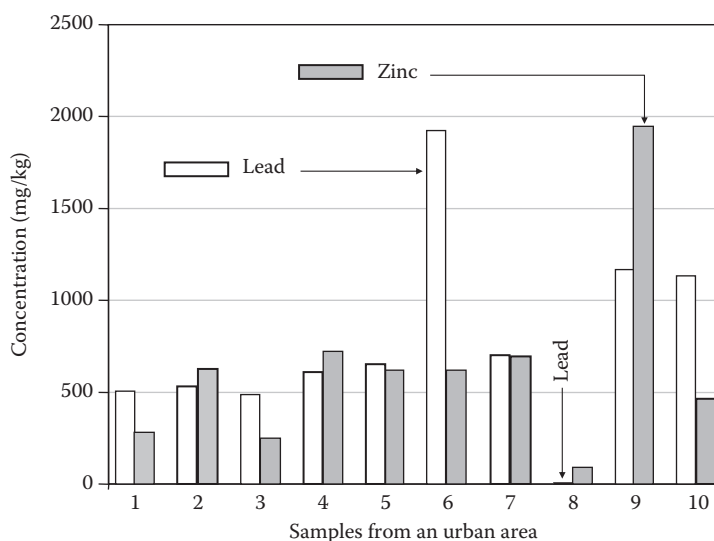
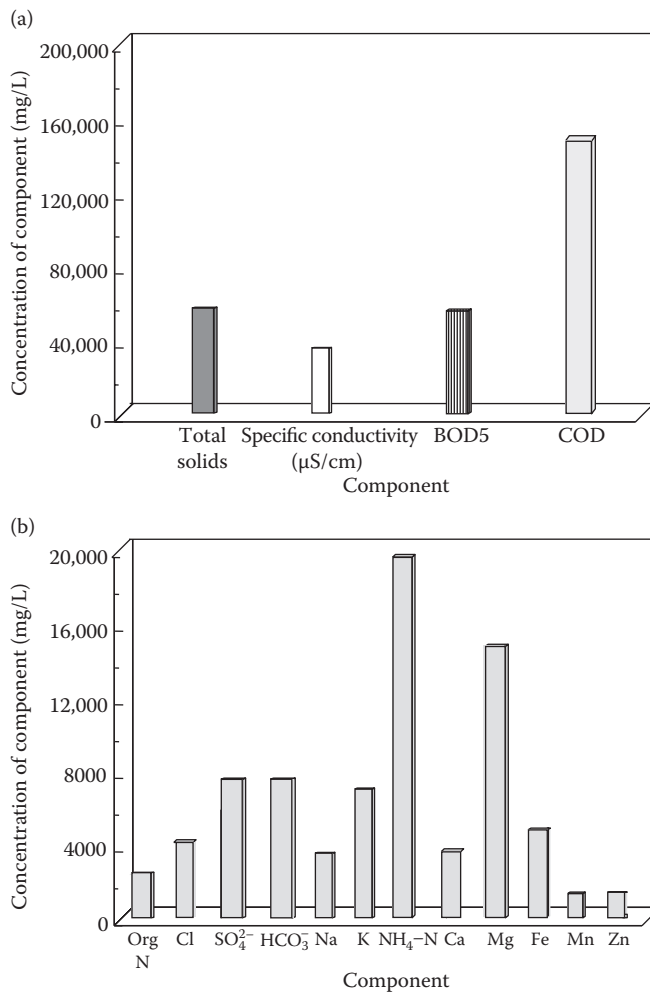


FIGURE 7.5

Lead and zinc concentrations of soil samples taken from various locations in the Montreal area (seven samples from communal garden and three samples from locations near it). (Data from Huang Y.-T., *Heavy Metals in Urban Soils*, MSc thesis, Concordia University, Montreal, Canada, 2005.)

**FIGURE 7.6**

(a, b) Range of selected components found in landfill leachate. (Adapted from data reported by Kjeldsen, P. et al., *Critical Reviews in Environmental Science and Technology* 32: 297–336, 2002.)

biogas is produced by a tonne of MSW (Genske, 2003). Volatile solvents, paints, and other chemicals such as toluene, phenol, ethyl-benzene, naphthalene, vinyl chloride, methylene chloride, xylene, and chloroform, will also evaporate. Dissolution processes involve chemical reactions between the various constituents in a wastepile, the end result of which will be transformed products and leachates. Hazardous waste dumping in the Love Canal in Niagara Falls, USA, in the 1940s and 1950s and subsequent use of the site as a hazardous waste landfill resulted in a situation (LaGrega et al., 1994), where the public was exposed to dioxin and other chemical fumes. Investigation of the many illnesses arising from the exposure showed that the chemicals causing the illnesses were neurotoxins, teratogens, fetotoxins, carcinogens, pulmonary toxins, and hepatoxins (Bridges, 1991).

Another case of illegal dumping of industrial wastes occurred on the island of Teshima in Japan, which had a low population of residents (Takatsuki, 2003). From 1978, a company was allowed to dispose of nonhazardous wastes on the island. However, because of

complaints of disposal of oil, shredder waste and open burning of wastes and a consequent investigation, the company halted disposal operations on the island but left large amounts of waste at the site. Leaching of the contaminants from the landfill and proper disposal of the contaminants (more than 600,000 tonnes) had to be addressed. Analyses showed contamination in the soil and leachate, surface, and groundwater (Table 7.4). Lead, benzene, and PCB in particular were notable. An impermeable wall was constructed on the north coast of the disposal area to prevent contaminated water from flowing out to sea. The industrial waste was then excavated (Figure 7.7) and brought to Naoshima Island where a melting furnace was constructed. The slag was to be reused as aggregate in concrete. Comprehensive environmental preservation measures and full environmental monitoring of sewage and emission gas are planned in Teshima

TABLE 7.4

Average Concentrations of Hazardous Contaminants in the Waste Leachate, Groundwater, and Surface Water at Teshima

Component	Leachate (mg/L)	Groundwater (mg/L)	Surface Water (mg/L)
Arsenic	0.048	0.004	0.02
Benzene	1.2	1.1	ND
Cadmium	0.022	ND	ND
1,3 dichloropropylene	0.54	ND	ND
Chromium (VI)	0.1	ND	0.03
Dioxins (ng TEQ/L)	8.0	0.031	0.18
Lead	6.1	0.804	0.12
Mercury	0.0017	ND	ND
PCBs	0.016	ND	0.0005
Tetrachloroethylene	0.19	0.0041	ND
Trichloroethylene	ND	0.003	ND

Source: Takatsuki, H., *Journal of Material Cycles and Waste Management*, 5, 26–30, 2003.

Note: ND, not detected.

**FIGURE 7.7**

Two views of the Teshima waste site with retaining wall where the waste and contaminated soil are contained before transfer to the treatment plant.

and Naoshima islands, with cleanup costs estimated to be in the order of 30 billion yen (approximately \$300 million).

7.3.6 Greenhouse Gases

Activities associated with urban living contribute significantly to the production of greenhouse gases. The combustion of fossil fuels is a major source of carbon dioxide production. Wood burning is another significant source. Methane released from anaerobic decomposition of organic waste in dumps and other sources contributes about 15% of the greenhouse effect. Chlorofluorocarbons (CFCs), used as refrigerants in air conditioners and as propellants, were produced in the 1950s. Their use has decreased significantly in developed countries, with the exception of developing countries, after the introduction of measures for their reduction. Concentrations of ozone, produced in internal combustion engines, have also increased. Levels have tripled in Europe and North America in the troposphere. The evidence indicates that human activities during urbanization have clearly increased these levels (greenhouse gases and CFCs), and that it is very likely that these will affect the geoenvironment in the future. If global warming happens, sea levels will rise as a result of ice cap melting and flooding of coastal regions will occur. This will disrupt coastal ecosystems and habitats. Permafrost melting will impact arctic ecosystems and will also cause considerable distress to physical structures because of terrain instabilities.

7.3.7 Impact on Ecosystem Biodiversity

The multitude of microorganisms and their diversity in the soil ecosystem is essential in maintaining and developing a healthy soil. Organic matter and nutrient recycling, mineralization, and decomposition are essential processes that have not been studied extensively in urban soils, particularly when compared with agricultural soils (Harris, 1990). Soil organisms include microbiota (bacteria, fungi, algae, protozoa), mesobiota (arthropods, nematodes, springtails, etc.), and macrobiota (earthworms, mollusc, larger arthropods, enchytraeids, etc.).

The impact of urbanization on soil properties and attributes includes great variability, compaction, bare top soil that is often water repellent, altered pH conditions, restricted aeration and drainage, altered nutrient cycling of the soil organisms, presence of other materials and contaminants in the soil, and altered temperature profiles (Craul, 1985). All these changes significantly impact on soil organisms. For example, trampling by humans in urban forests can significantly reduce the numbers of earthworms. More information is needed, however, on species diversity and numbers in urban soils and the impact of recreation, disturbance, compaction and contamination on these numbers. This microbial community can be used as an indicator of soil quality.

Chemicals from wastes, leaks, and emissions enter the soil ecosystem. They can accumulate in organisms via bioaccumulation as higher animals on the food chain eat lower contaminated organisms. As the contaminants increase in the species, the species may become compromised, causing an imbalance in the whole system. Anecdotal evidence indicates that fewer organisms, less biomass, and fewer species of organisms are found in urban soils. Assuming the evidence to be valid, this would be an indication of the stress on these organisms caused by the impact of human activities on urban soils. Although direct measures of the level of degradation or impairment of the quality of urban soils are not available, an argument could be made in support of the use of sensitive soil fauna and microflora as indicators for urban soil quality.

7.4 Impact Avoidance and Risk Minimization

As cities grow, the problems and stresses created by human–urban activities on the land environment will escalate. The requirements to satisfy the classical “food, shelter, clothing, and recreation” needs of the community impose several demands and stresses on the urban environment and its contiguous regions. To a very large extent, the main challenges for an urban society are linked to (a) sensible land management, (b) energy utilization–consumption and management, (c) nonenergy-type resources (food, minerals, building materials, etc.) consumption and management, (d) waste management, (e) reduction of contamination to air and water, and (f) water resources management.

7.4.1 Waste Management

7.4.1.1 Contamination Management and Prevention

Waste generation (urban and industrial) is a large problem. New land must be acquired for classical waste disposal techniques involving landfills when older landfills become filled and are decommissioned. Modern requirements for environmentally sensitive waste disposal and treatment require considerable resources. The essence of these requirements is embodied in the 4Rs: recycle, reuse, reduce, and recover. Reduction of waste entering landfills is the stated objective of almost, if not all communities and municipalities. Since 2000, Europeans (Eu-27) on average generate 520 kg of household waste per capita, which has stabilized despite economic growth until 2008 (European Environment Agency, Municipal waste generation CSI016/waste 001, published December 2011), Japan also produces a steady amount (1990 to 2007) at 400 kg per capita, whereas Canada continues to increase production (777 kg per capita) to twice the amount of Japan. Since 2005, the United States has begun to decrease its production (Conference Board of Canada, January 2013). In Switzerland, a family of four generating 100 tonnes of household waste would require 200 m³ of landfill volume. Reduction in land required for waste landfills can be obtained through implementation of the other 3Rs (recycling, reuse, and recover) together with incineration. Historically, landfills used to be located on the outskirts of cities. However, with the expansion of cities and suburbs in particular, these landfills are now part of the urban–suburban landscape. Although incineration is cleaner and energy efficient and can substantially reduce the volume of waste, incinerator facilities without benefit of modern burning systems and efficient scrubber units can emit contaminants into the air and produce toxic materials and ash that require disposal. Hazardous wastes such as solvents, oils, medical wastes and highly contaminated soils are often treated by incineration. With present capabilities and efficiencies in incineration and scrubber systems that can clean and properly capture contaminants before emission discharge, incinerators are being considered as the disposal system of choice since they can be located in or near cities. The system in the city of Vienna, Austria, is an example.

Contamination prevention is a method to reduce damage to the environment for future generations. Practices such as pesticide addition to lawns, city parks, etc., should be modified or eliminated. New methods to control pests should be introduced such as biological control. Many cities have banned the use of pesticides for private use. The use of less harmful or hazardous products can reduce contamination through substitution. A key example where this should have been practiced is the case of CCA-treated wood. Although it has only recently been banned for use in many countries, wood previously

treated still exists in service. Chromated copper arsenate (CCA) is a major wood preservative that was used in North America for many years for lumber treatment against insects and microorganisms because (a) it was inexpensive, (b) it left a dry, paintable surface, and (c) it bonded well, and was thus relatively leach-resistant. Primary utilization was for decks, playground equipment. Even today, it would not be unusual to find that outdoor wooden facilities with CCA treatment. CCA associated with playground equipment is particularly problematic since children are directly exposed through physical contact and subsequent oral contact by ingesting food with hands having previously been in contact with CCA contaminated wood. The U.S. Consumer Product Safety Commission (CPSC) has stated that this might even cause cancer in children (Green Building News, 2003). There is increasing concern about potential environmental contamination from leaching of Cu, Cr, and As from treated wood in service and from wood removed from service and placed in landfills and composted material. Open burning of this type of wood is also potentially hazardous. Proper incineration procedures are necessary. The life cycle of treated wood is estimated to be about 25 years, and the wood is then discarded as waste. By 1995, more than 90% of 67 million kg of utilized waterborne preservatives were CCA-treated (Solo-Gabriele and Townsend, 1999). The quantity of removed treated wood from services has been estimated by the Forest Products Laboratory (FPL) in Madison, Wisconsin, to increase from 6 million to 16 million m³ by the year 2020 (Cooper, 1993).

Moghaddam and Mulligan (2008) tested CCA-treated gray pine species wood for leaching using a modified TCLP method to determine the leaching of the three metals under various conditions. To obtain the results, samples of ground wood were soaked in acetic acid (0.1 N) at pH values of 3, 4, or 5, temperatures were 15°C, 25°C, or 35°C and leaching time was 5, 10, and 15 days. The amounts of chromium as chromium oxide (III) (CrO₃), copper as copper oxide (CuO), and arsenic as arsenic oxide (III) (As₂O₃) leached from the wood were determined to be 49% CrO₃, 34% As₂O₃, and 17% CuO. The study also examined the effects of pH and temperature on the leaching of the three metals, from the wood, for a 5-day period, and found that measurable amounts of chromium, copper, and arsenic in the leachates. Arsenic was found to be the least resistant metal to leaching when the temperature increased and chromium was the most resistant. In addition, there was more leaching of all three elements as the pH decreased. The effect is shown for pH 4 in Table 7.5. The results of the study showed that there is the risk of soil, water, and environmental contamination by chromium, copper, and arsenic, wherever chromated copper arsenate treated wood is used or disposed of in a landfill. Chromium was leached the least despite being present in the greatest proportion. Disposal must be in a lined landfill to avoid contamination of the groundwater.

TABLE 7.5

Results of Leaching Tests with Acetic Acid under Various Conditions

Conditions	Chromium (mg/L)	Copper (mg/L)	Arsenic (mg/L)
TCLP regulatory level	5.0	Not on the list	5.0
Experimental data at 35°C, pH 4			
5 days	0.6	4.9	4.5
10 days	1.1	5.9	5.7
15 days	1.4	6.4	5.5

Source: Adapted from Moghaddam, A.H. and Mulligan, C.N., *Waste Management*, 28, 628–637, 2008.

Since CCA-treated wood was exempt from the Toxicity Characteristic Leaching Procedure (TCLP) developed by the EPA, few reports concerning tests on these substances are available. Wilson (1997) tested CCA-treated wood and found that it failed to meet safety requirements for arsenic and barely passed for chromium. Since the ash also failed the test, one would conclude that CCA-treated wood cannot be burned in incinerators since the metals will remain in the ash. Arsenic can vaporize and be captured by air control equipment or escape into the atmosphere, but chromium and copper will stay in the ash. Mixing the CCA-wood with mulch for landscape purposes is also problematic because of the potential for arsenic leaching. Wood-burning power plants cannot accept this type of wood if they use their ash for application onto agricultural fields. The ash becomes hazardous if 10.7% or more of the wood is CCA treated. Although landfilling in municipal landfills is an option, it is not uncommon to find the waste (ash) sent to unlined *construction and demolition (C&D)* landfills—a practice that leads to contamination of groundwater. Recently, an alternate method was examined involving acid digestion followed by ethanol production by fermentation (Moghaddam, 2010). A slightly lower amount of ethanol from CCA treated than untreated wood was produced (6 and 7 g/L, respectively). In general, it suggests that production of ethanol from a hazardous waste (CCA treated wood) could assist in the disposal of CCA treated wood while generating a clean fuel as a source of energy.

Attempts at the removal of CCA treatment in the wood before reusing the wood have not been very successful. However, disposal of these products in the future is still uncertain. As landfilling in lined landfills is the only current option, the production of CCA-treated wood will be limited and was phased out from consumer application at the end of the year 2003 in the United States—as an agreement with manufacturers and the EPA. European countries had already banned this type of treated wood. Other alternatives such as ammonium copper quaternary (ACQ) and copper boron azole (CBA), alkaline copper quaternary compounds (ACQ), copperazole (CuAz), ammoniacal copper zinc arsenate (ACZA), copper citrate, and copper HDO (CuHDO) preservatives may be used.

7.4.1.2 Waste Reduction

Reduction of the wastes or reduction of the source of waste is the key to reducing emissions from landfills and other waste management techniques. Life cycle analysis (LCA) has been identified as a tool to help achieve sustainable consumption as it accounts for the emissions, and resource uses during production, distribution, use, and disposal (ISO, 1997). Three steps are involved: (1) the processes of the life cycle, (2) the environmental pressures of the processes (Figure 7.8), and (3) the environmental impact of the use, including the use of impact indicators. Although ISO 14040:2006 (reviewed and confirmed in 2010) defines the inventory analysis and impact assessment steps, the other steps involving definition of the process and the interpretation of the results are not necessarily simple “steps.” Several databases such as EcoInvent (version 3.0) and SimaPro are now available for some materials, but data are lacking. Other LCA software include Aveny GmbH, AMEEdiscover, eBalance, EMIS, GaBi, iPoint Compliance Agent LCA Module, Life Cycle Tracker, opn LCA, Quantis Suite 2.0, Regis, TEAM 5.1, and Umberto. In addition, life cycle impact assessment methods are being developed for minerals, land use, and toxic chemicals. *Life-Cycle Initiative*, a joint initiative of UNEP and the Society for Environmental Toxicology and Chemistry (SETAC) was

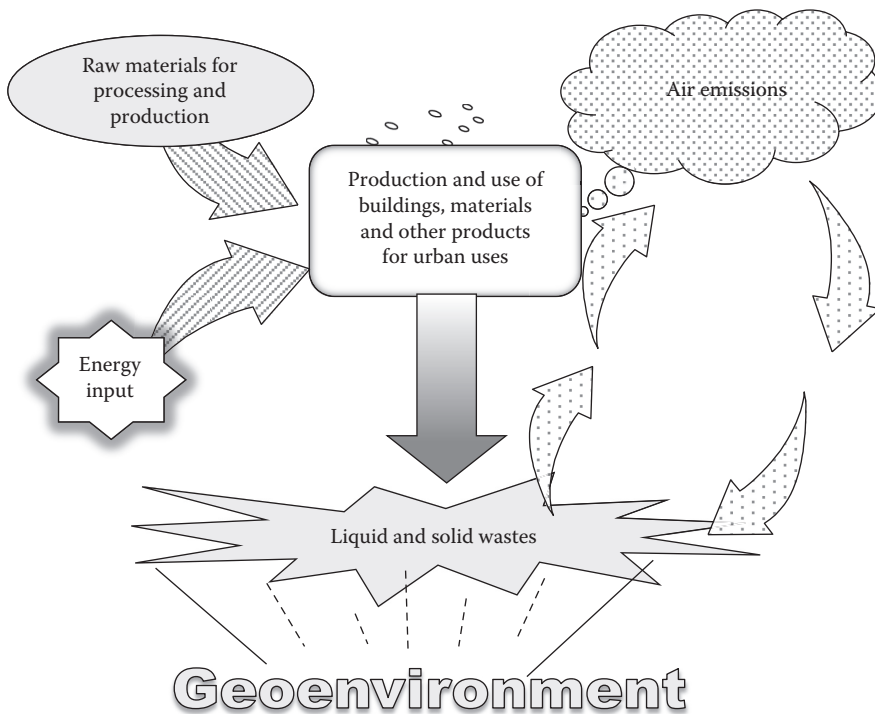


FIGURE 7.8
Elements of a life cycle assessment.

launched in 2002 and was formed to promote the development of standard methods and exchange of information (UNEP, 2004). For example, waste management experts can determine which wastes are causing problems and inform the public on alternatives or methods for waste reduction; however, most of the current information for LCA methods has been in regard to energy analysis (Hertwich, 2005). In Phase III (2012–2016), one of the main objectives is toward mainstreaming the use of life cycle approaches.

Some currently available tools are

- *BilanProduit*: helps to assess and reduce the environmental impact of a product
- *Carbonostics*: an online, carbon accounting and product life cycle assessment for the food sector
- *OGIP*: a tool to achieve an architecturally and ecologically optimized overall project within a budget.
- *ECODESIGN+*: a tool for supporting Product Carbon Footprint (PCF)
- *WRATE* (Waste and Resources Assessment Tool for the Environment) software: determines the environmental impact of different municipal waste management systems.
- *Eco-Bat4.0*: a tool for quickly performing a thorough life cycle impact assessment of a building

- *novaEQUER*: an LCA tool based on the description of a district/building, the dynamic thermal simulations by Pleiades+COMFIE and the behavior of the occupants
- *LEGEP*: a calculation tool for integrated design of sustainable buildings

7.4.1.3 Recycling

Recycling, reuse of wastes, and incineration reduce the volumes of waste entering landfills. It is clear that Canada, whose per capita waste generated is continually increasing (from 510 kg per capita in 1980), must increase efforts through recycling and waste to landfill reduction. Countries such as Finland and Japan have initiated aggressive waste management plans. Application of waste limits could be implemented as a “polluter-pays” mechanism. Although recycling and reduction of the amount of wastes, and thus the sources of contamination, has made inroads, particularly in advanced countries, a lot more progress is required. Although difficult to achieve, 100% recycling should be the goal for all materials including those for construction (asphalt, concrete, wood, etc.). Collection of paper, plastics, glass, trees, and other materials for recycling can reduce energy, material requirements, and landfill spaces. Backyard composting can substantially reduce organic waste transport, collection, processing, and disposal, while providing a fertilizer for home gardens.

Sewage sludge or biosolids is produced by wastewater treatment plants. The amount of sludge depends on the amount of water treated by the city, town, or municipality. The sludge is typically treated to remove water, and stabilization is by thickening, digestion, conditioning, dewatering, drying, and incineration. After drying/incineration, the sludge can be reused as a powder for manufacturing bricks, or mixed with Portland cement and stabilized ash. Land application for agricultural uses or for land reclamation is also possible. Pathogen and heavy metal concentrations must be removed to protect groundwater quality and public safety.

Sewage sludge has been used as an amendment to urban and agricultural gardens for organic carbon and nutrients. The sludges generally contain about 45% organic matter, 2.0% nitrogen, 0.3% phosphorus, and 0.2% potassium (Bridges, 1991). These sludges have been known to contain up to 3000 ppm of zinc, 2000 ppm of chromium, 1400 ppm of copper, 385 ppm of nickel, 240 ppm of lead, 60 ppm of cadmium, and 60 ppm of arsenic. Repeated application of this sludge leads to an accumulation of heavy metals in the soil. More recently, the metal content of biosolids was evaluated in Canada (Table 7.6). Although the levels are lower, they still can be problematic for Cd, Co, Cu, and Se, which are higher than Quebec regulations for fertilizer use.

Glass is dense and takes up significant landfill space. Increasing recycle rates is required. However, separation of colored glasses is difficult and they must not be contaminated with other materials such as ceramics. Crushed glass can be processed to reach the characteristics of gravel or sand. It can thus replace aggregate in backfill, road construction and retaining walls. The use of mixed glass as glassphalt is another possibility to replace aggregate in asphalt. More engineering tests (compaction, durability, skid resistance) will need to be performed on the properties of glassphalt and other materials. TCLP tests would need to be undertaken to determine the leachability of heavy metals from the glass. Lead has been shown to leach below the USEPA levels (CWC, 1998).

Plastics are used in many everyday items such as containers, packaging, and trays. Polystyrene, polypropylene, and polyvinyl chloride (PVC) are some of the plastic materials.

TABLE 7.6

Heavy Metals from Biosolids from a Canadian
Wastewater Treatment Plant in 2007

Heavy Metals	Concentration (mg/kg)
As	6
Cd	9
Co	19
Cr	131
Cu	477
Hg	1
Mo	7
Ni	35
Pb	105
Se	9
Zn	596

These can constitute around 10% of MSW. There are numerous problems with disposal, as it is not very biodegradable. It is a hazard in the marine ecosystem and occupies substantial volumes in landfills. Recycling can be achieved with generic plastic, mixed plastics to regenerate raw materials. New products can be formed from recycled polypropylene and polystyrene by injection molding, blow molding, and foam molding. The construction industry uses PVC for piping, and baseboard moldings. Polyethylene can be used for trash containers, book binders, bags, and other household applications. Biodegradable plastics are another alternative that is increasing in use.

Scrap tires are environmental threats (a) as mosquito hazards from accumulation of rain water and (b) as fire hazards, since they are difficult to extinguish and can burn for months, creating substantial contamination in the air and ground. Landfilling is difficult since landfills (a) are not compactable, (b) require hundreds of years to decompose, and (c) occupy substantial amounts of space. Contaminants may also leach into the soil. Heavy metals, PAHs, and TPHs have leached out under various conditions. This has limited the reuse of tires as artificial reefs and other environmental applications. The type of tire shredding can substantially affect the leaching results. Various applications for reused tires are shown in Table 7.7. Since there will be restriction for tire-derived fuel in the future, the engineering applications for tires are the most promising. Shredded tires, known as Tire Derived Aggregate (TDA), have many civil engineering applications such as a backfill for retaining walls, fill for landfill gas trench collection wells, cover material in landfills, backfill for landslide repair projects, and vibration damping material for railway lines. Ground and crumb rubber, also known as size-reduced rubber, can be used in both paving type projects and in moldable products.

Demolition debris and concrete are wastes from infrastructure renewal and building demolition. It has been estimated by the U.S. Environmental Protection Agency (USEPA, 2009) that 170 million tonnes of building-related waste were generated in 2003 in the United States (a 25% increase from 1996). Approximately 39% of this was of residential origin. It was also estimated that 49% was generated by demolition, 42% by renovation, and 9% by new construction. Approximately up to 75% of the wood, concrete, masonry, metals, and drywall are potentially recyclable. Overall, in 2003, 48% of C&D was recovered

TABLE 7.7

Applications of Recycled Scrap Tires

Tire Form	Application
Tire chips	Embankments, aggregate materials retaining walls, bridge abutment backfills Reduction in frost penetration due to low thermal conductivity Adsorption of organic chemicals in leachate collection systems, for gas migration control trenches, gas collection and venting layer in caps, leachate recirculation trenches, drainage layer in covers in landfills Low-height retaining structures
Whole tires	Highway applications for stabilization of road shoulders or noise barriers
Rubber	Rubberized asphalt concrete with long life and decreased thermal cracking
Crum rubber	Rubber is molded to form panels for railway crossings that fit between tracks instead of timber crossings
Tire shreds	VOC movement reduction in groundwater by addition to bentonite slurry walls
Ground tires	Sorption of VOCs from wastewater in wastewater treatment plants

Source: Sharma, H.D. and Reddy, K.R.: *Geoenvironmental Engineering*. 2004. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

and the remaining was discarded (USEPA, 2009). The promotion of environmentally sound waste disposal and treatment methods for construction debris constitutes one of the programs of the United Nations Agenda 21 (1993). Concrete can be recycled into aggregates of concrete, base foundation, new pavement, road shoulders, or backfill. Scrap wood can be used for landscaping (wood chips, mulch, groundcover), wood-based geotextiles for landfills as fuel or in building products (fiberboard products, rigid boards, plastic lumber). Asbestos, lead-based paints, PCBs, and CCA and pentachlorophenol (PCP) leaching from treated wood may be a concern. Cardboard, dry wall, rubble can be used as aggregate. The publication WasteSpec (Triangle J Council of Governments, Research Triangle Park, NC, 1995) provides specifications for waste reduction, material recovery, and reuse and recycling of construction waste. WasteSpec includes waste reduction techniques during construction, reusing waste material on site, salvaging waste material at the site for reuse or resale, returning unused material for credit, and delivering waste material for recycling.

Composting is one of the simplest of processes that can be used for treatment of organic wastes. It can also be very sophisticated. At the present time, it is used mainly for food wastes. However, composting materials can include garden and vegetable cuttings, paper and cardboard, garbage, and any decomposable organic matter. It is applicable for home owners, individual institutions, and even communities. It has increased in popularity significantly due to consumer awareness in decreasing the amount of wastes going to landfills. Moisture and oxygen levels, pile temperature and odor must be monitored throughout the process. Carbon to nitrogen ratios are the other important factors that must be optimal to ensure the success of the process. Composted products can be used as soil conditioners. The use of in vessel systems or biofilters with aerated piles will reduce odor levels considerably.

Anaerobic digestion is the microbial stabilization of organic materials without oxygen to produce methane, carbon dioxide, and other inorganic products. It is the most common biological treatment method used for high-strength organics in the world. At present, the technique is used for industrial, commercial, and municipal sludges (Mulligan, 2002). It

will continue to be popular since it produces methane that can be recovered and used for energy. Solids concentrations up to 35% can be processed. In addition, less carbon dioxide is produced in comparison to aerobic processes. This could become an important consideration due to the reduction requirements of the Kyoto Protocol and international treaty on global warming. This amendment to the United Nations Framework Convention on Climate Change (UNFCCC) reaffirms sections of the UNFCCC to reduce emissions of carbon dioxide and five other greenhouse gases from countries that ratify this Protocol.

Solids from anaerobic digestion can be composted. Supernatants from the sludge often have high organic contents and need to be treated further. Anaerobic digestion of MSW organics is performed at solids concentrations of 4% to 10%. Higher concentrations must be diluted. Gas production is 1.5 to 2.5 m³/m³ reactor or 0.25 to 0.45 m³/kg of biodegradable volatile solids. Retention times are approximately 20 days. Most reactors operate under mesophilic conditions.

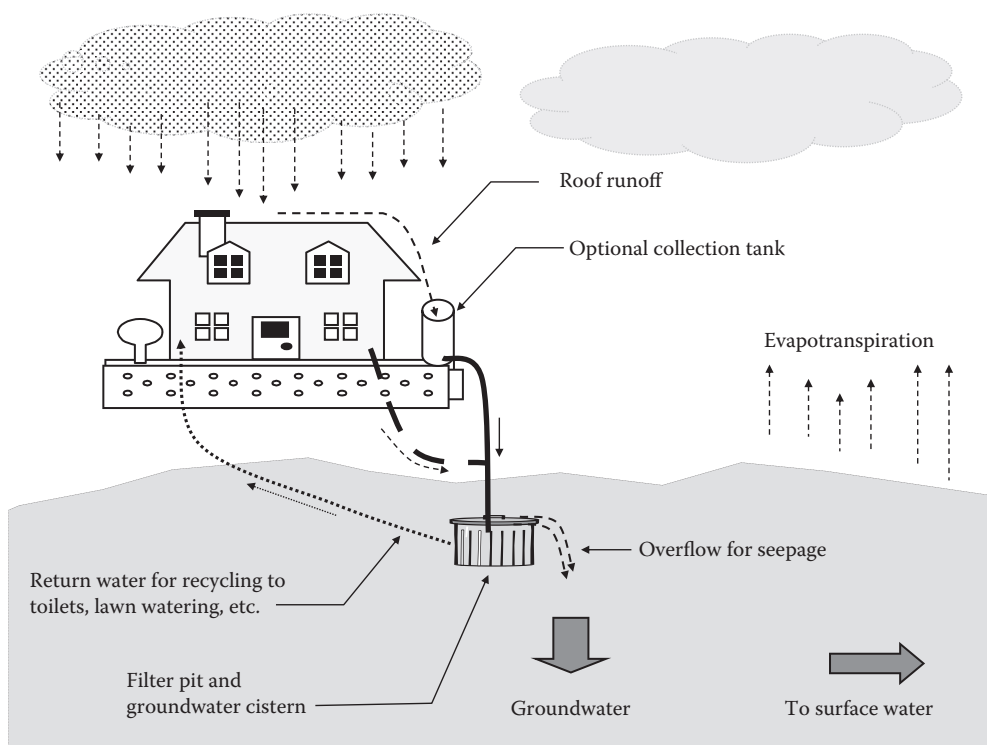
Aerobic digestion is a highly stable process that can be operated so that nitrification can also occur. Because of aeration requirements, it is more suitable for small- and medium-sized plants. Capital costs are less than costs for anaerobic digestion, and operation is safer since there are no explosive gases produced. Supernatants are also of higher quality. Thermophilic digestion is becoming increasingly popular due to pathogen destruction, and low space requirements and high sludge treatment rates. As an example, International Bio-Recovery Corp. (North Vancouver, BC) has developed a technology named autogenous thermophilic aerobic digestion (ATAD) that converts organic waste (food waste, sewage sludge, and animal manure) into single-celled protein organic fertilizer after 72 h.

7.4.2 Water Resources Management

As up to 90% of human sewage in developing countries is untreated, this is a growing threat to the health of surface water and groundwater. The capacity of rivers to absorb these contaminants without irreparable impairment of water quality is being exceeded. A combination of regulations and consumer incentives is needed to remedy the situation. Infrastructures must also be improved to reduce leakage from water supply systems. Since water quality monitoring is nonexistent in many countries, the impact of urbanization on water quality and water ecosystems is largely unknown—a situation that must be remedied.

The lack of clean water on the one hand and flooding on the other hand are problems that beset many cities worldwide. Development of dams upstream instead of policies for water sustainability, has led to water supply problems for downstream cities. We have previously discussed some of these problems in Chapter 3. Reuse of wastewater to reduce contaminant discharges into water systems may also be beneficial. Introduction of taxes or tax credits can also promote reduction in water use. Various other approaches have been proposed by König (1999) including the use of plant roofs to adsorb roof runoff with a combination of seepage or delayed drainage areas to allow rain water to return to the groundwater. Roof runoff could also be collected for use in toilets as shown in Figure 7.9.

In 2002, water consumption in Canada per capita was approximately 1500 m³ per capita as compared with less than 197 for Denmark. Through national efforts, a water conservation program was introduced that included leak detection and repair, changing water taxation and pricing, metering and water-saving devices, and public education. Water consumption decreased from 1997 to 2006 by 18.5% (Danish Water and Wastewater Association, 2007).

**FIGURE 7.9**

Recycling of roof and wastewater to replenish groundwater and provide nonpotable water for housing. (Adapted from information in König, K.W., Rainwater in cities: A note on ecology and practice. In T. Inoguchi, E. Newman, G. Paoletto (eds.), *Cities and the Environment: New Approaches for Eco-Societies*, United Nations University Press, Tokyo, pp. 203–215, 1999.)

7.4.3 Reduction in Energy Usage, Ozone Depletion, and Greenhouse Gases

As the burning of wood, coal, petroleum, and natural gas leads to substantial production of greenhouse gases and promotion of acid rain, it is obvious that reduction in the use of these energy sources is essential—as a step to fulfilling the requirements of the 1997 Kyoto Protocol. Although many different other steps are needed to meet the requirements, and whereas this is an essential step in the right direction, it is recognized that combustion of fossil fuels is not a sustainable practice. Other sources of energy such as solar, wind, geothermal, hydrothermal, and hydroelectricity produce less greenhouse gases than the above-mentioned fuels. In the case of acid rain, the choice of fuels with lower sulfur and nitrogen oxide contents can also minimize acid fallout and damage to soil, water, fauna, and humans. Nuclear energy is a clean energy. However, the problems of spent fuel rods and other radioactive waste materials are substantial and have yet to be fully resolved. A recounting of the repository disposal of high level nuclear wastes and the technological tools for managing such wastes can be found in Pusch and Yong (2005) and Yong et al. (2010). Biogas from waste dumps should be recovered and used for heating purposes. For example, the St. Michel Environmental Complex, in Montreal, Canada, recovers, at the landfill, approximately 20 MW of electricity, which is enough to power 12,000 homes.

CFCs can be replaced with other gases. Reforestation and increases in forest growth will increase carbon dioxide sink capacity. Sustainable energy generation and low-energy consuming practices for transportation, heating, and so on must be practiced, although they are not without political implications. Green buildings for houses and commercial use to reduce energy use are now being constructed. Eco-building codes and architecture will need to be developed and improved. Santa Monica, California, for example, replaced city building electricity with geothermal electricity in 1999, and Austin, Texas, offers a *GreenChoice* option for consumers that includes renewable electricity from wind, solar, or biogas (Portney, 2003).

Biodiesel is gaining popularity as a renewable fuel. It is made from the oil of various crops including palm, mustard, rapeseed (canola), sunflower, and soybeans (Weeks, 2005). Rapeseed, which produces the highest yield, is the most common source in Europe, whereas soybean is the most common in the United States. Waste frying oil can also be used. All emissions (with the exception of NO_x) are reduced when biodiesel is burned in comparison to petroleum diesel. Spills are of less impact since biodiesel degrades faster in the environment. In addition, wastewater and solid waste generation rates are lower.

7.4.4 Minimizing Impact on Biodiversity

The encroachment of cities into natural landscape areas has a detrimental impact on biodiversity. To mitigate this impact, one needs to have access to a base inventory of the natural places and biodiversity existing within the target areas so as to develop a basis for determination of the nature and extent of potential impacts. This base inventory also forms the basis for planning for urban expansion that is sensitive to the need to (a) prevent introduction of invasive species, (b) protect endangered species, and/or (c) protect the natural habitats. Cities such as San Francisco, California, are looking at ways to understand biodiversity, protect, and restore the natural ecosystems, protect sensitive plants and animals through education, purchasing green spaces, developing pest management programs, and enforcing environmental regulations (Portney, 2003).

7.4.5 Altering Transportation

Although some might argue otherwise, there is a consensus that automobiles have facilitated transport and contributed to economic progress. However, there are many environmental and sustainability issues related to transportation that need to be addressed. The method of delivery of urban transportation needs (buses, cars, trucks, etc.) require modification if ozone production is to be reduced. Cities should be planned in an optimal manner to minimize transportation requirements. Bicycles and walking should be facilitated instead. Walking is a completely sustainable transportation mode. Copenhagen was one of the earliest cities to promote pedestrian streets (Vega, 1999). Numerous cities within Europe are promoting pedestrian areas and others such as Amsterdam are promoting cycling. Public transportation will also need to be improved. Electric cars are another alternative as no emissions are produced.

7.4.6 Brownfield Redevelopment

New policies are being developed in various countries to reduce greenfield consumption. In the United Kingdom, regulations require that 60% of all housing must be on brownfields

by 2015. Germany is aiming to reduce greenfield consumption by 75% by 2020 (Genske, 2003). The USEPA made special efforts since 1998 to encourage brownfield redevelopment—in line with the goals of sustainability (USEPA, 1999a). Three cities, Baltimore (Maryland), Portland (Oregon), and Chattanooga (Tennessee) were selected as EPA pilot cities. Aspects of these programs included (a) an inventory of the brownfield sites, (b) development of awareness programs, (c) cleanup and redevelopment criteria, and (d) finding financing mechanisms for cleanup. The aims of these programs were to (1) catalyze business, (2) create jobs, (3) clean up the environment, (4) rebuild the community, (5) promote land use, and (6) reduce urban sprawl as a means to reduce contamination.

An overview of the action plan devised by the USEPA (1999b) regarding brownfield development is shown in Figure 7.10. The first part of the evaluation is the collection and assessment of the environmental information for the site. The data will determine what cleanup may be required depending on the intended use of the land. These data will need to be compared with regulatory levels to determine if the contaminant levels in the site are above or below regulatory limits. The National Brownfield Program has resulted in the assessment of over 20,000 sites, 872 cleanups, and almost 16,200 hectares made ready for reuse (USEPA, 2014).

Once a cleanup option has been chosen for a brownfield, the technology will be implemented and monitored to determine if cleanup levels are reached. Additional contamination

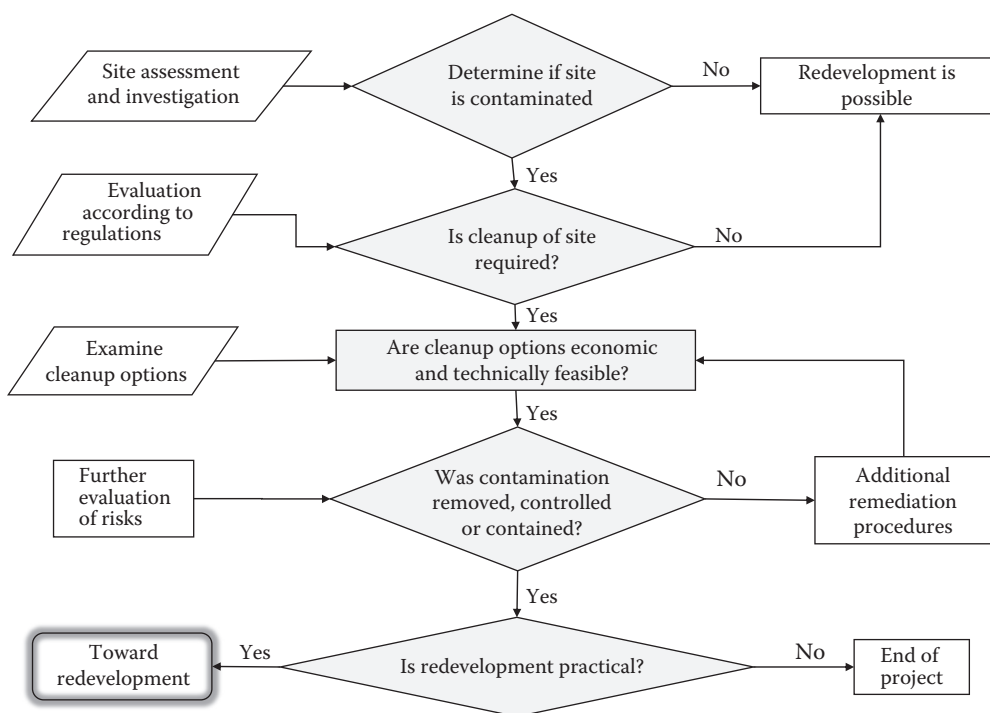
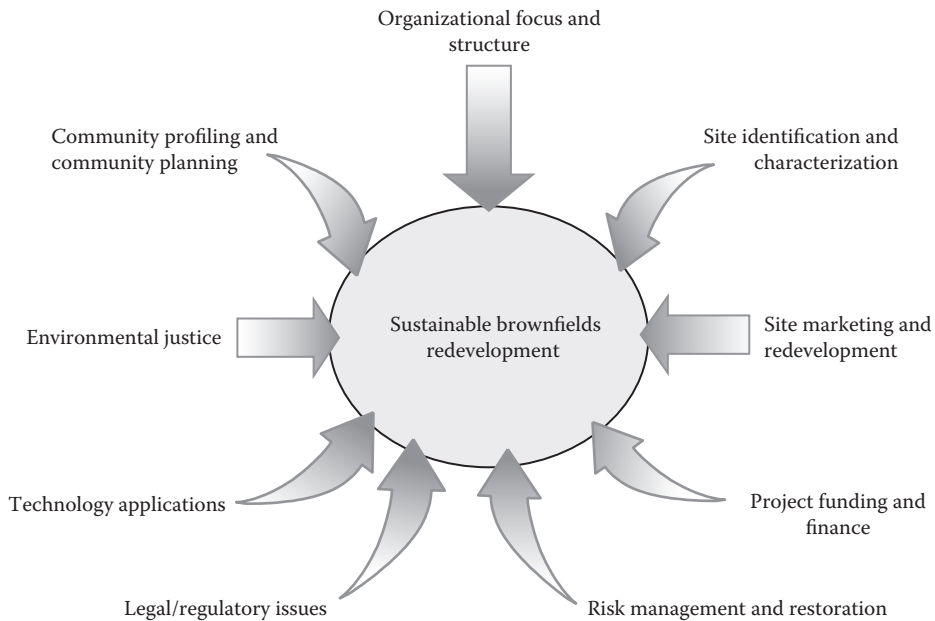


FIGURE 7.10

Evaluation of a brownfield project. (Adapted from USEPA, *Road Map to Understanding Innovative Technology Options for Brownfields Investigation and Cleanup*, 2nd ed., U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, EPA, 542 B-99-009, 1999b.)

**FIGURE 7.11**

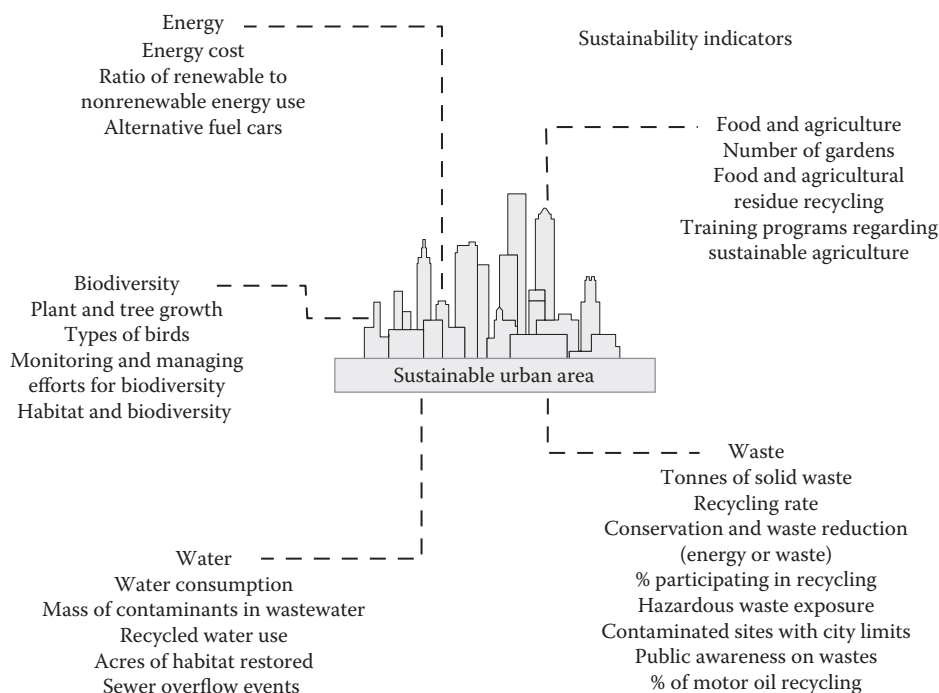
Elements to be incorporated into a sustainable brownfields redevelopment. (Adapted from USEPA, *A Sustainable Brownfields Model Framework*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, EPA, EPA500-R-99-001, January 1999.)

may be found that was not initially discovered. Long-term monitoring, particularly for natural attenuation, may be required. The site can only be developed when the regulatory levels have been achieved.

The USEPA (1999a) organized various elements into a model framework (illustrated in Figure 7.11). Many of the principles of sustainability are incorporated into this process to enable the project to be sustainable for the community in the future. The framework is designed to assist municipalities, planners, and developers to undertake brownfields projects. The technologies used should incorporate resource conservation, materials reuse, public safety and mobility, and information availability. Factors to measure sustainability should be incorporated in the future and projects should be reevaluated every few years to monitor progress and failures.

7.4.7 Sustainability Indicators for Urbanization

Indicators are useful for determining progress and comparisons with other cities or practices. There has been considerable effort in recent years to create indicators as a measure of the sustainability of cities. Most of the indicators presently available deal with easy-to-obtain data such as recycling information. Cities such as Seattle (Portney, 2003) use a wide range of indicators such as air quality, biodiversity, energy, climate change, ozone depletion, food and agriculture, hazardous materials, human health, parks and open space, economic development, environmental justice, education, etc. (Figure 7.12). An example of an

**FIGURE 7.12**

Selected sustainability indicators for the city of San Francisco that affect the geoenvironment. (Yong et al., 2006.)

indicator system is the Global City Indicators Program (GCIP) funded by the World Bank (GCI, 2014).

Environmental indicators are generally associated with such elements or parameters as water, energy, solid wastes, air, and land use. For example, in regard to waste, one is interested in quantities (a) generated, (b) disposed, and (c) recycled. Other indicators regarding urban planning are (a) areal size of informal settlements as a percentage of city area, (b) green area (hectares) per 100,000 population. Water indicators track (a) wastewater treatment facilities with primary, secondary, and tertiary treatment, (b) water consumption (c) water loss, and (d) water service interruption per household. For energy, the indicators are generally concerned with (a) use of energy and its form (less polluting energy sources are favored) and (b) amount of energy used, (c) power interruptions (d) % of city population with electrical service. Air quality indicators seek to provide controls on (a) PM10 concentration and (b) GHG emissions due to transportation, industry, and the energy sector. A water quality index, greenhouse gas index, and total energy use indices are under development. Others for land quality and use should also be included.

Table 7.8 shows an index value system developed for Amsterdam (Jonkhoff and van Eijnatten, 2012). The indicators are valued equally and use 2010 as the base that is indexed at 100. As the value decreases, this indicates a more sustainable city that was occurring as a preliminary basis in 2011.

TABLE 7.8

Sustainability Indicators for Amsterdam

Type of Indicator	Indicator
General indicators	CO ₂ emissions per inhabitant (tonnes) NO _x emissions per inhabitant (µg/m ³)
Climate and energy	Energy use (households) (GJ) per inhabitant Sustainable energy production (GJ) per inhabitant (inverse)
Sustainable mobility and air quality	Bicycle share in (%) of total of bicycles, mopeds, motorbikes, and cars Share clean trucks and lorries (%) with Euro 4 or cleaner engine
Climate and energy	Attractiveness of Amsterdam for new companies (according to ECM ranking) Energy use per added value (MJ/€)
Sustainable innovative economy	Amount of residual household waste (kg) per inhabitant Liveability indicator (x/10) given by inhabitants when asked how satisfied they were with their neighborhood on a scale of 1 to 10

Source: Adapted from Jonkhoff, E. and van Eijnatten, W., *Measuring Sustainability: The Amsterdam Sustainability Index Sustainable Cities, Building Cities for the Future*, Green Media, Long, pp. 27–28, 2012.

7.5 Mitigation and Remediation of Impacts

7.5.1 Mitigation of Impact of Wastes

Proper daily covering of wastes deposited in active landfills can mitigate odor, dust, fires, and pests. A common technique is to use a granular-type soil fill material cover that is compacted on the daily load of waste brought to the landfill. Techniques for placement of wastes in landfills, using compartments, for example, have been developed and are well illustrated in many handbooks dealing with disposal of wastes in landfills. The details of the interactions between wastes and the land environment are discussed in Chapter 9.

For landfill surface closure, a waterproof cover system as shown previously in Figure 1.11 in Chapter 1, will prevent water infiltration and reduce the requirement for treatment of the leachates. This is the technique of landfill construction and closure that is called a *dry garbage bag* system. The intent of this system is to keep the material entombed in the land with liners surrounding the entire waste that is designed to be impermeable to water. Since water is the carrier for contaminants—i.e., contaminants cannot be transported into the surrounding ground without water—there is a school of thought that argues that denial of water will not only obviate dissolution processes, but will also deny production of leachates. Along this line of reasoning, a dry garbage bag system will presumably keep the contained wastes in a dry state “forever.” However, reality forces one to accept the fact that engineered liners and barriers have a life span for secure containment that sometimes will have flaws, the result of which will admit water to the system and ultimately generate leachates that will find their way into the surrounding ground. In recognition of that fact, and in support of the thesis that if one could generate a bioreactor system with water entering the wastepile, leachate recycling into the wastepile would accelerate dissolution of the waste material in the landfill. The outcome of this kind of strategy is to obtain faster dissolution of the wastes in the landfill, and a quicker return of the landfill to more fruitful and beneficial land use.

For closures that are designed to prevent moisture entry into the wastepile, a vegetative cover on top of the impermeable barrier can assist in reducing dust generation. The roots of the plants need to be short to avoid penetrating the waste that would inhibit their growth. Biogases at active landfills should be collected for energy recovery—as done, for example, in the landfill in the city of Montreal. Other gases generated in the wastepile will need to be collected to avoid problems—as seen in the Love Canal problem discussed previously.

Wastes are treated in many ways according to the regulations in the country where it is generated. In many ways, unsorted MSWs can be treated as a resource containing discarded bottles, paper, glass, and cans that can be recovered and recycled. Construction wastes contain many items that are recyclable, for example, broken concrete elements crushed and used as granular fill and scrap lumber and wood chips that can be converted to particle board and paper into cardboard. Organic wastes can be converted via composting or anaerobic digestion. (Mulligan, 2002). One tonne of green waste produces 0.3 tonnes of compost and 0.12 tonnes of biogas.

Mixed wastes can be very difficult to treat and thus may require incineration. However, this reduces the weight of the waste to one third and the volume to one fifth of the original volume. In addition, 1 tonne of household waste can produce an equivalent energy value of 120 L of heating oil or 200 kg of coal (Genske, 2003). Despite these positive aspects, wastes generated from incinerators include gaseous emissions (74%), bottom (23%) and fly ashes (3%), and process water. These ashes must be stored and properly disposed of since exposure to acidic solutions enhances metal leaching that will find its way into aquifers or surface water. If these ashes are recycled, the heavy metals must be immobilized. Volatile substances such as dioxin are produced during incineration and can accumulate in animals, plants, and humans. Filtration and chemical methods are needed to reduce emissions of dioxins and other hazardous components such as sulfur compounds that lead to acid rain, and carbon and nitrogen oxides that can contribute to the greenhouse gas effect. The calorific value of the waste also must be sufficient to run the incinerator in a sustainable manner.

Treatment of liquid wastes is by physical and chemical means. Deep underground injection and storage is a method that has been used. However, in addition to possible compaction and ground subsidence, groundwater contamination may also result. Modeling and experimental investigations to predict the consequences of long-term storage are required.

7.5.1.1 Fresh Kills Urban Dump, New York City, New York, USA

As an example of sustainable practice, we can take a brief look at the Fresh Kills urban dump. Fresh Kills Landfill is 7500 ha in area and was established in 1948 on Staten Island for the disposal of waste for the 20 million people living in New York (Chamley, 2003). Although more than 21,000 tonnes were dumped daily in the 1980s, this decreased to 13,000 tonnes per day by the 1990s, mainly due to sorting and recycling. The dump was closed in 2001 with the exception of the waste from the rubble from the September 2001 World Trade Center disaster. As the site was originally a wood, meadow- and saline-soil mixed coastal landscape, plans are underway to restore the site. Local vegetation has been planted on a new 100-m hill, with an ultimate objective of transformation of the site into a nature and leisure place. It will be an 890-hectare park that is three times the area of Central Park and will emphasize sustainability and ecological restoration. The first part of the park (Schmul Park) was opened in October 2012 (City of New

York, 2013). Storm water management and reduced water and energy consumption are practiced. As 90% of the wetlands in New York–New Jersey Harbor Estuary were lost, an effort is underway to restore the wetlands. The process consists of using goats to graze on invasive species and installing biodegradable coir (coconut fiber) fiber logs with mussel shells and native wetland plants to reduce erosion and dissipate wave energy. Freshkills Park played a role in absorbing and slowing Hurricane Sandy in 2012 (Kimmelman, 2012).

7.5.1.2 Vertical Barriers and Containment

In Chapter 3, we have seen how vertical barriers can be used to isolate and contain the contaminants in groundwater. When a landfill is in contact with the groundwater or when a landfill leachate contaminates the groundwater, an available treatment option is to install vertical barriers to confine the contaminants. A low permeability base is required to key in the cutoff walls. If this does not exist, an artificial base will have to be added. For older landfills where liners have degraded or do not exist, other means may be required to reduce the potential for contaminant leaching into the groundwater as shown in Figure 7.13. Silicate gels, pozzolamics, or cements can be injected into the soil under the landfill to form an impermeable layer, thus immobilizing the plume. Groundwater levels may also need to be lowered by pumping to maintain their level below the landfill and the seal-off area. Pump and treat systems for treating the groundwater may also be necessary. Land

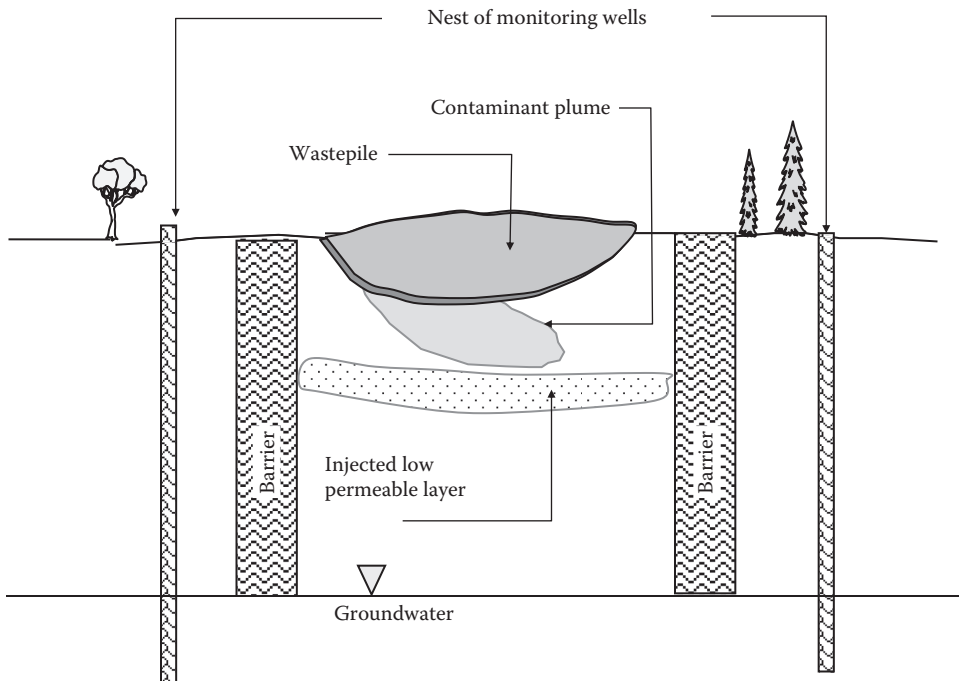


FIGURE 7.13

Vertical barriers and injections for an artificial low permeable layer under a landfill. (With kind permission from Springer Science+Business Media: *Urban Land, Degradation, Investigation and Remediation*, 2003, 331 pp., Genske, D.D.)

settlement and decreased plant growth may result from lowering of the water table. Long-term monitoring is required to ensure that the system performs according to requirements specified by the indicators prescribed for safe performance.

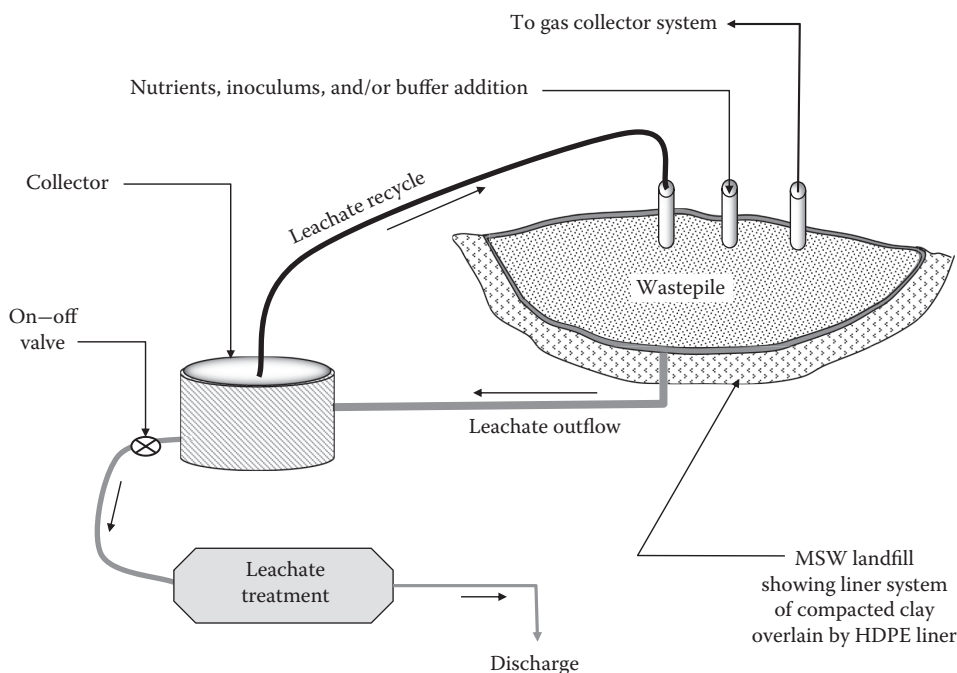
7.5.1.3 Excavation

Excavation, partially or totally, to remove offending landfills can be a solution to decreasing contaminant generation and allow land reuse. The waste can be recycled, incinerated, or dumped in a safe landfill. Handling and transport of these wastes is not without risk. Corroded drums are not easy to handle. The excavated landfill can be filled with clean or recycled soil and subsequently used for construction of buildings. Numerous measures have to be instituted to ensure worker safety and protection of the environment during the excavation work. Health and geoenvironmental threats arise from breaking bags, dust, emission of harmful gases or liquids, and unstable waste.

7.5.1.4 Landfill Bioreactor

Landfills traditionally have been operated without addition of liquid; they have been operated under the “dry garbage bag” concept. Increasing the moisture content of the waste, however, can increase waste degradation and methane production since most of the conversion processes are anaerobic. This concept is known as a landfill bioreactor and is becoming increasingly used worldwide. Experience with this type of landfill shows that gas recovery can be increased up to 90%, and that wastes can be stabilized within 10 years instead of 30 to 100 years (Block, 2000). Landfills can be designed to be aerobic, anaerobic, or anaerobic–aerobic bioreactors. Anaerobic bioreactors maintain moisture content of 10% to 20% to optimize anaerobic degradation conditions. Aerobic reactors require injection of air or oxygen with vertical or horizontal injection wells. Although wastes can be stabilized in 2 years by aerobic landfills, injection of the air can be costly and can lead to fires and thus is not practiced often. The hybrid or anaerobic–aerobic bioreactor takes advantage of aerobic and anaerobic bacteria. The upper layer of waste is aerobically treated before burial and subsequently treated with anaerobic bacteria. In all cases, moisture control is the most important parameter. Other factors include pH, waste pretreatment such as shredding, nutrient addition, settlement, cellulose content, leachate quantity and quality, and temperature control. Monitoring of these factors is essential. There is also the potential for mining the dredged waste for humic material and other recyclables. Figure 7.14 shows the major elements of a waste landfill bioreactor system. In addition to recycling of the collected leachate back into the wastepile, the option of addition of inoculum, nutrients, and other dissolution aids is provided. Gas generated from the wastepile is collected in a collection system for treatment.

In the United States, according to the EPA subtitle D rule, landfill bioreactors can only be used for landfills with composite liners such as 0.61 m of clay covered with a high-density polyethylene (HDPE) liner, as shown in Figure 7.14. Most installations increase the moisture content through recirculation of the leachate. Recirculation assists biodegradation by enhancing the transport of nutrients through the waste, redistribution of methane bacteria, buffering, dilution of inhibitory components, and retention of the constituents of the leachate in the landfill. It can be accomplished by spray application, infiltration ponds, horizontal or vertical injection wells, or trenches. Accumulated amounts of leachate will depend on (a) regulatory requirements, (b) how much is needed for each landfill compartment, and (c) minimization of quantity of leachate requiring disposal. Older areas in

**FIGURE 7.14**

Schematic of a landfill bioreactor. Leachate can be directly fed back to the wastepile in the landfill without treatment or after treatment in the *leachate treatment* facility. The use of on-off valves will facilitate choice of treated or untreated leachate for recycling. (Adapted from Mulligan, C.N., *Environmental Biotreatment*, Government Institutes, Rockville, MD, 395 pp., 2002.)

the landfill can serve as seeds for new areas. Ideally, other liquids will have to be added to increase the moisture content to 30% to 40%. However, a balance must be made such that organic acids or other components do not accumulate and inhibit methane production (Pohland and Kim, 2000). Leachate and gas monitoring are integral to the success of the process. In terms of heavy metal concentration in the leachate, pH is a major factor in mobility of the metals. Mobility of the metals increases as the pH decreases. In addition, organic and inorganic agents can serve as ligands, promoting metal transport. However, the mechanisms of precipitation, encapsulation, and sorption ensure that the heavy metals are captured in the waste.

Solubility, volatility, hydrophobicity (k_{ow}), biodegradability, and toxicity influence the behavior of organic contaminants in the landfill. Compounds such as dibromomethane, TCE, 2-nitrophenol, nitrobenzene, PCP, and dichlorophenol tend to be highly mobile and thus are found in the leachate and gas phase (Pohland and Kim, 2000). They will also be biologically altered by reduction, complexation, complete, or partial degradation. Other compounds such as hexachlorobenzene, dichlorobenzene, trichlorobenzene, lindane, and dieldrin are more hydrophobic and thus will remain in the waste and are available for biodegradation (Table 7.9).

The EPA (USEPA, 2007) reviewed the literature and evaluated five full-scale operating bioreactor landfills. They found that the bioreactors complied with existing solid waste regulations and technical guidance and that the addition of leachate and other liquids requires appropriate design to allow the injection systems to distribute the moisture

TABLE 7.9

Conversion or Transport of Inorganic and Organic Components in a Landfill Bioreactor

Component	Transport or Conversion Mechanism
Heavy metals (Cd, Cu, Cr, Fe, Hg, Ni, Pb, Zn)	Reduction of Fe, Cr, Hg Complexation with organic or inorganic components and mobilization Precipitation as hydroxide (Cr) or sulfides (Cd, Cu, Fe, Hg, Ni, Pb, and Zn) after sulfate reduction Sorption and ion exchange with waste Precipitation under alkaline conditions
Halogenated aliphatics including PCE, TCE, dibromomethane	Volatilization and mobilization in leachate due to high vapor pressure and solubility
Chlorinated benzenes such as hexachlorobenzene, trichlorobenzene, and dichlorobenzene	Volatilization and sorption on waste due to low solubility and high k_{ow}
Phenols and nitroaromatics such as dichlorophenol, nitrophenol, and nitrobenzene	Low volatility, vapor pressure, and k_{ow} , with high solubility in leachate
PAHs and pesticides (lindane and dieldrin)	Low volatility and mobility due to low vapor pressure and high k_{ow}

Source: Adapted from Mulligan C.N., *Environmental Biotreatment*, Government Institutes, Rockville, MD, 395 pp., 2002.

uniformly within the waste. The design of leachate collection systems was able at all sites to maintain leachate levels of under 30 cm of head on the liner. Slope stability was not problematic and any issues were easily corrected but proper design and operations were necessary to provide for slope stability. As there was more potential for fires in aerobic landfills than anaerobic, monitoring, and liquid addition without delay are essential. Fires or “hot spots” appear to have greater potential in aerobic landfills but can be managed with good monitoring of temperature and aeration and subsequent addition of liquids. Issues for the anaerobic bioreactors were similar to regularly operated landfilled.

In summary, the development of landfill bioreactors will continue due to its advantages over conventional landfills. Further efforts will be necessary to optimize leachate recirculation, gas generation, and removal of recalcitrant compounds. There are still many challenges including regulator reluctance, ability to wet the waste uniformly, and availability of design criteria. Slope stability and settlement will differ from traditional landfills due to the increased moisture content and degradation rates and thus will need to be properly monitored.

7.5.1.5 Natural Attenuation

Although we discussed natural attenuation and its application for groundwater in Chapter 3, and will be discussed in greater detail in Chapter 9, we want to turn our attention here to the use of monitored natural attenuation (MNA) of soil to reduce the toxicity and concentration of contaminants in a soil–water system. This subject has been treated in detail by Yong and Mulligan (2004). This concept of passive remediation has gained acceptance by many jurisdictions and regulatory agencies. To ensure effectiveness, monitoring guidelines and criteria have been (or are being) established. The soil and the contaminants must be compatible to ensure the reactions of effective and optimum partitioning of the contaminants with the soil solids and the reactions and interactions to reduce the toxicity of

the contaminants. Target concentrations must not be exceeded to protect the environment and biotic receptors.

To a certain extent, this is true because the soil attenuation layer of an engineered barrier system is often composed of soil materials that are chosen for their attenuation capability—a designed soil–water system, which is generally called an *engineered clay barrier*. Figure 7.15 shows a general view of an engineered barrier system used for containment of a waste pile. The details of the filter, membrane, and leachate collection system and the nature and dimensions of the contaminant attenuation layer are specified by regulatory *command and control* requirements or by performance requirements. The nature of material comprising the engineered clay barrier that underlies the synthetic membrane is determined on the basis of a maximum permissible hydraulic conductivity performance expressed in terms of the Darcy permeability coefficient k . There is an implied understanding (not always well founded) that the minimum specified hydraulic conductivity is somehow related to the attenuation capability of the engineered soil.

The basic idea in the design details of the engineered barriers is that if leachates inadvertently leak through the HDPE membrane and are not captured by the leachate collection system, the contaminants in the leachate plumes will be attenuated by the engineered clay barrier. The engineered clay barrier serves as the second line of defence or containment. Although the specifications refer only to a maximum permissible k value (generally in the order of 10^{-9} m/s) for the engineered clay barrier material, it is prudent to conduct additional tests of the material. These tests, which determine the contaminant assimilation capability of the clay material, are part of the protocol in the *evidence of EngNA capability*

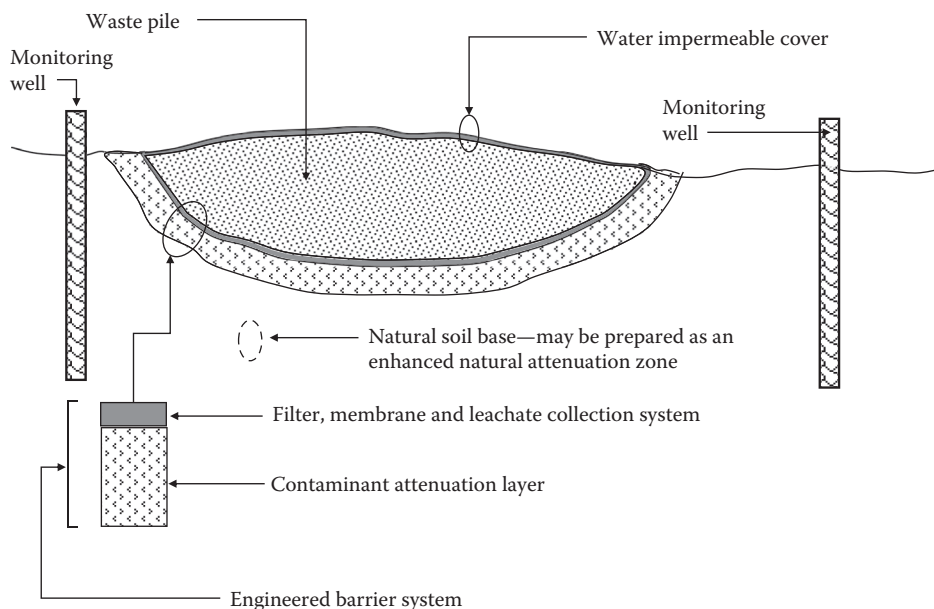


FIGURE 7.15

Contaminant attenuation layer constructed as part of an engineered barrier system. The dimensions of the attenuation layer and the specification of the various elements that constitute the “filter, membrane and leachate collection system” are generally determined by regulations or by performance criteria. (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

that assesses the capability of the engineered clay barrier material to attenuate the contaminants in the leachate plume. This will be discussed in Section 7.5.2.

The EngNA as a direct link from NA is also used as the foundation base for the double-liner barrier system for landfill containment of hazardous waste. There are several options for the foundation base seen in the diagram. Since a fully compacted foundation base is a standard requirement—to provide support for the material contained above—one has the option of working with the native material if it has the proper assimilative potential, or with imported fill material. Again, the purpose of the foundation base is to provide attenuation of contaminants should leakage of contaminants through the double-liner system occur. This in essence constitutes a third line of defence against contaminant transport into the subsurface soils.

One of the significant benefits in applying the protocols for *evidence of EngNA capability* is the determination of the required thickness of the contaminant attenuating layer and the engineered clay barrier shown in Figure 7.16. This specification can be obtained from the calculations from fate and transport models using the results of supporting laboratory research on partitioning and other attenuating phenomena. Since the dimensions for the engineered clay barriers specify “greater than or equal to” designations, application of the protocols for *evidence of EngNA capability* will likely provide dimensions that should satisfy regulatory requirements.

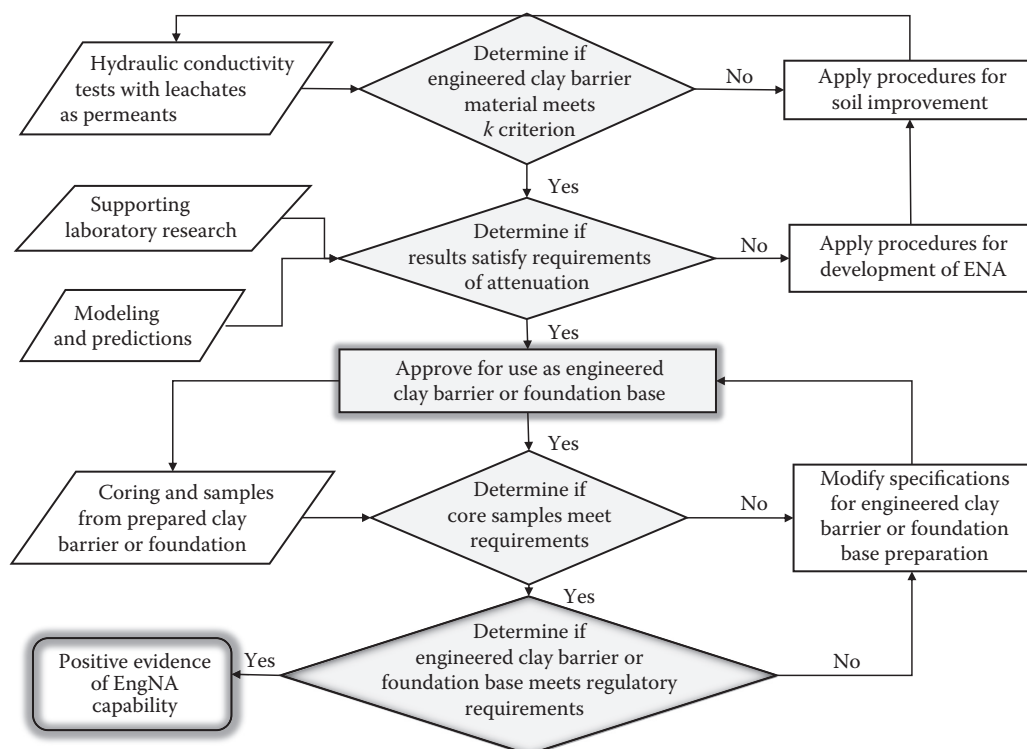


FIGURE 7.16

Protocol for determination of *positive evidence of EngNA capability* as required for use of engineered clay barriers or as foundation base material for double-liner systems. (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

TABLE 7.10

Application of Natural Attenuation at Landfill Sites

Location	Geology	Chemicals	Electron Donors	Microbial Process	Studies
Farmington, NH landfill (1995 to present)	Silty sand (up to 22 m below surface) Bedrock	TCE, DCE, VC, trace ethane, DCM, TEX, ketones	TX, DCM, ketones	Acetogenesis, methanogenesis Cometabolic oxidation	NA investigation in groundwater, laboratory studies
Niagara Falls, NY (1994)	Overburden, fractured bedrock	TCE, DCE, VC, DCA, CA, CT, CF, DCM, CM, ethene ethane	Landfill leachate, other chemicals	Methanogenesis Sulfate reduction	NA investigation in groundwater,
Cecil County, MD (1995–1996)	Sand and fill over fractured saprolitic bedrock	VC release	VC	Aerobic oxidation Anaerobic oxidation	NA investigation in groundwater

Source: Sharma, H.D. and Reddy, K.R.: *Geoenvironmental Engineering*. 2004. Copyright Wiley-VCH Verlag GmbH & Co. KGa. Reproduced with permission.

Water quality in the vicinity must remain acceptable despite contaminant dilution, degradation, and sorption processes. According to the Action Plan for *Switzerland Towards a Sustainable Development* (FOEFL, 1997), these controlled leachate landfills fall within the concept of sustainable development since few resources are consumed. Contact with the waste is not necessary. As with all bioreactor-type landfills, a proper monitoring program is necessary—to ensure that fugitive leachates are captured and treated effectively with natural attenuation processes. To date, although little hard documentation exists regarding the use of MNA for remediation of fugitive leachates from landfill sites, the limited options available favor its use. Examples of its use are shown in Table 7.10. Christensen et al. (2000) has suggested that there are five critical factors:

1. Local hydrogeological conditions
2. Size of the landfill and the variable nature of the leachate plume or plumes
3. Complexity of the leachate plumes
4. Long time frame for evaluation of the attenuation capacity of the soil
5. Demonstrating the effectiveness of natural attenuation based on a mass reduction basis

7.5.2 Remediation of Urban Sites

There are numerous benefits to restoring contaminated urban and brownfield sites. They include reducing sprawl, providing tax revenue, improving land and public health by improving air quality, removing threats to safety, and reducing greenhouse gas emissions (NRTEE, 1998). The United States and United Kingdom have national efforts in place for brownfield redevelopment. In addition, transportation costs can be reduced by up to \$66,000/ha/year if brownfields are redeveloped compared with greenfields by reducing urban sprawl (NRTEE, 2004). Also 4.5 ha of *greenland* can be preserved for

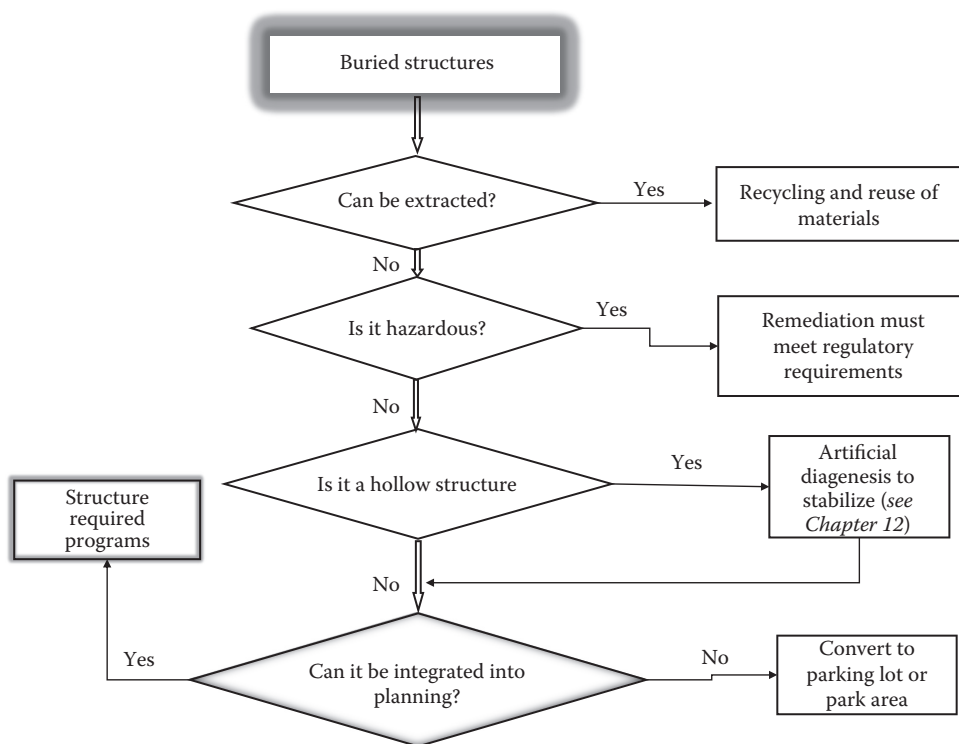
every hectare of brownfield restored. Land use is more compact, thus increasing city competitiveness. The Revi-Sols program in Montreal and Québec, Canada led to the cleanup and development of 153 projects for a total of 220 ha of land by the year 2004. The tax revenues in Montreal increased by \$25.6 million and 3400 new housing units were established.

One example of the restoration of a former contaminated site is the Angus Shops in Montreal (NRTEE, 2004). Between 1904 and 1992, the site was used as an area for railway and military maintenance and the construction of new equipment. Approximately one-third of the sites (309 acres out of 1240 acres) were contaminated with heavy metals, petroleum hydrocarbons, and PAHs. All hazardous wastes were disposed of off-site. Recyclable materials, all debris and contaminated soil were removed. Backfill consisted of clean on-site soil. The cleanup cost a total of \$12 million. Five hundred houses, a supermarket, and an industrial mall have been built, with a biotechnology center under construction. Property taxes have increased to \$2.2 million a year and more than \$391 million has been invested by private parties.

To restore urban contaminated sites, various parameters need to be considered. These include the characterization of the soil (mineral, texture, geochemical characteristics), the factors influencing fate and mobility of the contaminants such as dilution, sorption/desorption, biodegradation, and transformation, and other factors such as climate, hydrology, and microorganisms present. As a first step in the remediation of land for redevelopment, an investigation will be required to determine underground heterogeneity and hidden objects and obstacles. This can be accomplished by studying historical records and conducting geophysical surveys. Sewers, cables, underground tanks, pipelines, foundations, etc., must all be identified. They should be grouped according to their ease of extraction. For example, large foundations cannot be easily extracted and may require blasting, whereas tanks and other similar objects are not difficult to remove. Another factor is the type of material. Wood piles can be cut off, brick foundations may be extracted, but concrete foundations require special procedures. Various strategies could also be used to reduce redevelopment costs and promote sustainability. These are summarized in Figure 7.17.

As noted in Chapter 3, a variety of remediation techniques exist. They include excavation, contaminant fixing or isolation, incineration, or vitrification, and biological treatment processes. In situ processes include (a) bioremediation, air or steam stripping, or thermal treatment for volatile compounds, (b) extraction methods for soluble components, (c) chemical treatments for oxidation or detoxification, and (d) stabilization/solidification with cements, limes, resins for heavy metal contaminants. Phytoremediation is a developing technique (Mulligan, 2002). The most suitable types of plants must be selected based on contaminant type and recovery techniques for disposal of the contaminated plants.

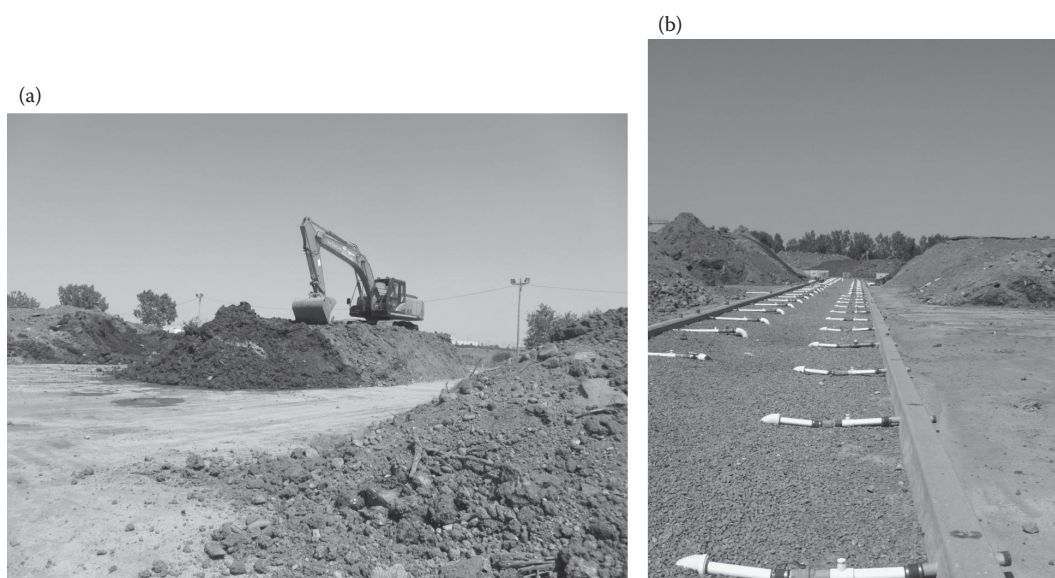
In Copenhagen, a soil treatment plant of 45,000 tonnes/year was recently established, mainly for oil-contaminated soils, with requirement for reduction of levels of 700 to 2000 mg/kg to below 50 mg/kg (Cooper, 1999). The treatment procedures call for green waste to be added to the soil in a 50:50 ratio and placed in a 1.5-m high windrow. Turning every week is required to maintain the temperature above 15°C even in the winter. Because of better air permeability characteristics, sandy soils are much easier to treat than clay soils. If the treatment is successful, the remediated soil can be used to grow vegetation in embankments or in construction projects. If the treatment fails or does not meet the required criteria, the soil must be sent to a special landfill.

**FIGURE 7.17**

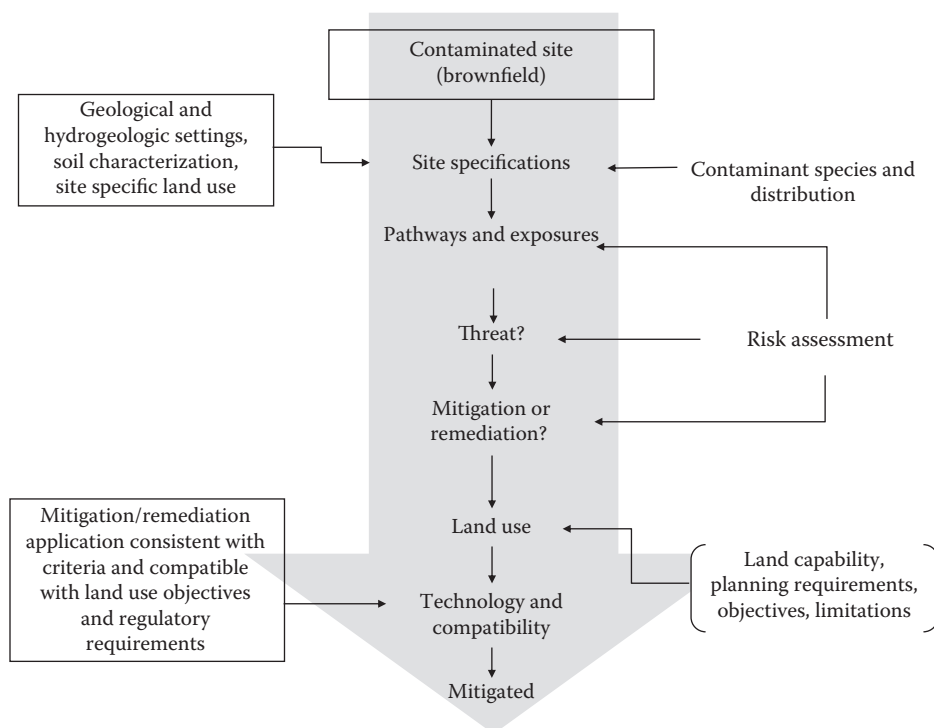
Schematic protocol for managing underground structures in a redevelopment plan. (With kind permission from Springer Science+Business Media: *Urban Land, Degradation, Investigation and Remediation*, 2003, 331 pp., Genske, D.D.)

In the provinces of Québec and Ontario, treatment centers for contaminated soil serve various clients including real estate developers (for example, conversion of a gas station to condos), excavation contractors, environmental consultants, government agencies, industries, and manufacturing companies. The process is an in situ biopile that uses microorganism to breakdown the contaminants while controlling aeration, humidity, and nutrient levels. The process is shown in Figure 7.18. Treated contaminants include petroleum hydrocarbons, volatile organic contaminants, PAHs, PCP, creosote, and phenol. Water and air emissions from the process can also be treated biologically via an aerated wastewater treatment system, wetlands, and a biofilter. Depending on the remaining contaminant levels, the treated soil may be able to be returned to the original site.

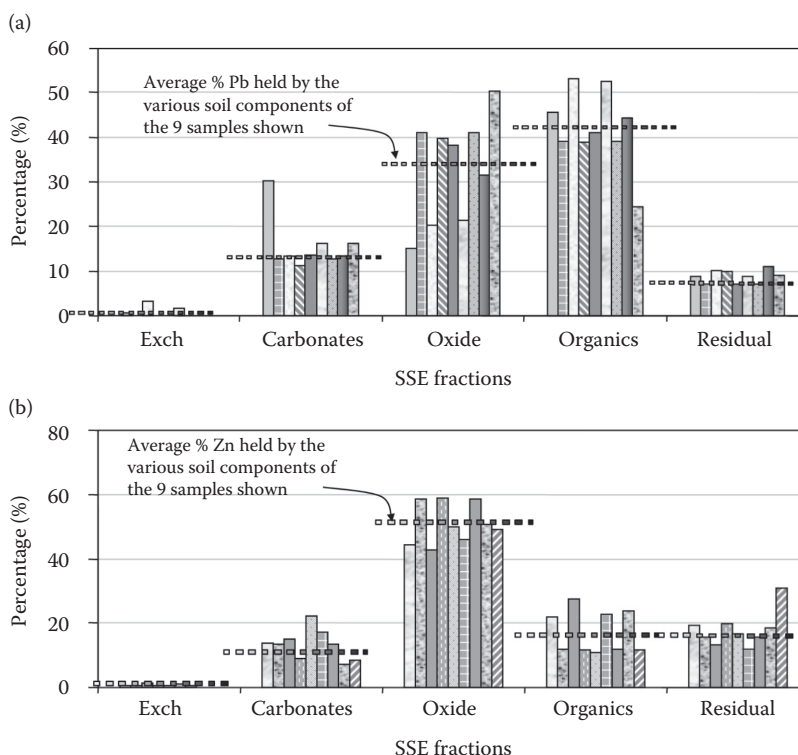
Regardless of the origin of the contaminants in the area, an evaluation of the threats to human health and the environment must be undertaken before the remediation process. Both the potential exposure time and level must be considered. Figure 7.19 gives a flow-chart that illustrates a simple procedure for evaluation and treatment. Techniques such as selective sequential extraction are useful in determining the likelihood that the heavy metals are mobile. Selective sequential extraction studies were performed on nine soil samples (Huang, 2005). Figure 7.20a and b shows the results for lead and zinc, respectively. It can be seen that both lead and zinc have different affinities toward different soil fractions. Both Pb and Zn have higher affinities toward the soil fractions of organic matter and oxides. Only a small fraction of both metals is associated with the exchangeable

**FIGURE 7.18**

Biopile contaminated soil treatment site with soil preparation (a) and aeration system (b).

**FIGURE 7.19**

Simple protocol for rehabilitation of a contaminated site. (Adapted from Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, 307 pp., 2001.)

**FIGURE 7.20**

Selective sequential extraction characterization of nine different soil samples for Pb (a) and Zn (b) retention by the different soil components and mechanisms. Note that *Exch* represents Pb or Zn held by cation exchange mechanisms, and *carbonates*, *oxides*, and *organics* represent soil components responsible for retaining the metals. *Residuals* represent “remaining” in the soil matrix. (Data from Huang Y.-T., *Heavy Metals in Urban Soils*, MSc thesis, Concordia University, Montreal, Canada, 2005.)

fraction. Metals bound to the exchangeable fraction of soil are mostly physically adsorbed (by electrostatic force) to the soil surfaces, and thus, the bonding is weaker compared with other binding mechanisms. The moderate to high degree of leaching by rainfall and the competition from other cations present in the leachate solution possibly explains why only a limited amount of Pb and Zn were retained by this soil fraction. There is a high degree of association of Pb and Zn with soil oxides and organic matter. The metals associated with oxides are particularly susceptible to oxidation–reduction reactions and solubilization upon a decrease in pH by acid rain.

Sequential extraction was performed on the untreated soil from a site slated for rehabilitation and construction (Okoro, 2006). The results (Figure 7.21) showed that copper existed mainly more in the organic fraction (50%), whereas zinc was mainly in the oxide fraction (36%) and nickel more in the exchangeable and carbonate fractions (50%). Some soil washing tests were performed with a series of five washings with biosurfactants, which enabled the oxide fraction of zinc, organic fraction of copper, exchangeable and carbonate fractions of nickel to be substantially reduced, compared with the control and the untreated soil. These results indicated the feasibility of removing heavy metals and the total petroleum hydrocarbon content of a mixed contaminated soil with the anionic biosurfactants tested.

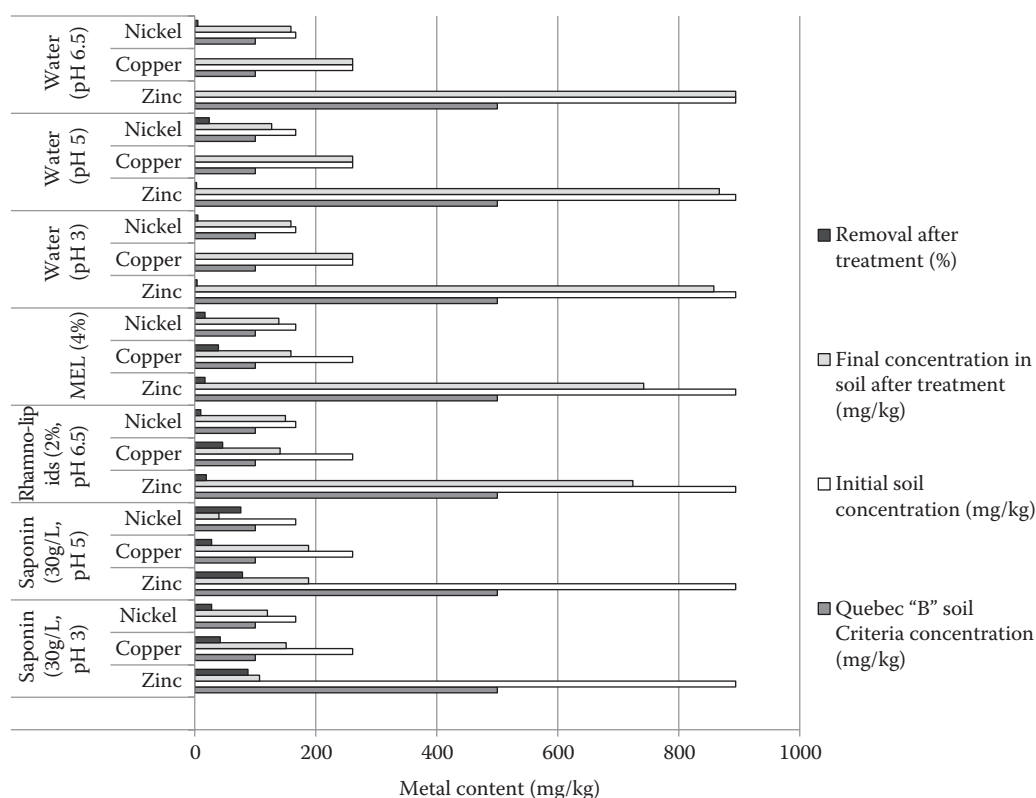


FIGURE 7.21

Remediation of a contaminated urban site using biosurfactants. (From Okoro C., *Biosurfactant Enhanced Remediation of a Mixed Contaminated Soil*, MASc thesis, Concordia University, Montreal, Canada, 2006.)

7.5.2.1 Case Study of a Sustainable Urban Area

The Federation of Canadian Municipalities (FCM; <http://www.fcm.ca>) provides various awards each year for a variety of concerns, including for innovative sustainability practices. One of the awards for sustainable communities is for restoration of brownfields. In 2013, the Brownfield project award was given to the City of Kingston in Canada for Belle Park, a 44-ha, multiuse recreational space. The site is a former landfill where the city uses pumps and extraction wells to capture the leachate that flows into the river. Since 2007, the city initiated a new practice to plant 12,500 hybrid poplar trees and over 16,000 live stakes, bareroot seedlings and potted shrubs as a means of capturing the leachate flowing to the river and in the groundwater. The poplars uptake large volumes of groundwater containing the contaminants. Less leachate is now reaching the river, and over the long term, there will be less need for the pump and treat systems. The solution is cost-effective and the area provides societal benefits due to the transformation of the grass area into one with many trees, and there are new pathways for walkers. There were various challenges for the project. Owing to the harsh former landfill environment, there were special requirements for tree care as regular irrigation methods could not be used as a result of the leachate infiltration. The trees needed to be planted early in the rainy season before the heat of the summer, to encourage growth as much as possible. In addition, early protection from

weeds and wildlife which was labor intensive was required to avoid the use of herbicides and pesticides. It was beneficial to select ornamental plants that will thrive alongside the trees, and tree varieties that are disease-resistant.

7.6 Concluding Remarks

Cities have significant impacts on the geoenvironment. Increasing urban population will increase pressures on the geoenvironment in the years to come. All aspects of the geoenvironment need to be protected. Optimal design of landfills is one of the methods to protect the urban environment. Natural attenuation of the landfill leachate plumes is a sustainable method of remediation. The operation of a landfill bioreactor has potential to increase methane production rates and waste degradation rates, which subsequently increases the life of the landfill. Although waste reduction and recycling programs exist in many cities, substantial improvements are needed to decrease wastes going into landfill and increase recycling rates. Life cycle analysis of products can be used to assist in determining which products have less impact on the environment. However, more data (particularly regarding emissions and leachates during production and disposal) is required to facilitate the comparison process.

Cities need to redevelop brownfields through remediation and other planning initiatives. This will substantially reduce the need for greenfields for future development projects. Few efforts have been made to protect the diversity of plants, animals, and microorganisms (i.e., biodiversity). Substantial efforts can be made to conserve resources such as energy. Electricity from geothermal and other renewable sources can be chosen. Buildings and their materials must also be energy efficient. Efforts must also be made regarding transportation to reduce its impact on the geoenvironment.

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8

Coastal Marine Environment Sustainability

8.1 Introduction

For many different reasons, the coastal marine environment can be considered to be an important part of the geoenvironment. It is the recipient of (a) liquid discharges from surface runoffs, rivers, and groundwater and (b) waste discharges from land-based industry, municipal, and other anthropogenic sources. It is also a vital element in the geoenvironment that provides the base for life-support systems. The combination of these two large factors, with their direct link to human population, makes it (the coastal marine environment) an integral part of the considerations on the sustainability of the geoenvironment and its natural resources.

8.2 Coastal Marine Environment and Impacts

The coastal marine environment is a significant resource. A healthy coastal marine ecosystem ensures that aquatic plants and animals are healthy and that these do not pose risks to human health when they form part of the food chain. In this chapter, we will discuss (a) the threats to the health of the coastal sediments resulting from discharge of contaminants and other hazardous substances from anthropogenic activities, (b) the impacts already observed, and (c) the necessary remediation techniques developed to restore the health of the coastal sediments.

8.2.1 Geosphere and Hydrosphere Coastal Marine Environment

The discussion in Section 1.2 in Chapter 1 on the inclusion of many elements of the hydrosphere in the geoenvironment points out that the coastal marine environment is included in the discussions on the receiving waters of the geoenvironment. This is because it is impacted by the outcome of anthropogenic activities. The sea provides the habitat for many living organisms and is an important ecosystem in the geoenvironment. Seawater is one of the major supply sources for our water resources through evaporation of the seawater and subsequent deposition on land as rainfall. Evapotranspiration constitutes the other major source of water for rainfall. Circulation and recycling of water on land is a very important process for preservation of the global environment and life support for all living organisms. This is not only because no living organisms can survive without water,

but also because many substances required for the preservation of the sea environment are transported with the circulation of water.

Nutrients, such as phosphorus, nitrogen, silicate, etc., are produced during the decomposition of plants by the actions of organisms and are transported into the sea by water. Phosphorus and nitrogen are produced from the decomposition of withered leaves, while silicate originates primarily from inorganic soils. These nutrients are essential to the organisms in the sea, and are basic elements of the ecosystems in the sea. In general, there are fewer nutrients in shallow coastal zones, in comparison to deep seawater. This makes deep seawater more attractive for fish farming and for creating fishing grounds. To increase the amount of nutrients in the fishing grounds, fishermen have begun to plant broad-leaved trees in mountainous areas as a means to increase production of phosphorous and nitrogen as decomposition products for eventual rainfall (land surface flow) transport into the sea. Recognition of the high mineral and nutrient values that can be obtained from deep seawater has led to harvesting of deep seawater for extraction of salt and other products.

8.2.2 Sedimentation

The sea bottom is the interface between the seawater as the hydrosphere and the sediments and rock as the geosphere. Sediments are formed from substances deposited in the hydrosphere or produced in the hydrosphere itself. Because of the concentration of cations in seawater, suspended clay particles can aggregate more easily and settle faster than in freshwater. In addition, most sediment solids have a specific gravity greater than that of seawater—which explains why most of the nonaggregated solids will finally settle to the bottom of the sea. The settlement or sedimentation of solids is probably one of the strongest agents responsible for the purification of seawater because

1. Various (harmful and noxious) substances sorbed or attached to the sedimenting substances (particles) will be sedimented with the particles—resulting in a measure of purification of the seawater
2. Turbidity is reduced and transparency is promoted

8.2.3 Eutrophication

In some closed sea areas, increased concentration of nutrients can be found. This phenomenon is called *eutrophication*. This can happen naturally. More often than not, this phenomenon is developed as a result of the input of additional nutrients due to anthropogenic sources. This is sometimes called anthropogenic eutrophication. The main sources of these nutrients are sewage effluents, nutrients washed out of farm land, golf courses, lawns, and deposition of nitrogen from nitrous oxide emissions. Low to moderate eutrophication is beneficial because it enhances production of microscopic plants called phytoplankton that live in the ocean. Because they (phytoplankton) are bait for zooplankton, they are the basis for the marine food chain, and their increased presence means a better food supply for the fish that rely on them as their source of food. However, when eutrophication is high, an excess amount of phytoplankton will be produced, and the resultant phytoplankton bloom will contribute to the reduction in the amount of dissolved oxygen in the immediate region—creating problems for the fish population as explained later in this section as red tide.

Resuspension of decayed algae and inorganic and organic particles will contribute to the turbidity of water, adding to the sunlight shading effect. Turbidity affects growth of

sea plants that need sunlight. Decay of algae by bacteria removes large amounts of oxygen from the water, and may kill living organisms. Oxygen deficiency will cause sediments to change from an aerobic to an anaerobic state. When this occurs, sulfides such as pyrite, can be formed (Fukue et al., 2003). Hydrogen sulfide is a hazardous substance for fish. The combination of oxygen depletion with hydrogen sulfide makes the seawater look blue or greenish-blue—a condition sometimes called *blue tide*.

Accelerated production of phytoplankton algae will lead to algae bloom—an overpopulation of certain types of algae that are readily distinguished on the water surface as patches of bloom because of their high population density. The red algae bloom known as *red tide* is a vivid demonstration of such an occurrence involving certain types of algae that contain red pigment. Some, but not all, of the red algae species are toxic. The prominent ones are the dinoflagellate *Alexandrium tamarens* and the diatom *Pseudo-nitzschia australis* (WHOI, 2014). Their production of neurotoxins makes them harmful to fish and other aquatic life forms—and even humans. Remediation treatment is needed if one wishes to maintain a healthy environment in the coastal marine ecosystem to counter the effects of the preceding.

Many countries, states, and communities have set up programs for monitoring of surface water quality. The term *surface water* is used here in the overall defining sense to mean all water that is naturally exposed to the atmosphere. This includes rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries, and all springs, wells, or other collectors directly connected to surface water. In general, the quality of surface water has a direct influence on its sediments, benthic organisms and plankton. Data obtained on surface water quality are used to structure measures to counter eutrophication and contamination of surface water.

8.2.4 Food Chain and Biological Concentration

Some organic matter, such as phytoplankton, deposited onto the sea bottom or suspended in seawater will be decomposed by microorganisms or will be consumed by small benthic animals called zooplankton. Phytoplankton is the first level in the marine food chain and zooplankton are the second trophic level. Decomposition of the phytoplankton and other organic matter will produce detritus. This is a good source of nutrients. The food chain starting from detritus is often called the *detritus food chain*, in contrast to the food chain starting from phytoplankton in seawater. These food chains are the most important process for the preservation of marine environment and living organisms such as fish, shellfish, sea plants, etc. These are important sources of protein and minerals for humans. However, the food source for these marine living organisms can contain toxic and hazardous substances bioaccumulated through uptake, for example, through the gills of fishes.

Bioaccumulation refers to the uptake and storage of a contaminant—generally, a toxic substance—by an organism in the food chain. Bioaccumulation in fish presents health problems to humans when these are ingested. Although uptake of a toxic substance is an important measure, we need to account for possible excretion of the substance and also metabolic transformation of the substance as factors that will reduce the uptake amount of the substance. Hence, storage becomes an important consideration. The literature shows that the term *bioconcentration* is quite often used in place of bioaccumulation. Bioconcentration is related to bioaccumulation, but is more specific in that it expressly refers to the uptake and storage of toxic substances from water. The term bioconcentration has also been used to indicate the condition when concentrations of a substance in a particular biota are higher than in the surrounding medium. For this discussion, we use the first meaning of the term

bioconcentration—uptake and storage of contaminants from water. When uptake and storage occur from water and also from food, the more general term bioaccumulation is used. Available evidence (Chiou, 2002) indicates that there is a correlation between bioaccumulation and the octanol–water coefficient k_{ow} (see Section 2.5.3 in Chapter 2) for many of the organic chemical contaminants reported in Section 2.3.2 in Chapter 2.

8.2.5 Contamination of Sediments

Historical discharge of contaminants and other toxic substances into the environment and the receiving waters from industrial development is a matter of record. This discharge became more significant during and after the industrial revolution at around the eighteenth century. Many of the discharges included such substances as heavy metals, PCBs, dioxins, polycyclic aromatic hydrocarbons, tributyltin, triphenyltin, etc., all of which are known toxicants. When these substances find their way into the ocean environment, some of them will dissolve. However, most of them will find their way onto the sea bottom through eventual sedimentation or attachment to suspended solids, a process that is considered as “dispersion” of noxious substances in the sea. Their effects on the human food chain can be deduced from Figure 8.1. This figure shows the food chain beginning with phytoplankton anchoring the lowest trophic level and progressing upward through the zooplankton, fish, and other marine aquatic species, and finally to humans. Mineral particles and organic matter settling in seawater can adsorb toxic and hazardous elements and compounds. The record shows that bioaccumulation of such elements and compounds as polychlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins/dibenzo furans/

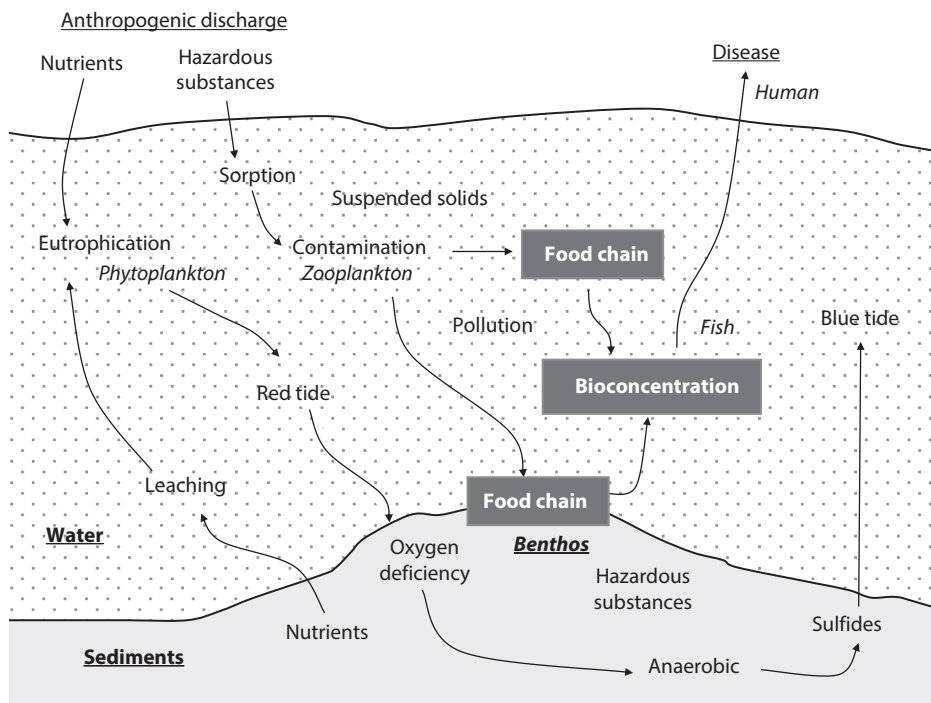


FIGURE 8.1

Various processes of dispersion and accumulation of substances in the sea.

dioxins, tributyltins (TBT), heavy metals, etc., in living organisms such as seaweed, sea turtles, shellfish, fish, etc. (Jensen et al., 2004; Gardner et al., 2003; Green and Knutzen, 2003). In some coastal areas and bays near urban centers, studies show that the sediments are heavily polluted with heavy metals and other hazardous substances (Jones and Turki, 1997; Kan-Atireklap et al., 1997; Fukue et al., 1999; Ohtsubo, 1999; Cobelo-García and Prego, 2003; Romano et al., 2004; Selvaraj et al., 2004). Makiya (1997) reports an intake of dioxins in the range of 60% to 70% from a one day ingestion of fish and shellfish. To eliminate the root of the human food chain problem requires one to decontaminate the contaminated sediments. This will eliminate the food source for the lower trophic levels. Until such is achieved, the danger of ingesting fish and shellfish that have bioaccumulated toxic and hazardous substances will always be present.

8.2.5.1 Some Case Studies of Sediment Contamination

Evidence of sediment contamination from land-based anthropogenic activities can be found in both marine coastal regions and also at the bottom of rivers, lakes, and other bodies of receiving waters. At a site in Germany, a lignite seam was found to accumulate aliphatic and aromatic chlorinated hydrocarbons downstream from a chemical plant (Dermietzel and Christoph, 2002). An initial fast desorption occurred from the outer surface of the sediment, followed by a slower diffusion-controlled released from the interior of the sediment.

Sediment samples from Lake Harwell, South Carolina, were taken at five places in 1998, to determine if natural attenuation of PCBs was occurring (Pakdeesusuk et al., 2005). From an analysis of the mole percentage of each congener of PCB and/or the total of *meta*-, *para*-, and *ortho*-chlorines and total chlorines per biphenyl, it was determined that solubilization and desorption were negligible according to mass balances since 1987. In situ dechlorination was occurring though after an initial rapid rate, followed by a slow rate since 1987. Microcosm studies supported the findings. There was a lack of information on organic matter and electron acceptors such as nitrate, sulfate, iron, and manganese, which made it difficult to predict optimal dechlorination conditions. To reduce the risk of bioaccumulation in fish, capping with fresh sediment may need to be increased.

In 1982, trichloroethene contamination in the groundwater was first detected at a Michigan National Priorities List site (An et al., 2004). Since then, samples were taken in 1991, 1992, 1994, 1995, and 1998, 100 m from the shore and, later, 3 m from the shore. Anaerobic degradation was indicated as the products of dichloroethene (DCE), vinyl chloride (VC), ethene, and methane were found. Analysis of the water within the lake sediments indicated natural attenuation.

At the Columbus Air Force Base, the fate and transport of jet fuel contaminants was evaluated in sixty sediment samples (Stapleton and Saylor, 1998). Using DNA probes, 10^7 to 10^8 organisms per gram of sediment were founds, compared with 10^4 to 10^6 organisms per gram by traditional methods. There was evidence of the degradation of BTEX and naphthalene, particularly after 5 to 7 days. Without nutrient addition, more than 40% of these ^{14}C -labeled compounds were mineralized in the sediments. Correlations of laboratory assay and field analyses are required, and thus, further field tests will be performed.

At the Dover Air Force Base, which was contaminated with chlorinated ethenes, low biomass levels ($<10^7$ bacteria per g sediment) were found (Davis et al., 2002). However, mineralization of vinyl chloride and *cis*-DCE was found to be occurring. The 16 S rRNA gene sequence indicated the presence of anaerobic microorganisms capable of anaerobic-halorespiration and iron reduction. It was concluded that microorganisms were the major mechanism for reductive and oxidative attenuation of the chlorinated ethenes.

A study of heavy metals in fish and shellfish was conducted in Port Philip Bay, Australia (Fabris et al., 1999), with the objective of determining the partitioning of heavy metals in dissolved and particulate species in the bay waters. Concentrations in the near-shore and estuarine areas were not higher than in the coastal marine waters despite a flushing time of 10 to 16 months in the bay. The mechanisms for partitioning were related to co-precipitation of iron and manganese oxyhydroxides with dissolved heavy metals. A strong correlation of iron with chromium, nickel, and zinc was seen in the particulates. Contrary to the metals, arsenic concentrations (as As(III)) increased in depth in the sediments and thus did not seem to be the result of anthropogenic activity. Near the surface layer of sediments, arsenic is oxidized to As(V) and leaves the sediments while Fe(III) can co-precipitate some of the arsenic and become trapped in the sediments.

8.2.5.2 Sediment Quality Criteria

Table 8.1 gives an indication of the different criteria or definitions structured by some countries for characterization of sediment quality. Although many countries and jurisdictions have established guidelines for water quality, and especially for drinking water, very few countries have set up sediment quality guidelines. The importance of available guidelines and criteria can be seen in the need to protect pollution of the sea from dumping and indiscriminate discharge of hazardous wastes—all of which will eventually find their way onto the sea bottom and ultimately into the human food chain. The 1954 International Convention on the Prevention of Pollution of the Sea by Oil, together with the 1958 Geneva Convention on the High Seas were the earliest formal attempts to regulate and control discharge of hazardous substances into the sea. These have been reinforced with more attention paid to discharge of various kinds of hazardous wastes, especially wastes originating from land sources.

TABLE 8.1

Outlines of Sediment Quality Guidelines

Country or Organization	Criterion or Standard for Guideline
USEPA	Screening concentrations for inorganic and organic contamination SQCoc: Draft sediment quality criteria; oc: organic carbon SQALoc: Sediment quality advisory levels ERL: Effects: range—low ERM: Effects: range—median AET-L: Apparent effects threshold—low AET-H: Apparent effects threshold—high TELs: Threshold effects levels PELs: Probable effects levels
U.S. National Oceanic and Atmospheric Administration (US-NOAA)	ERL: Effects: range—low ERM: Effects: range—median
Canada	ISQs: Interim sediment quality guideline PEL: Probable effects levels
Australia	ISQG-low: Interim sediment quality guidelines—low ISQG-high: Interim sediment quality guidelines—high
The Netherlands	Target value Intervention value

8.3 London Convention and Protocol

The London Convention and Protocol consists of the original London Convention 1972. This expanded the Oslo Convention for North-East Atlantic to cover marine waters worldwide, except for the inland waters of the various 80 states that were signatories to the convention. The Oslo Convention came into force in 1974 and the expanded Oslo Convention (to worldwide marine waters), which became the London Convention that came into force in 1975. With this Convention, elimination of future marine contamination from deliberate discharge of industrial and other wastes is to be achieved through regulation of dumping of wastes at sea. The wastes of concern included the original oily wastes from the 1954 and 1958 conventions, dredging spoils and wastes, and industrial wastes (i.e., land-based generated wastes).

Adoption of the *1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972*, 2006 (IMO, 2006) essentially strengthened the London Convention with the *Precautionary Approach* and the *Polluter Pays Principle*. With the precautionary approach, the burden of responsibility for determining whether a waste designated for ocean dumping is potentially hazardous is now borne by the originator of the waste. The annex in the *1996 Protocol*, "Assessment of wastes or other matter that may be considered for dumping" states that "acceptance of dumping under certain circumstances shall not remove the obligations under this Annex to make further attempts to reduce the necessity for dumping." The wastes or other matter that may be considered for dumping in accordance with the objectives of the protocol and the precautionary approach include

1. Dredged material
2. Sewage sludge
3. Fish waste, or material resulting from industrial fish processing operations
4. Vessels and platforms or other man-made structures at sea
5. Inert, inorganic geological material
6. Organic material of natural origin
7. Bulky items primarily comprising iron, steel, concrete, and similarly nonharmful materials for which the concern is physical impact, and limited to those circumstances where such wastes are generated at locations, such as small islands with isolated communities, having no practicable access to disposal options other than dumping

For dredged material and sewage sludge, the goal of waste management should be to identify and control the sources of contamination. This should be achieved through implementation of waste prevention strategies and requires collaboration between the relevant local and national agencies involved with the control of point and non-point sources of pollution. Until this objective is met, the problems of contaminated dredged material may be addressed using disposal management techniques at sea or on land.

Apparently, dredged material from the sea bottom has always occupied a special position under the convention—to a large extent because dredging is an important requirement and a necessity for keeping navigation routes open, and also for ports and harbors. The volume of dredged materials is considerable. However, there is incontrovertible

evidence to show that a significant portion of the dredged material ports, harbors, and coastal regions is highly polluted. This realization has now energized many countries to begin considering dredged sediments as contaminated–polluted and to insist that proper disposal of dredged materials be obtained.

8.4 Quality of Marine Sediments

Changes in seawater quality occur quickly over a very short period because of the effect of currents and dilutions. Although these effects may lead to low concentrations of contaminants in seawater, the record shows that contaminants can be (and will be) adsorbed onto suspended and sedimenting particles. This is especially true when the settling particles are of biological origin—since they have the capability for sorbing heavy metals. This sorption process is known as biosorption, and the sorbent is called a biosorbent. Generally speaking, a biosorbent refers to the capability of a biomass to sorb heavy metals from solutions. Of particular importance is the fact that biosorbents have a combination of functional groups such as those described in Section 2.6.2 and Figure 2.13 in Chapter 2 for organic chemicals. The combination of functional groups endows the combined group with significantly enhanced biosorbent capability to sorb various kinds of heavy metals—as opposed to monofunctional groups. Microalgae, for example, are well known biosorbents (Wilde and Benemann, 1993). The study reported by Inthorn et al. (2002) on 52 strains of microalgae and their capabilities for removal of Pb, Cd, and Hg from various solutions showed that both green algae and blue-green algae functioned well in removing the heavy metals. Although deposition of the contaminant-associated settling particles onto the seabed may serve to remove a proportion of the waterborne contaminants from seawater itself, the accumulation of contaminated particles in the sediment presents a significant problem for the benthic population.

Determination of the quality of marine sediments is required for at least two different purposes:

1. Preservation of the ecosystem. Knowledge of the types and nature of the contaminants in the sediments is essential, to enable one to structure the necessary measures for remediation and management of the quality of the sediments in conformance with established guidelines for sediment quality.
2. Safety assurance for the lower trophic levels in the marine-derived human food chain. Since phytoplankton and zooplankton are the first and second trophic levels, respectively, in this marine-derived human food chain, preservation of the quality of these trophic levels means eliminating or reducing the concentrations of contaminants in the sediments—inasmuch as these can be bioaccumulated or bioconcentrated by the organisms that occupy these trophic levels. The record shows that organisms such as benthos, fish, and mammals have been more or less contaminated through the food chain and through bioconcentration (Kavun et al., 2002; Do Amaral et al., 2005; Moraga et al., 2002). Although guidelines have yet to be established, it is evident that in the absence of detailed records and tests, specification of allowable concentrations will likely be severely conservative, in the interest of eliminating health threats to the human population.

8.4.1 Standards and Guidelines

8.4.1.1 Guidelines

Guidelines have been established in some countries for the purpose of evaluating sediments contaminated with toxic chemicals. The aim of these guidelines is to limit the concentration of toxic chemicals using various criteria—such as those shown in Table 8.1. As with all criteria based on observed effects on human health, differences exist between the guidelines used by the various countries. To a large extent, this is because of the different means for determination of the effective levels, and also in the perception of what constitutes an acceptable risk. For example, since apparent effects threshold (AET) values are essentially determined by a single result (i.e., the highest nontoxic sample) as opposed to the entire distribution of results (e.g., as with threshold effect levels TEL or probable effects level PEL), the final AET values used by the regulatory agency may vary substantially depending on the outcome of their analyses. A considerable amount of work remains to be done in this area. The use of interim values as preliminary values at the present time recognizes the fact that additional technical work on individual AET values together with reliability analyses and discussions with other involved agencies are required.

8.4.1.2 Chemicals

The guidelines issued by the various countries and agencies for environmental quality for sediments include trace and heavy metals and different types of organic chemical compounds. There is no definitive common listing of elements and chemicals between the agencies and countries, and no common agreement as to criteria used to evaluate and target the listed elements and chemicals. An example of sediment quality guidelines can be seen in the interim sediment quality guidelines (ISQG) and probable effect level (PEL) values given in the 2003 Canadian Environmental Quality guidelines (Table 8.2). The U.S. National Oceanic and Atmospheric Administration (NOAA), meanwhile, has established sediment quality guidelines that contain 9 trace metals, 13 individual polycyclic aromatic hydrocarbons (PAHs), 3 classes of PAHs, and 3 classes of chlorinated organic hydrocarbons. As an example, for lead the ERL (effects: range—low) is 46.7 ppm dry weight, ERM (effects: range—medium) is 218 ppm dry weight, and the incidence of effects is 90.2% when the concentration is higher than the ERM. When concentration exceeded the ERM values, the incidence of adverse effects increased from 60% to 90% for most trace metals and 80% to 100% for most organics. However, the reliability of the ERMs for nickel, mercury, DDE, total DDTs, and total PCBs are much lower than those for other substances.

8.4.2 Background and Bioconcentration

8.4.2.1 Background Concentration

As discussed in Section 2.3 in Chapter 2, the elements shown in Table 8.3 are known to exist naturally in the environment, generally in the form of compounds and minerals such as sodium chloride, copper carbonate (azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, and malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$), magnesite (for magnesium), and in food sources such as spinach and nuts (for magnesium). Not all the elements shown are toxic or totally harmful to human health. In the listing shown in Table 8.3, both lead (Pb) and cadmium (Cd) are known as toxic elements and can be safely identified as contaminants. There are no acceptable daily intake values for these. The rest of the elements shown in Table 8.3 are known

TABLE 8.2

Environmental Quality Guidelines for Sediments

Substance	Fresh Sediments		Marine Sediments	
	ISQG (µg/kg)	PEL (µg/kg)	ISQG (µg/kg)	PEL (µg/kg)
Arsenic	5900	17,000	7240	41,600
Cadmium	600	3500	700	4200
Chlordane	4.5	8.87	2.26	4.79
Chromium	37,300	90,000	52,300	160,000
Copper	35,700	197,000	18,700	108,000
DDD (2,2-bis(<i>p</i> -chlorophenyl)-1,1-dichloroethane; dichloro diphenyl dichloroethane)	3.54	8.51	1.22	7.81
DDE (1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl)-ethene; diphenyl dichloroethylene)	1.42	6.75	2.07	3.74
DDT (2,2-bis(<i>p</i> -chlorophenyl)-1,1,1-trichloroethane; dichloro diphenyl trichloroethane)	1.19	4.77	1.19	4.77
Dieldrin	2.85	6.67	0.71	4.3
Endrin	2.67	62.4	2.67	62.4
Heptachlor (heptachlor epoxide)	0.6	2.74	0.6	2.74
Lead	35,000	91,300	30,200	112,000
Lindane (hexachlorocyclohexane)	0.94	1.38	0.32	0.99
Mercury	170	486	130	700
PCBs	34.1	277	21.5	189
Arochlor 1254	60 ^a	340 ^a	63.3 ^a	709 ^a
Polychlorinated dibenzo- <i>p</i> -dioxins/ dibenzo furans (PCDD/Fs)	0.85 ng-TEQ/ kgdw	21.5 ng-TEQ/ kgdw	0.85 ng-TEQ/ kgdw	21.5 ng-TEQ/ kgdw
Acenaphthene	6.71	88.9	6.71	88.9
Acenaphthylene	5.87	128	5.87	128
Anthracene	46.9	245	46.9	245
Benzo(<i>a</i>)anthracene	31.7	385	74.8	693
Benzo(<i>a</i>)pyrene	31.9	782	88.8	763
Chrysene	57.1	862	108	846
Dibenzo(<i>a,h</i>)anthracene	6.22	135	6.22	135
Fluoranthene	111	2355	113	1494
Fluorene	21.2	144	21.2	144
2-Methylnaphthalene	20.2	201	20.2	201
Naphthalene	34.6	391	34.6	391
Phenanthrene	41.9	515	86.7	544
Pyrene	53	875	153	1398
Toxaphene	0.1 ^b		0.1 ^b	
Zinc	123,000	315,000	124,000	271,000

Source: Adapted from Canadian Environmental Quality Guidelines. Available at <http://st-ts.ccme.ca/>, 2003.

^a Sediment quality guideline for Arochlor 1254: provisional; 1% TOC; adoption of severe effect level of 34 µg/g TOC from Ontario (Persaud et al., 1993).

^b Sediment quality guideline for toxaphene: 1% TOC; adoption of the chronic sediment quality criterion of 0.01 µg/g TOC of the New York State Department of Environmental Conservation (NYSDEC, 1994).

to be essential elements, and the lack of any of these can be harmful to human health. However, ingestion of concentrations of these essential elements in excess of acceptable daily intake (ADI) can be harmful to human health. Table 8.3 shows some of the effects to human health for some of the essential elements when ingested concentrations are deficient (*lack of*) or in excess (*toxic*). All the harmful effects shown in the last two columns are not meant to be totally definitive. They should be considered as *potential effects* since very few totally controlled studies have been conducted to fully isolate the noted *harmful effects*.

The record shows that background concentration of many of these elements and several other known toxicants exist in the environment and especially in the coastal marine environment and sediments—naturally derived and more likely due to anthropogenic

TABLE 8.3

Average Daily Intake of Some Inorganics in Typical North American Adults Compared with Typical Dosages in a Common Dietary Supplement

Element	Daily Intake (mg/day) ^a		Possible Effects from Deficiency ^b	Possible Toxic Effects ^b
	Typical Average Value for Adult	Typical Dosage in Dietary Pills		
Potassium	3750	32	Hypokalemia, muscle weakness, abnormal heart rhythms	Diarrhea, nephrotoxicity, hyperkalemia, muscle fatigue, cardiac arrhythmia
Calcium	420	530	Loss of calcium from bone, muscle spasms, leg cramps	Calcium deposition in soft tissue, kidney stones
Sodium	5660		Muscle cramps	High blood pressure
Phosphorous	1500	400	Weakness, rickets, bone pain	Kidney/liver damage
Magnesium	375	100	Electrolyte imbalance of Ca and K	Muscle weakness
Zinc	13	22.5	Reduced appetite and growth	Irritability, nausea
Iron	19.5	12	Anemia	Gastrointestinal irritation
Chromium	0.115	0.027	Atherosclerosis	Tubular necrosis of the kidney
Fluoride	3		Possible osteoporosis	Dental fluorosis, possible osteosclerosis
Copper	1.7	2	Anemia, loss of pigment, reduced growth, loss of arterial elasticity	Disorder of copper metabolism, hepatic cirrhosis

Source: Adapted from Yong, R.N., Waste disposal, regulatory policy and potential health threats. In S.P. Bentley (ed.), *Engineering Geology of Waste Disposal*, Geological Society of London Special Publication No. 11, pp. 325–340, 1996.

^a Information from Lappenbusch, W.L., *Contaminated Waste Sites, Property and Your Health*, Lappenbusch Environmental Health, Virginia, 360 pp., 1988.

^b Deficiency and toxicity effects are *probable effects* and are very much dependent on initial health, diet, local environment, cultural attitudes, body features, physiology, etc.

discharges. Exposure to concentrations of these elements and toxicants that are higher than the probable effects level (PEL) or effects: range—median (ERM) raises questions relating to safety and risks to human health. Since the PEL and ERM types of criteria and guidelines have been provided for determination of the direct toxic effects on aquatic life, the potential risk to human health resulting from bioconcentration (of toxicants) have yet to be fully evaluated. Excessive bioconcentration in marine species constituting seafood for humans will pose problems to human health, and may well result in chronic or acute poisoning. The Minamata disease was an unhappy happening that originated from methyl mercury contamination of fish. This is discussed in greater detail in a later section.

Target concentrations reflecting maximum allowable background values for sediments are necessary to provide the necessary protection for both aquatic species and human health. These have yet to be set because (a) data on present backgrounds are not available, (b) the links between these and bioconcentration in aquatic species and human health are also not available, and (c) the highly variable nature of background concentrations of a substance. The variability and changing nature of background concentrations are functions of many factors, such as sediment characteristics, local geology, mineralogical aspects of soils near the deposited place, and discharges from land-based industries. Isolating discharges from land-based industries allows one to consider the deviation of the background concentrations with sediment type as an indication of a range of tolerable intake.

8.4.3 Sulfide and Its Effects on Marine Life

8.4.3.1 Toxic Sulfide

An excess of sedimentary organic matter might lead to high bacterial sulfate reduction rates, oxygen depletion, and the subsequent release of toxic hydrogen sulfide, especially during the warm season (Magni et al., 2008). The effects of eutrophication on marine benthic communities have been well documented (Pearson and Rosenberg, 1978). A significant reduction in survival time is obtained when individual macrobenthic species are subjected to hypoxia and sulfidic conditions (Rosenberg et al., 2001; Gamenick et al., 1996). In general, sulfide combined with hypoxia is more toxic to benthic animals than hypoxia alone (Diaz and Rosenberg, 1995). Effects on infaunal benthos are also more acute than on epifauna because of their frequent burrowing activities and, hence, exposure to severe hypoxia and sulfidic conditions (Hagerman, 1998).

In the Seto Inland Sea, in Japan, the qualities of seawater and sediment were degrading up to 1970. Since the Act on Special Measures Concerning Conservation of the Environment of the Seto Inland Sea was issued in 1973, the quality of seawater has been considerably improved. However, to date, organic matter and nutrients have accumulated in the sediments, resulting in the production of organic matter in the sediments, and toxic hydrogen sulfide. In Japan, this situation is similar for other sea areas including ports and harbors.

For example, the sulfide concentrations for the Harima-nada sediments are plotted against ignition loss (Figure 8.2). The original data were obtained by the Ministry of Land, Infrastructure, Transport, and Tourism (MLITT). In Figure 8.2, solid circles and squares show sandy sediments, and the triangles indicate silt–clay sediments. The figures show no significant relationship between sulfide content and ignition loss because of the varied nature of the organic content and sediment age.

The details are explained as follows: New organic sediments are possible under aerobic conditions because they initially contact dissolved oxygen. An excess of sedimentary

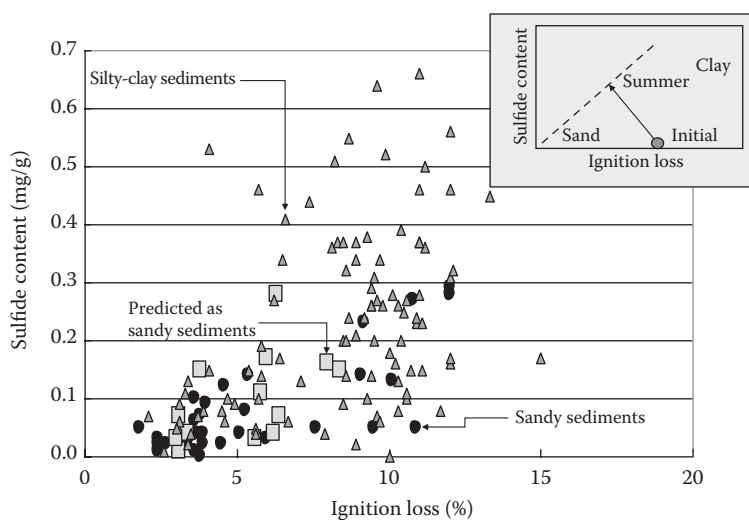


FIGURE 8.2

Sulfide content versus ignition loss for the Harima-nada sediments. (Data from Ministry of Land, Infrastructure, Transport and Tourism, Japan. Available at <http://www.pa.cgr.mlit.go.jp/chiki/suishitu/download/input.htm>.)

organic matter leads to high bacterial sulfate reduction rates, oxygen depletion, and subsequent release of toxic hydrogen sulfide from summer to autumn (Magni et al., 2008; Rosenberg et al., 2001). At this stage, the ignition loss tends to decrease and the sulfide content will increase (Yamamoto et al., 1997). The trend is indicated by the arrow in Figure 8.2.

The concentration of the sulfide in sediments depends on many factors, such as the type of sediment, organic content, pH, redox potential, dissolved oxygen, water and sediment temperature, etc. The physical and chemical properties of Seto Inland Sea sediments, reported by Yamamoto et al. (1997), are shown in Figure 8.3 plotted in terms of redox

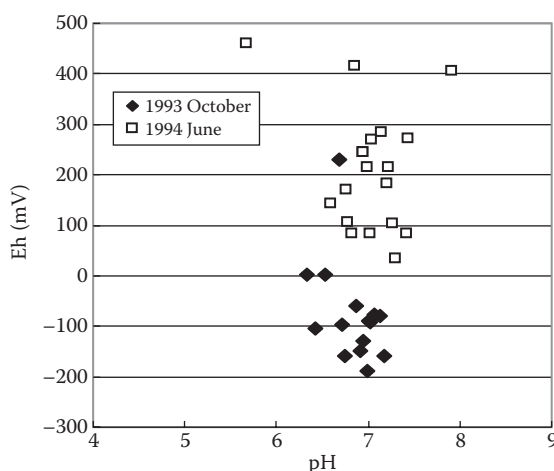
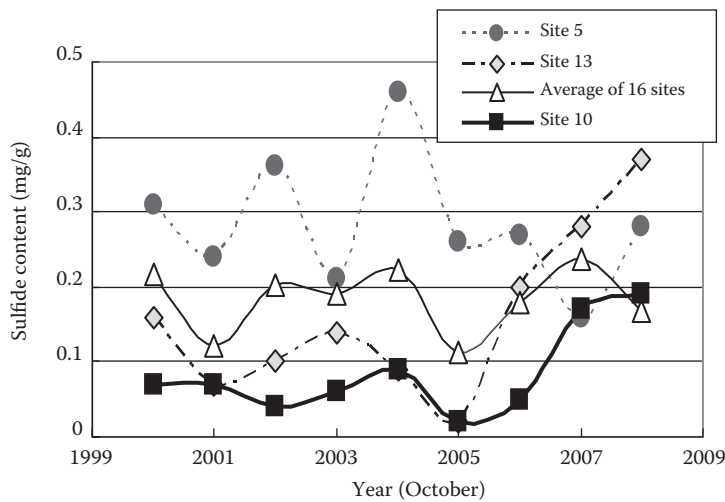


FIGURE 8.3

Comparison between redox potentials in October 1993 and June 1994. (Data from Yamamoto, T. et al., *Journal of the Faculty of Applied Biological Science, Hiroshima University*, 36: 43–49, 1997.)

**FIGURE 8.4**

Annual changes in sulfide content for the Harima-nada sediments. (Data from Ministry of Land, Infrastructure, Transport and Tourism, Japan. Available at <http://www.pa.cgr.mlit.go.jp/chiki/suishitu/download/input.htm>.)

potential versus pH values for the period between October 1993 and June 1994 for various sites in the Seto Inland Sea.

Figure 8.4 shows the changes in sulfide concentration obtained from Harima-nada in the month of October between 2000 and 2008. The concentration and its fluctuation are unpredictable. The data for site 10 were obtained from fine sand, which had a relatively low level (less than 0.1 mg/g) of sulfide (between 2000 and 2006) and a rapid increase to 0.2 mg/g after that.

8.4.3.2 Guidelines for Sulfide for Surface Water and Sediments

The Quality Criteria for Water (USEPA, 1976) concluded that the hazard from hydrogen sulfide to aquatic life is often localized and transient. Available data indicate that water containing concentrations of 2.0 µg/L undissociated H₂S would not be hazardous to most fish and other aquatic wild life, but concentrations in excess of 2.0 µg/L would constitute a long-term hazard.

Hydrogen sulfide has an adverse impact on aquatic life, especially to crustacea. The standard level provided by the Japanese sediment guideline for fish is 0.2 mg/g. Herein, the sulfide content is defined by the percentage of sulfide/dry weight of sediment. If the pore space of sand is the habitat of marine life, the conventional definition of sulfide should be modified for an aestivating fish such as sand lance.

The comparison between both the guidelines for water and sediments mentioned above indicates that the value of the criterion for sediments will be somewhat higher than that of water, even if the difference between the densities of sediments and water is considered.

8.4.4 Connecting Problems of Geoenvironment and Bioenvironment

It is well understood that the marine geoenvironment is directly connected to the bioenvironment through the food chain. Eutrophication of marine geoenvironment often results

from the blooming of phytoplankton—with the latter event (phytoplankton blooming) being the result of human activities.

Guidelines and/or criteria are necessary requirements in addressing environmental problems. It is important to realize that in respect to the bioenvironment, environmental change is often irreversible, with no prospect for recovery or rehabilitation. A specific example of adverse effects of eutrophication most likely responsible for extinction of marine life in the bioenvironment is shown below.

Japanese sand lance (*Ammodytes personatus*), also called sand eel, is one of about 18 species of marine fish of the family *Ammodytidae* (order Perciformes). Sand lances are slim, elongated, usually silver fish that are especially abundant in northern seas. Individuals range from about 8 to 20 cm in length. They have a forked tail, a long head, a long dorsal fin, and peculiar skin folds on the lower sides, as shown in Figure 8.5. They live in schools, often under the sand below the surf (aestivation) in summer, which means that they can be affected by sediment quality. They lay their eggs in sand, and the eggs hatch in winter. The fry become a target of fishery for about 1 month in the spring.

The haul of sand lance in the Seto Inland Sea has continued to decrease since 1970. This is considered to be mainly due to the decrease in sand beach and tideland. Sand was harvested from the bottom of the Seto Inland Sea for use as aggregates for concrete. This also decreased the habitat for sand lance and their egg-laying sites. According to a report by the Ministry of Economy, Trade, and Industry and the Ministry of Land, Infrastructure, Transport, and Tourism, about 10,000 to 20,000 m of sand were harvested annually from the bottom of the Seto Inland Sea from 1971 to 2004. During this period, a large coastal area was reclaimed from the sea, as shown, for example, by the reclamation of 16 km of coast in the Okayama and Kagawa Prefecture facing the middle of Seto Inland Sea. This has resulted in the loss of sand lance habitat. The haul of sand lance, which has not recovered since harvesting of sand at the bottom was prohibited, continues to decrease, with large fluctuations. There has been no explanation for this phenomenon. Because of anthropological activities, various kinds of solutes and solids have been discharged into the Seto Inland Sea. In particular, organic matter has caused eutrophication. The organic matter discharged from land has spread over the areas of the Seto Inland Sea, except for straits with a strong current. In this situation, the clean sand of the sea bottom has changed to sand with clay or silt fractions and organic matter.

The sedimentary rate in the Seto Inland Sea determined using the ^{210}Pb method varies between 0.11 and 1.13 g/cm² (Hoshika and Shiozawa, 1987). The sedimentary rate is

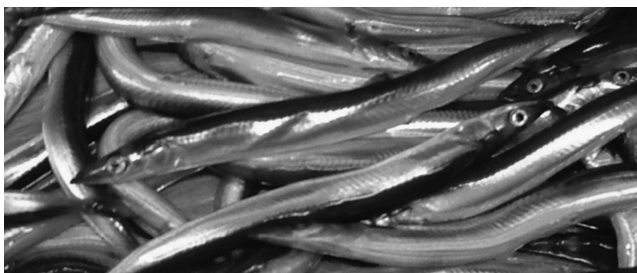


FIGURE 8.5

Japanese sand lance.

relatively high in the central parts of Osaka Bay, Harima-nada, and Hiuchi-nada. These areas are also the habitat of sand lance. Water quality might be one of the governing factors for the health of the population of sand lance. This area had the worst water quality around 1970. Although water quality has been improved since 1970, red tide still occurs. The biodegradation of dead bodies of phytoplankton accumulating on the bottom and penetrating into the pore spaces of sediment renders the sediment anoxic. This creates a critical condition for sand lance because they must aestivate in the sand during the summer.

The fishery and haul of sand lance are now strictly controlled by the local governments. Even under management and control, the population and haul of sand lance are still decreasing, as shown in Figure 8.6. The data of another prefecture, Hyogo Prefecture, showed a decrease of 76% in the haul of sand lance and of 28% in the haul of other fish (Kobe Newspaper, 2010, 5.10). However, no explanation could account for the abrupt drop of the haul. Note that sand lance is a key member of the food chain in the Seto Inland Sea. If sand lance disappears from the sea area, the kinds of fish will be completely changed. It will also damage the food culture in the anthrosphere through biosphere and geoenvironment, starting from the anthrosphere. For fishery resources in the Seto Inland Sea to recover, it is necessary to increase the population of sand lance. The detailed study showed that the decrease in population of sand lance in the Seto Inland Sea was due to the sulfide concentration in the pore mud water of sandy sediments (Fukue et al., 2012a), where the pore mud water means the organic mud water in sandy sediments. This was examined by converting the sulfide concentration of sediments to that of the pore mud water of the sediments. Figure 8.7 shows the conversion of sulfide concentration from sediment to pore mud water. The figure shows that aestivating sand lance will be killed or damaged by the toxic sulfide in summer to autumn because the concentration of converted sulfide content (in pore mud water) is considerably higher than the Japanese criteria for fish. To counter this problem, the resuspension technique developed and described by Fukue et al. (2012b) in Section 8.5.4 can be applied.

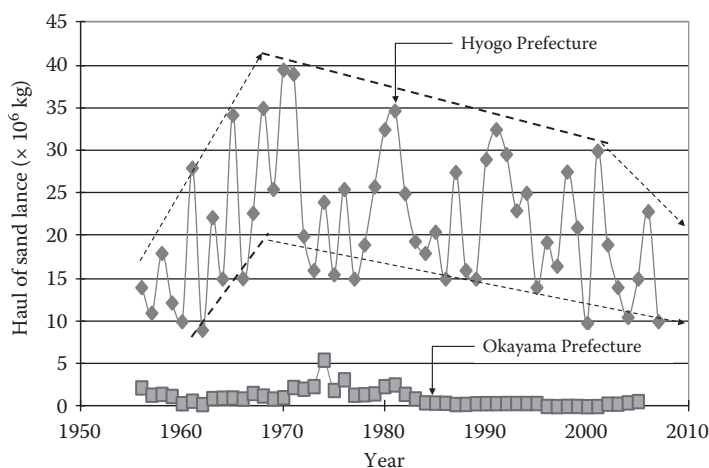
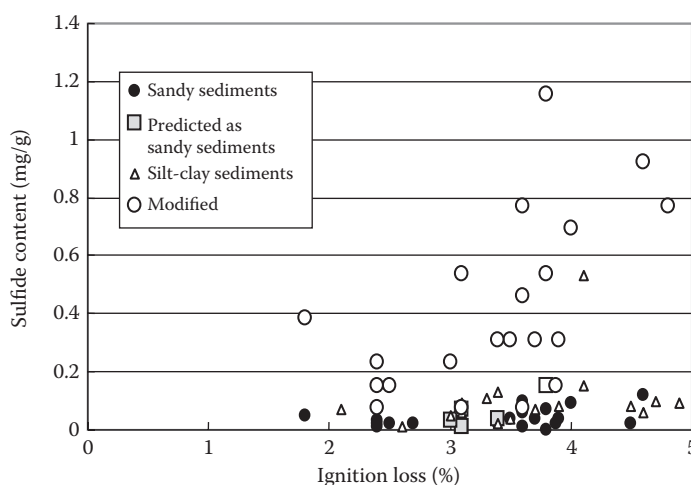


FIGURE 8.6

Fluctuation of haul of sand lance as published by Okayama and Hyogo Prefectures.

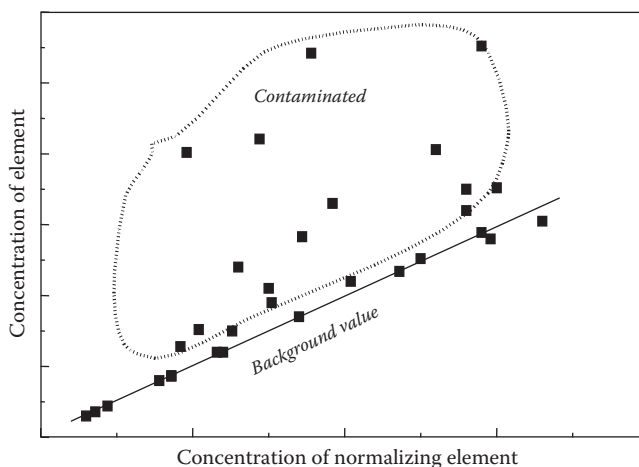
**FIGURE 8.7**

Conversion of sulfide concentrations from sandy sediments to the pore mud water. (Data from Fukue, M. et al., Evaluation of adverse effects of anoxic sediments on aestivating sand lance [*Ammodytes personatus*], Contaminated Sediments, 5th Volume: Restoration of Aquatic Environment, STP 1554, ASTM, pp. 159–174, 2012a.)

8.4.5 Heavy Metals

Many heavy metals are trace metals. These are metals that exist in extremely small quantities and are almost at the molecular level. They reside in, or are present in, animal and plant cells and tissue and are a necessary part of good nutrition, as shown, for example, in Table 8.3. Because excess intake of heavy metals may cause damage to human health, it is necessary to take into consideration the background concentrations in sediments in structuring safe limits for ingestion of aquatic species. We define the *background concentrations* (values) as the concentrations of substances under natural condition without any significant input or effect from human activities.

Background values of metals were found to agree well with average values for gneisses rocks (Carral et al., 1995). However, the background values for copper, zinc, lead, and cobalt do not necessarily agree with previously obtained values. Various techniques have been used to reduce data scattering and to allow for a more accurate statement of background values. Fukue et al. (1999) used carbonates as the normalizing substance in their measurements. Cobelo-García and Prego (2003) obtained the baseline relationships between the concentration of iron and contaminant, whereas Din (1992), Cortesão and Vale (1995), and Santschi et al. (2001) used aluminum to normalize heavy metals. Titan has also been used as a normalizing element. Fukue et al. (2006) calculated the specific surface area of sediment particles assuming them to be spheres and that the specific surface areas will be related to the background values of heavy metals. This is consistent with the thesis that the amount of metals sorbed onto particles is to a large extent dependent on the particle size. The results reported by Fukue et al. (2006) using these normalization characteristics were found to be reasonable. Santschi et al. (2001) reported that concentrations and fluxes of most trace metals found in sediment cores recovered from Mississippi River delta, Galveston Bay, and Tampa Bay in the United States, when normalized to Al, were typical for uncontaminated Gulf Coast sediments. Similar results can be cited with other normalizing elements. The concept for the normalization technique is shown in Figure 8.8. The drawback of these methods is

**FIGURE 8.8**

Concept of a normalization technique for obtaining a background value.

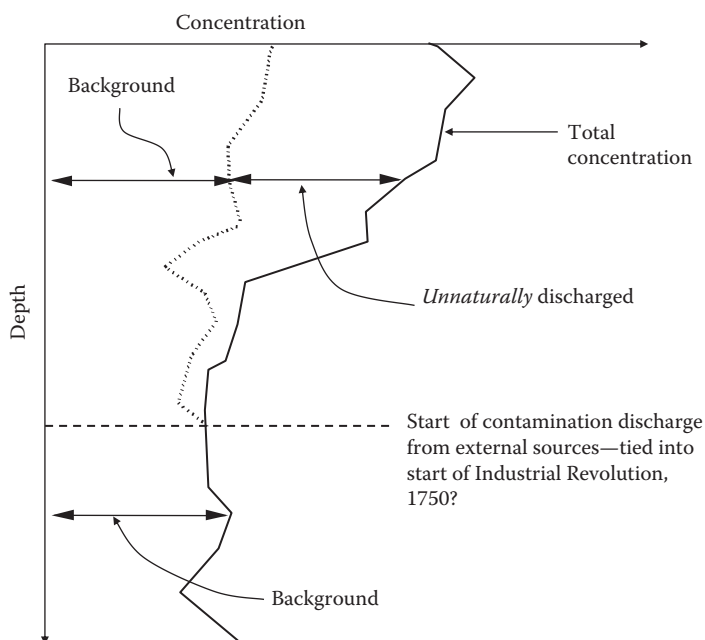
that noncontaminated sediment samples are required in order that relationships between normalized substances and the objective concentrations can be constructed. If the depth and extent of sampling are insufficient, normalization characteristics cannot be obtained.

Many contaminants in water are sorbed on sorbates that may be inorganic and organic particulate materials. These particulates, together with the sorbed contaminants eventually settle to form sediments on the seabed. The properties and surface characteristics of the soil solids that comprise the particulate materials have been discussed briefly in Sections 2.4 and 2.5 in Chapter 2 in respect to contaminant–particle interactions. Some of the more pertinent surface activities include such parameters as charge density, CEC, specific surface area, the equilibrium (natural) concentration of contaminants, etc. A more detailed explanation of all of these surface properties and their interactions with contaminants can be found in Yong (2001). The background concentration values of sediments will be directly related to the inherent properties and characteristics of the constituents.

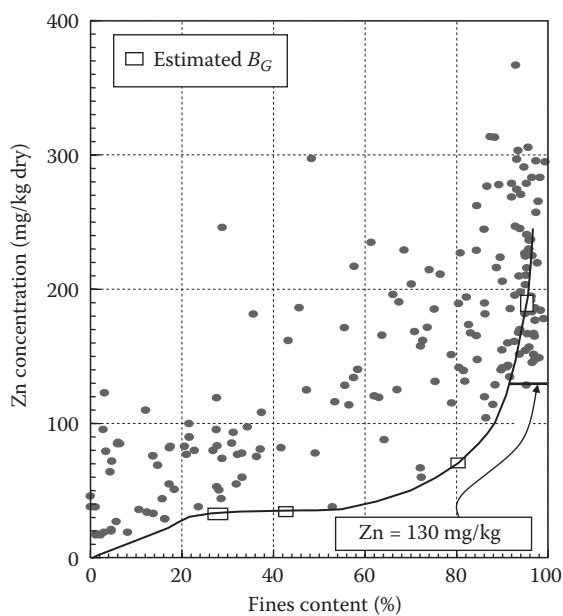
There are two concepts of background concentration: (1) concentration in the mother rocks and (2) mother rock concentrations together with sorbed substances under natural conditions during transport process and deposition. The second concept is more appropriate when background concentrations are used to evaluate the risk to human health, especially when bioconcentration is factored into risk evaluation.

8.4.5.1 Profile of Heavy Metal Concentration

Most profiles of metal concentration for sediments show trends similar to those portrayed in Figure 8.9. The total concentration consists of the background and contributions from the discharges originating from land-based industries. Beginning from the bottom of the profile shown in Figure 8.9, the total concentration consists only of the background values. As one progresses upward, toward the top of the sediment, the total concentration begins to include contaminant discharge contributions from land-based industries. The beginning point shown in the diagram assumes that this can be tied to the start of the Industrial Revolution in about 1750. The total concentration increases as one progresses upward in the sediment, indicating increased discharge of contaminants into the marine environment. As an example, Figure 8.10 shows zinc (Zn) concentrations in various sediments

**FIGURE 8.9**

Concept of background value of metal concentrations in sediments. The *unnaturally* discharged concentrations are likely due to discharges from land-based industries and land-based non-point contamination sources.

**FIGURE 8.10**

Deviation of zinc concentration in various sediments. B_G , background concentration.

obtained from coastal regions in Japan. Because the sediment samples were obtained from various depths in the total sediment layer, the concentration levels were not uniform, and some of the shallower samples were contaminated. The background concentrations can be obtained using a normalizing factor. The procedure adopted for the zinc concentrations shown in Figure 8.10 was to use the fines content as the normalizing factor. The fines content refers to the fine particle sizes in the sediment, generally clay and silt, and is defined as the content of clay and silt fractions <0.075 mm. The line representing the approximate lower limit shown in Figure 8.10 can be defined as the background zinc concentrations for the sediments. The detailed theoretical approach to obtain the background line has been reported by Fukue et al. (2006).

Similar relationships with lead (Pb) and copper (Cu) have been obtained, as shown in Figures 8.11 and 8.12. Fukue et al. (2006) have used relationships between calculated specific surface area and fine content and also limitation of sorption of fine particles under a relatively low equilibrium concentration. This is due to the limited concentrations of the substance in nature. The background values for Zn, Pb, and Cu shown in the figures are lower than the values presented as the ISQGs in Table 8.2. When the background concentration B_G is known, the degree of contamination, P_d will be obtained as

$$P_d = (C - B_G)/B_G, \quad (8.1)$$

where C is the current concentration of specific substance or element (Fukue et al., 1999).

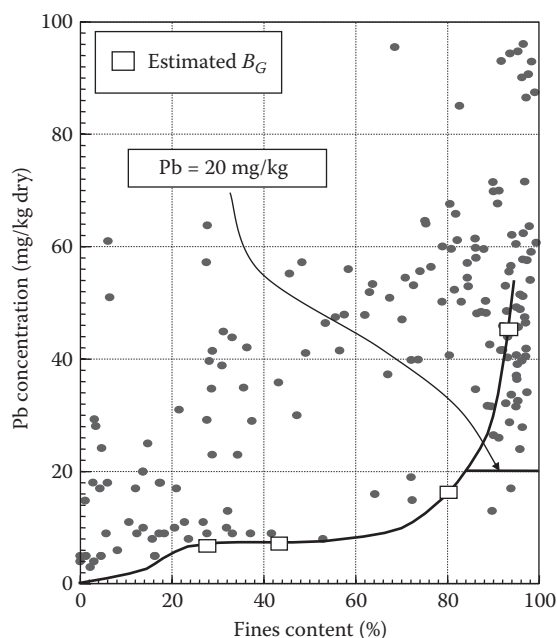


FIGURE 8.11
Deviation of lead (Pb) concentration in various sediments.

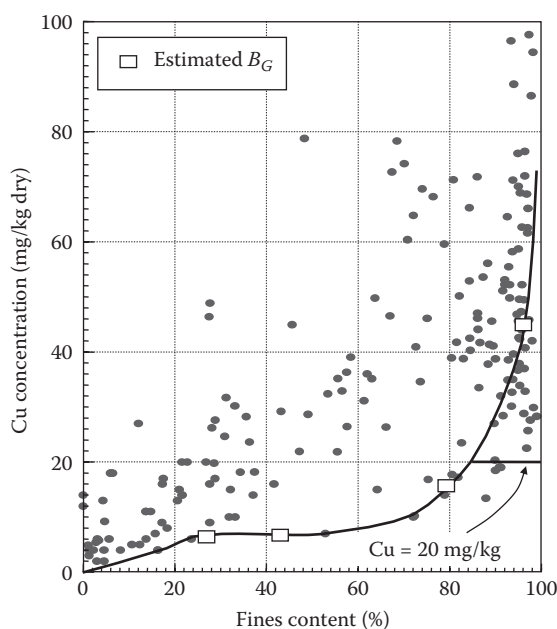


FIGURE 8.12
Deviation of copper (Cu) concentration in various sediments.

As stated in the previous section and shown in Table 8.3, there is a risk that the intake of hazardous substances beyond the PEL values may be harmful to human health.

8.4.5.2 Minamata Disease

In the 1950s, a significant number of people succumbed to a disease, later identified as Minamata disease, that was traced to ingestion of poisoned fish and shellfish in Minamata Bay in Kyushu Island (Japan). Measurements of methylmercury chloride showed very high concentrations, up to approximately 50 ppm in fish and 85 ppm in shellfish from the contaminated areas in Minamata Bay. The more than 100 people that ingested the contaminated fish and shellfish showed initial symptoms of numbness of the limbs and areas around the mouth, sensory disturbance, lack of coordination, weakness and tremor, speech, and audiovisual difficulties. Progressive worsening of all of these with time led to general paralysis, convulsions, brain damage, and death. Traces of mercury poisoning were also found in animals living around the bay. Many of these animals also died. More details of this terrible demonstration of the impact of polluted sediments can be found in <http://www.env.go.jp/chemi/minamata.html> (Ministry of Environment, Japan, 2014) and <http://unu.edu/publications/books/filter/publisher=42&ref=/unupbooks/uu35je/uu35ie0c.htm/> (United Nation University, 2014).

It is useful to note that although Minamata disease is well documented and serves as a dramatic demonstration of the chain of effects originating from polluted sediments, discovery and diagnosis of the health problems and source of the health problem took some considerable time, effort, and tracking. There are undoubtedly countless cases of poisoned

aquatic animals in the first level of the food chain serving the human population, and unreported or undiagnosed (underdiagnosed?) poisoning of the affected population.

8.4.6 Organic Chemical Contaminants

8.4.6.1 Organotins

Other than from direct, and indirect discharge of land-based industrial waste contaminants and leachates from waste piles, some hazardous substances enter the marine environment through direct contact and use, such as organotins used as antifoulants for ships, quays, buoys, etc. Organotins are compounds of tributyltin (TBT). They are highly toxic chemicals comprising of tin combined with organic molecules. They are used not only as antifoulants, but also as wood preservatives, slimicides, and biocides. In the context of a coastal marine environment, organotins are used essentially as biocides to prevent the buildup of barnacles and algae. They are self-polishing co-polymers and generally have a service life between 3 to 5 years—meaning that they have to be reapplied to the marine structures at the end of their service lives. They are poisonous to marine life including whales, dolphins, seals, fish, and sea birds. Linley-Adams (1999) reports that concentrations in bottlenose dolphin liver from the U.S. Atlantic and Gulf Coasts found in the period between 1989 and 1994 ranged from 110 to 11340 ng/g wet weight. He further reports on the presence of organotins in sea otters in California waters and harbor porpoises in Turkish coastal waters in the Black Sea. TBT has been reported to result in the development of imposex, a pseudo-hermaphroditic condition in female gastropods (snails) at ng/L levels of concentration (Horiguchi et al., 1994). The U.K. guideline provides 0.002 µg/L of TBT for sea water quality, and 0.008 µg/L for seawater quality for triphenyltin (TPT) guideline. The Canadian environmental guideline for seawater quality is 0.001 µg/L for TBT.

TBT can enter the marine environment through (a) leaching of the antifoulant paints, (b) during application of TBT as an antifoulant, and (c) when the paint is removed from the pieces of equipment painted with the antifoulant. The degradation of TBT is relatively slow in sediments. The half-life of TBT in sediments has been reported to be approximately 2.5 years (de Mora et al., 1995), whereas it is only a week or so in marine waters (Seligman et al., 1988). Since 1990, their use have been banned for all vessels in certain countries (Japan, Australia, and New Zealand), and in some other countries, their use have been restricted to vessels with lengths greater than 25 m. The IMO (International Maritime Organisation) in 2001 adopted the International Convention on the Control of Harmful Anti-Fouling Systems—a convention that prohibits the use of harmful organotins as antifoulants. The Convention came into effect at the beginning of 2003 for all ships and was expanded to include all floating platforms, floating units, floating production and storage units at the beginning of 2008.

8.4.6.2 Chlorinated Organic Microcontaminants

Chlorinated organic microcontaminants have been accumulating in sediments and sea animals for many years. These contaminants are highly toxic and direct or indirect ingestion of these will be life-threatening. The particular group of chemicals known as CDDs (chlorinated dibenzo-*p*-dioxins) is perhaps the one that has gained the most attention and concern, since it is known to enter the geoenvironment and into the marine environment from many sources. Of the more than 70 chemicals that make up the CDDs, the one known

as 2,3,7,8-TCDD or more simply as TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) is considered to be one of the most toxic. The WHO (World Health Organization) has designated this as a known human carcinogen. In general, CDDs find their way into the land and marine environment as waste discharges from some processes that employ chlorine, such as paper mills that use chlorine bleaching processes (see Section 7.4 in Chapter 7), manufacturing of chlorinated organic intermediates, and water treatment plants. Generically, CDDs are known as dioxins. They also occur naturally and are discharged when materials containing such substances are degraded and combusted, as in forest fires. Dioxins released as atmospheric emissions from forest fires, combustion of fossil fuels, and from incinerators serving industrial plants and municipal and hazardous waste facilities will subsequently be deposited onto land and water bodies at points distant from their sources. In water bodies, they will be attached to the suspended and sedimenting particles and will form part of the sediment. A limit of 3×10^{-5} µg of 2,3,7,8-TCDD per liter of drinking water (30 picograms per liter; i.e., 30 pg/L) has been set by the EPA.

Dioxins generally occur in the environment with chlorinated dibenzofurans (popularly known as furans). They are ubiquitous, and have been found in all media: air, water, soil, sediments, animals, and food (Johnson, 1992). They fall into the class of POPs (persistent organic pollutants) and are bioaccumulative. Since they have a strong affinity for soil and sediment particles, their presence in the media containing these POPs pose significant health threats. To determine the risks resulting from exposure to these POPs, many environmental regulatory bodies, such as the U.S. Environmental Protection Agency (USEPA) have adopted an evaluation technique that uses *toxicity equivalency factors* (TEFs). This technique compares the toxicity of designated dioxins and furans to that of the most toxic dioxin, i.e., the 2,3,7,8-TCDD. With this technique, the TCDD establishes the height of the toxicity bar and is given a TEF value of 1, and all other organic chemical compounds being scrutinized as assigned TEF values according how toxic they are perceived to be. Determination of toxicity intake (or uptake) of a particular organic chemical contaminant requires the use of *toxicity equivalents* (TEQs). A TEQ for a particular organic chemical contaminant ingested is determined by the product of the contaminant weight (in grams) and its assigned TEF, and the units are grams TEQ. As an example, Makiya (1997) stated that 60% to 70% of daily intake of dioxins (approximately 3.5 TEQ pg/kg/day) is obtained from fish and shellfish. The tolerable daily intake (TDI) established in Japan is 4 TEQ pg/day per kg weight. The Japanese standard value for soils contaminated with dioxins is 1000 pg-TEQ/g or less, whereas the corresponding standard value for sediments is 150 pg-TEQ/g. This value drops to 1 pg-TEQ/L or less for water—in accordance with the Ministry of Environment (Japan) standards. Sediments containing dioxins that are more than the standard value are required to be treated. The classical remediation techniques used are dredging and disposal on land—procedures that are most often costly and sometimes prohibitive when dredged materials have to be treated before land disposal.

8.5 Rehabilitation of Coastal Marine Environment

Several techniques have been tried and used in the rehabilitation of coastal marine environments. Table 8.4 gives a short summary of some of the recent procedures used to treat contaminated seawater and sediments and also measures taken to create coastal

TABLE 8.4
Various Techniques Developed for Remediation of Contaminated Seawater and Sediments

Technology	Name	Feature	Example of Use	Economics	Durability	Maintenance	Comments
<i>Seawater</i> Aeration	Air bubble curtain	Aeration	Developing	Needs electricity	Durability of hardware	Clogging due to organisms	
		Aerobic condition Convection of seawater					
	Microbubbling	Aeration	Oyster farms				
	Aerator	Very small bubbles					
		Aeration	Developing	Needs electricity			
Filtration	Special seawall	Mixing of seawater					
		Natural bubbling	Developing				
	Air mixing flow	Mixing of seawater					
		Aerobic condition of deep seawater	Developing				
	Filtration	Mixing of seawater Control and management of eutrophication	Many examples	Exchange of filter materials	Depends on instruments	Exchange of filter materials	Enclosed water area
Gravel oxidation	Control and management of eutrophication Removal of suspended solids Actions of microorganisms	Developing		Removal of filtered materials			
Inclined wall	Control and management of eutrophication	Used in rivers		Exchange of filters	Removal of sediments		

Adsorption	Artificial leaves	Removal of suspended solids Filtration	Used in sediment ponds	Removal of sediments	Muddiness due to spraying agent Impact on living organisms Impact on environment from aggregation agents
	Clays	Control and management of eutrophication	Many examples	Removal of sediments	
	Aggregation agent	Control and management of eutrophication	Many examples	Removal of sediments	
		Promotion of sedimentation			
Lime strewing	Adsorption of sulfide Increase in pH	Many examples		Fossil limestone	Fossil limestone
Sorption / accumulation	Accumulation of plants	Reduction of eutrophication	Lakes	Recovery of plants	Management of aquatic plants
	Bioaccumulation of shellfish Silt fence	Removal of suspended solids	Well known		
Isolation	Oil fence	Prevention of diffusion of suspended solids	Many examples	\$500– 2000/m \$50/m	Treatment of adhesive organisms
Sediments Cultivation		Promotion of settlement of suspended solids			
		Oxidation		Simple and easy	

(continued)

TABLE 8.4 (Continued)

Various Techniques Developed for Remediation of Contaminated Seawater and Sediments

Technology	Name	Feature	Example of Use	Economics	Durability	Maintenance	Comments
In situ solidification and dredging and disposal Trench	Capping of sand	Solidification of seabed	Established	Expensive			
		Removal of contaminants	Many examples	\$300/m ³			Disposal using bags
		Collection of mud in trench with about 2 m depth	Needs experience		Influenced by waves	Removal of sediments	Need disposal sites
Artificial tidal land	Lime strewing	Capping of sand	Many examples	Easy task with a simple machine			Not for navigation route of ships
		Sand beach	Many examples	Lack of sand materials	Influenced by waves		
		Adsorption of sulfide	Many examples		Short term	Strew often when no effects are observed	
Phyto-remediation	Creation of Ecosystem	Heavy metals, TBT, etc.	Developing				
			Need seawater purification				
		Biological diversity	Many examples	High cost			Difficulty in evaluation
Artificial wet lands	Seagrass	Biological diversity, Increase in haul of fish and shellfish					
		Recreation in seaside					
		Biological diversity					Easy
Tidal pool	Artificial coral reef	Biological diversity, Increase in haul of fish and shellfish					
Artificial fish compartment		Biological diversity, Increase in haul of fish and shellfish					

marine ecosystems. The methods used include (a) removal of the contaminants and hazardous substances by various techniques, (b) immobilization and isolation of these substances, and (c) neutralization and detoxification. The techniques for treatment of seawater include aeration, filtration, adsorption, accumulation, isolation, etc. Common treatment techniques for contaminated sediments include dredging and capping. Other lesser-used techniques include cultivation and lime strewing. The essence of the various techniques, together with present capabilities, economics of operation, and requirements are also briefly noted in the table. The ultimate aim of sediment and seawater treatment procedures is to remove the threat posed by contaminants and hazardous substances in the water and sediments.

8.5.1 Removal of Contaminated Suspended Solids

8.5.1.1 Confined Sea Areas

In confined sea areas, accumulation of hazardous substances and eutrophication are significant problems. A major factor in the constitution of seawater quality is the amount of suspended solids in the seawater. These solids include mineral particles, plankton, organic matter, and others kinds of particulate matter. The sorption characteristics and properties of suspended solids make them useful tools for sorption of hazardous substances such as heavy metals, PAHs, chlorinated organic compounds, etc., in the seawater. Bacteria such as colon bacilli may also be found on the surfaces of suspended solids. Table 8.5 provides an example of the concentration of heavy metals adhering to some typical suspended solids. Removal of the contaminated suspended solids will be a step toward obtaining better seawater quality. Together with the process of bioaccumulation, these suspended solids can be removed from the seawater using pumping and filtration techniques, e.g., released phosphorus (into the sea) initially taken by phytoplankton and algae will be removed when the phytoplankton and algae are themselves subsequently removed. Figure 8.13 gives a schematic illustration of this simple concept. The ultimate aim is to ensure that the concentrations of the hazardous substances are lower than the allowed values in the guidelines. Improved seawater quality provides for (a) greater transmission of light to sea bed, (b) acceptable water quality for leisure use by the local coastal community, (c) reduction of potential for eutrophication and reduced capability for development of red tide, and (d) better sediment quality and also further reduction in potential for eutrophication, benthic contamination, and development of blue tide. Technology and procedures for removal of suspended solids in closed sea areas using filtering techniques should be determined by the targeted final requirements and results of site investigation.

TABLE 8.5

Examples of Metal Concentrations in the SS of a Coastal Sea Area (mg/kg dry)

Element	Concentration	Element	Concentration	Element	Concentration
Fe	8000–30,000	Cu	240–500	P	2600–3000
Al	14,000–44,000	Pb	26–97	Mg	9600–14,000
Ti	1000–32,000	Cd	2.6–3.0	Ca	9000–90,000
V	40–53	Ni	2.8–36	K	9500–15,000
Zn	350–940				

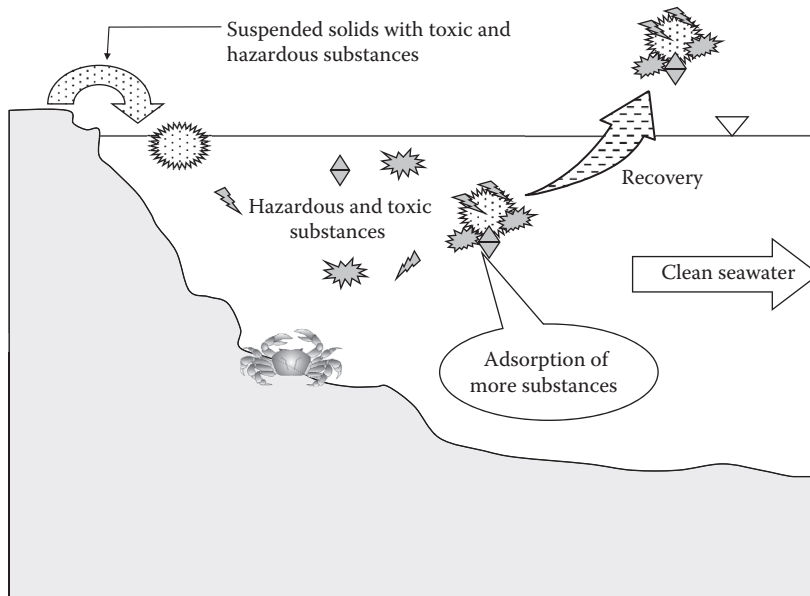


FIGURE 8.13
Concept of removal of suspended solids (SS).

8.5.1.2 Large Bodies of Water

To treat large bodies of seawater, filter units consisting of beach sand and steel slag have been used successfully to remove the suspended solids. These units were installed on a vessel (approximately 2500 tonnes), as shown in Figure 8.14. The case study conducted with thirty eight filter units (1.5×3.6 m) for purification of seawater in closed sea area achieved a purification capacity of about $6000 \text{ m}^3/\text{day}$. The quality of the treated (purified) seawater satisfied the regulatory requirements for allowable SS, COD, pH, DO, etc. (Fukue et al., 2004). A comparison of the nature of the suspended solids showed that these contained large amounts of substances, as much as the underlying sediments. Figure 8.15 shows the results of removal of the suspended solids. The left-hand plastic cylinder with a height of 30 cm contains the seawater with suspended solids. That is why no circular lines on the bottom of the cylinder can be seen. The right-hand picture shows that removal of almost 100% of suspended solid from the contaminated seawater produced transparent seawater that, to all intents and purposes, was devoid of suspended solids and all the substances adhering to the suspended solids. Studies show that this technique can be used for purification treatment water in various kinds of marine applications including dredging, and treatments to prevent development of red tide and blue tide.

8.5.1.3 Continuous Removal of Suspended Solids

In some closed sea areas, land-based hazardous substances are continuously discharged and delivered by rivers, etc., to the coastal marine waters. Filter units similar to those used in the purification vessel, mounted on semipermanent pier fixtures can function well to remove the hazardous substances adhering to the suspended solids.

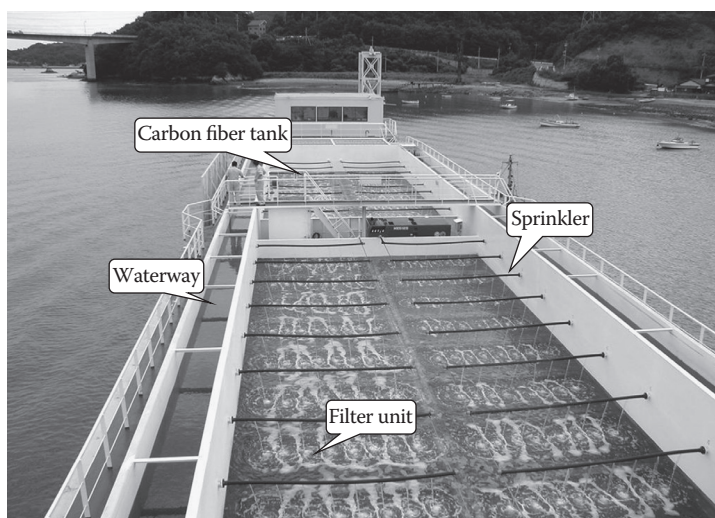


FIGURE 8.14
Purification vessel to remove suspended solids from seawater.

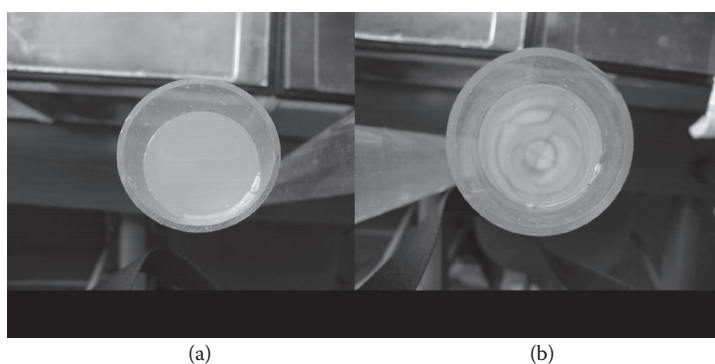


FIGURE 8.15
(See color insert.) Plastic cylinders showing (a) nonfiltered and (b) filtered seawater obtained with purification units in the purification vessel.

8.5.2 Sand Capping

Containment and isolation of nutrients and hazardous substances in sediments will discourage eutrophication and prevent uptake of hazardous substances. Two methods in use are (1) sand capping and (2) dredging removal and dumping on land. Sand capping is a procedure that places a bed of clean sand on the contaminated sediment. It may be the easiest and one of the most economical ways to restore the health of the bottom environment. In situ capping refers to placement of a covering or cap over an in situ deposit of contaminated sediment (Palermo et al., 1998). The cap may be constructed of clean sediments, sand, gravel, or may involve a more complex design using geotextiles, liners, and multiple layers, as used for the capping of landfill waste disposal sites. This capping isolation procedure not only prevents resuspension of polluted fines and other

sediment particles, but also reduces the flux of contaminants into the water column above.

A sand cap can provide a new sand beach and tidal flats that will serve as a habitat for various kinds of organisms, from bacteria in pore spaces to macro-benthos such as bivalves, sea cucumber, and seaweed. These organisms consume a large amount of nutrients. When sand is obtained from regions distant from the capping site, organisms and small animals may exist in the transported sand that are not native to the capping site. This is especially true when the source of the sand is land-based. Newly created sand cap beaches can function as physical purification units, i.e., filtration, through the action of waves and tides. Removal of suspended solids from the seawater and decomposition of organic matter adhering to the suspended solids by microorganisms in the pores are additional benefits obtained in sand capping.

For sand capping to be robust and successful in providing the necessary isolation capability, the following must be accounted for in the design and construction of the cap:

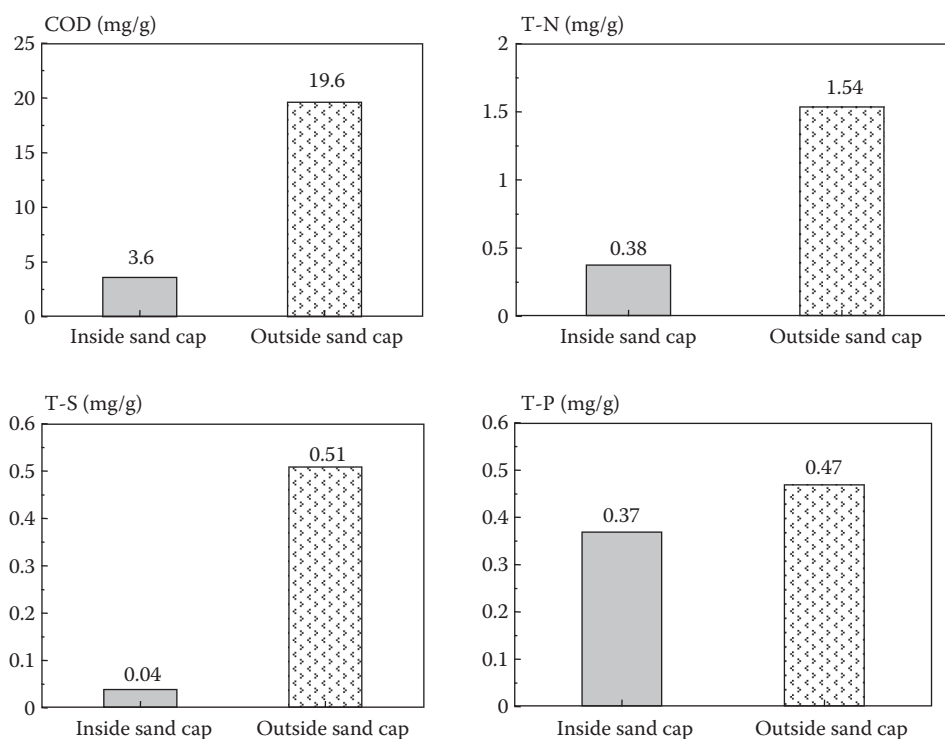
- a. Nature and type of currents, waves, flood, etc., that would cause drifting of the sand during and after emplacement. The record shows that hurricanes and typhoons are capable of dramatically altering the near-shore bottom conditions.
- b. Possible movement of some benthic organisms through the sand cap.
- c. Disruption of the food chain.

Table 8.6 shows a sampling of some recent major sand capping projects. The benefits from sand capping are shown in Figure 8.16. Data reported by the Port of Kanda, Ministry of Land, Infrastructure and Transport, Japan, for COD, T-N, T-S, and T-P following sand capping indicate environmental benefits such as less COD, less sulfide, and a lesser amount of nutrients in the sand cap, in comparison to that of the surrounding silty seabed. From the viewpoint of biological diversity, there is every indication that the sand cap is better than the surrounding silty seabed.

TABLE 8.6

Purification Projects Using Sand Caps

Project Location	Contaminants	Site Conditions	Cap Design	Construction Methods	Reference
Kihama Inner Lake, Japan	Nutrients	3700 m ²	Fine sand, 5 and 20 cm		
Akanoi Bay, Denny Way, Washington	Nutrients PAHs, PCBs	20,000 m ² 1.2 ha near shore with depths from 0.6 to 18.3 m	Fine sand, 20 cm Average of 80 cm of sandy sediment	Barge spreading	Sumeri, 1995
Simpson Tacoma, Washington	Creosote, PAHs, dioxins	6.8 ha near shore with varying depths	1.2 to 6.1 m of sandy sediment	Hydraulic pipeline with "sandbox"	Sumeri, 1995
Hamilton Harbor Ontario	PAHs, metals, nutrients	10,000 m ² portion of large, industrial harbor	0.5 m sand	Tremie tube	Zeman and Patterson, 1996
Eitheim Bay, Norway	Metals	100,000 m ²	Geotextile and gabions	Deployed from barge	Instanes, 1994

**FIGURE 8.16**

Effects of a sand cap (Port of Kanda, the Ministry of Land, Infrastructure and Transport, Japan). COD, chemical oxygen demand, T-N, T-S, and T-P, total nitrogen, total sulfides, and total phosphorous, respectively.

8.5.3 Removal of Contaminated Sediments by Dredging

8.5.3.1 Dredging

Dredging has historically been used (a) for beach reclamation, (b) to remove bottom sediments to deepen channels, waterways, and harbors and ports, (c) for maintenance of desired water depths for sea routes, and (d) to obtain materials for reclamation. Regardless of the type of equipment used (cutter wheels, augers, bucket wheels, pumping, suction hopper, self-propelled, automatic, etc.), dredging is a very invasive and destructive procedure. When used for removal of contaminated sediments, total disruption of the bottom ecosystem occurs. To return the benthic layer to full functionality, replacement of the food supply for benthic organisms is necessary. Removal of the first trophic level in the food chain will have severe consequences on the higher trophic levels. In that regard, planning for dredge removal of the contaminated bottom layer must include restoration of the functionality of the benthic layer.

8.5.3.2 Treatment of Dredged Sediments

Two options are available for disposal of dredged contaminated sediments: (1) disposal in a secure landfill and (2) treatment of the contaminated sediments and reuse of the treated sediments. Option (1) is not an option that has many proponents. Treatment of contaminated

sediments (option 2) can be an expensive procedure, especially when the quantities are large. An expedient procedure is to perform gravity separation of the contaminated sediment and to remove the coarse fractions for treatment and reuse as construction material. A useful technique for sediments that do not contain much organic matter is to form larger particles by promoting aggregation of the fines with lime. Contaminated fine fractions can be treated or disposed in secure settling ponds. These settling ponds are not unlike those obtained in natural resource extraction processes (Chapter 5). Techniques for dewatering and hastened sedimentation of the suspended fines that constitute the fine fractions of the sediment were discussed in Chapter 5. In the case of the fines in sediments, solidification, and compression by filter pressing can be used (Yamasaki et al., 1995).

8.5.4 Removal of Contaminated Sediments by Resuspension

Dredging of the sediments is necessary to facilitate the passage of the vessels or remediate contaminated sediments. However, disturbance of the contaminated sediments can spread the contamination. Alternatively, a two stage resuspension method is suggested as a new in situ method for remediation of highly contaminated sediments (Fukue et al., 2012b) (Figure 8.17). In the first stage, air jets are used in the confined water column to create a strong turbulent flow to suspend the sediments. After a certain period, the coarser sediments are allowed to settle, whereas the finer sediments remain suspended. In the second stage, the fine

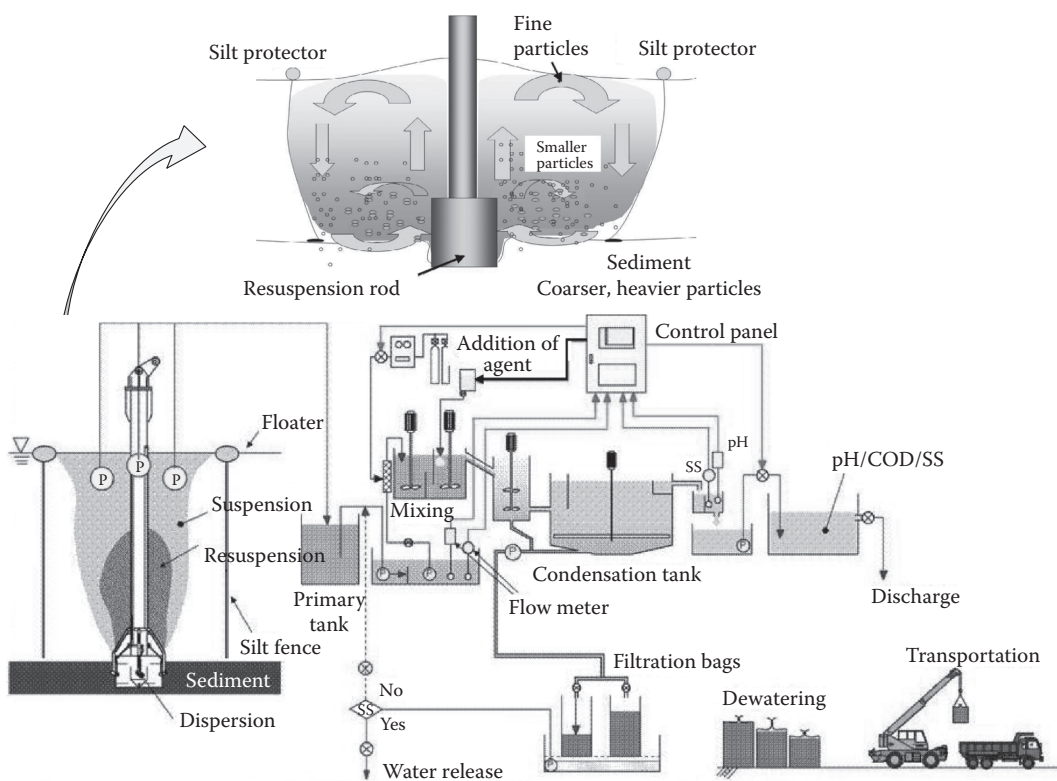


FIGURE 8.17

Schematic drawing of the entire resuspension process. The top drawing is a “blow-up” illustration of the resuspension principle.

suspended sediments are then pumped from the water and filtered. Recently a pilot test in Japan was evaluated in an area of 3000 m² with a high organic content (30% loss on ignition) with hydrogen sulfide production. About 11 tonnes of wet resuspended solids were removed during the resuspension pilot test. In the test, 50 cm of the bottom sediment layer was resuspended and 3% of the organic and smaller particles were removed. Analyses showed that full scale implementation would enable the removal of about 10% of the resuspended solids, and reduce COD by 95%, T-P by 50%, T-N by 100%, and sulfide by 75% for the redeposited sediments compared with the untreated sediments. Further tests were performed in Canada on samples obtained from a harbor. In total, 17 samples (surface and core samples) were taken at selected stations near the dock and the breakwater area. Sediment size distribution, water content, and loss of ignition were determined and the concentrations of the heavy metals were measured before and after the tests. Final results indicate an improvement in sediment quality. Aeration reduced the concentration of pollutants (mostly organic), and by removing the fine sediments, the heavy metal concentrations were decreased for some metals.

8.6 Creation of a Natural Purification System

8.6.1 Creation of Sand Beaches and Tidal Flats

Artificial sand beaches and tidal flat are created for one of the following purposes:

- a. Formation of clean beach for resort areas and parks
- b. Farming for shellfish
- c. Recovery of beach following reclamation
- d. Rehabilitation of coastal marine environment

Sand beaches and tidal flats possess natural capabilities for cleaning seawater under repeating waves and tides. This capability arises from a combination of their ability to filter a large amount of suspended solids (mostly organic matter), and the dissolution of the suspended solids by microorganisms. Although the organic matter entrapped in the sand pores is food for microorganisms and benthic animals, there are no easy means to quantify the process and its benefits. Evaluation of the impacts arising from construction of the tidal flats and beaches cannot be readily performed. In part, this is due to the dynamic processes initiated by the actions of currents and waves. Stabilization of the new beaches and tidal flats will be a long-term process. The use of breakwaters on beaches brings problems of decreasing redox in the region due to the dead organisms and excrements. Figure 8.18 shows one of the three tidelands (Kansai Rinkai Park, 270,837 m²), created artificially by the Tokyo Metropolitan Government in 1965, at a time when Tokyo Bay was losing its valuable natural environment. The area incorporates vast tidelands, which were once the breeding areas for birds and were also once abundant with fish and shellfish.

8.6.2 Creation of Seaweed Swards

Eelgrass (*Zostera marina*) is a water plant with long grasslike leaves. Figure 8.19 shows a dense sward of eelgrass. There are many different species of eelgrass. Shallow intertidal



FIGURE 8.18
An example of creation of an artificial tideland.



FIGURE 8.19
Dense sward of eelgrass (*Zostera marina* L.) in a coastal region.

water eelgrass has shorter and narrower leaves, whereas deeper subtidal water eelgrass has longer and wider leaves. They tend to grow in tidal creeks, sandy bays, estuaries, and on silty–sandy sediments and are a vital part of the food web chain for the coastal marine ecosystem. In dense swards of eelgrass, silt and clay particles tend to be deposited with organic matter. Decomposition of organic matter will render the seabed anaerobic, and the color of the sediments will become black because of the effect of sulfide.

The eelgrass family is one of the few flowering plants that lives in salt water, and the long grass blades are home to various kinds of small marine plants and animals. They are

TABLE 8.7

Comparison of Heavy Metal Concentrations in Sediments with and without Eelgrass (Seto Inland Sea, Japan)

Sampling Point		Heavy Metal (mg/kg)		
		Cu	Pb	Zn
A	With eelgrass	11	20	76
B	Without eelgrass	13	10	83
C	With eelgrass	11	25	69
D	Without eelgrass	14	130	90
E	With eelgrass	15	17	77
F	With eelgrass	16	18	82
G	Without eelgrass	27	17	110
H	With eelgrass	17	18	83
Average with eelgrass		14	19.6	77.4
Average without eelgrass		18	52.3	94.3

the breeding ground and habitat for all kinds of marine animals including crabs, scallops, and other kinds of shellfish. They not only serve to foster and stabilize the benthic habitats, but they also have the potential for phytoremediation. Eelgrass can absorb trace metals and organotins (Brix and Lyngby, 1982; Francois et al., 1989).

Table 8.7 gives a comparison of concentrations of various heavy metals in sediments with and without eelgrass. The sediments that were taken from a small eelgrass sward at an estuary of Kasaoka Bay in Seto Inland Sea, Japan, consisted of a number of small communities, with bare parts between the communities. The total area of the eelgrass sward was 1491 m². The sampling points from A to H were located in the bare parts and communities. The results show that the sediments with eelgrass contain a lesser amount of heavy metals—most likely attributed to heavy metal absorption (uptake) by the eelgrass. Since eelgrass grows from spring to summer, and their dead leaves drift upward to the sea surface at the end of their growing season, collection of the dead leaves can be simply implemented. This means that if eelgrass is used for phytoremediation, the absorbed heavy metals can be harvested with the dead seagrass leaves.

Reclamation and other near-shore industrial activities can negatively impact the coastal habitat, particularly on the seagrass beds that form the seaweed fields. Reduction of seaweed fields not only decreases the habitat of marine living things but will also result in a marked decrease in the haul of inshore fish. For example, in Japan, approximately 6000 ha of seaweed field have disappeared since 1978, and about one third of this is due to the impact of reclamation projects.

8.7 Sea Disposal of Waste

Dumping or discharging land-based industrial waste into the sea is essentially prohibited—with the burden of responsibility resting on the waste generator to ensure that any waste material entering the sea must be nontoxic and nonhazardous. Section 8.2 has discussed the strict prohibitions articulated in the London Convention and Protocols. Since many countries and jurisdictions with restricted land areas do not have sufficient land space for

TABLE 8.8

Examples of Sea Disposal of Various Kinds of Waste

Site	Area (ha)	Volume of Waste Disposal (million m ³)				Total
		Municipal Waste	Industrial Waste	Soils from Construction Site	Dredged Materials	
Off-Amagasaki	113.0	2	3.9	5.8	4.1	16.0
Off-Izumi-Otsu	203.0	4	9.4	12.7	4.8	31.0
Off-Kobe	88.0	5	7.3	3.0		15.0
Osaka Port	95.0	5	6.3	2.8		14.0
Total	499.0	16	26.9	24.3	8.9	76.0

land disposal of waste, controlled and regulated discharge of municipal and industrial wastes into the sea remains as the option of last resort. When such a need arises, waste disposal sites in the sea must be constructed to meet safety and health protection requirements. Isolation of the waste from contact and dispersion into the sea is a prime requirement. In some countries, artificial islands have been constructed for the principal purpose of emplacing secure disposal facilities. These island-based disposal sites must conform to all the regulations that attend land-based disposal sites, with the strict requirement for monitoring and control to ensure no escape of leachate into the sea.

In some other cases, actual disposal sites have been constructed in the sea using seawalls as containment walls to prevent escape of waste and leachates into the surrounding sea. Typical examples are seen in Tokyo Bay and Osaka Bay. Table 8.8 give a short summary of the waste disposal sites and materials disposed in four sites in Osaka Bay, constructed under the auspices of the Phoenix Project. The objectives of the project not only focused on the proper and safe disposal–discharge of the wastes in Osaka Bay, but also on preservation of the coastal marine ecosystem, and development of the regional area through environmentally acceptable reclamation of shoreline.

8.8 Coastal Erosion

Coastal erosion is a problem that has confronted coastal communities for a long time. Some will argue that this is a natural phenomenon and that the “problem” arises when the human population occupies the coastal regions and imposes various requirements on the coast, such as building structures, infrastructures, wharfs, etc. Alteration of the coastline is a natural phenomenon, and erosion is a major factor in the alteration process. This alteration process becomes a problem because of the requirements and expectations imposed by the human population. Erosion arises not only from the aggressive action of waves and currents, but also from diminished sediment recharge from streams and rivers feeding into the sea. Flood control dams and other river restoration projects can curtail the flow of suspended particulates and sediments. Without this sediment recharge and with erosive forces acting on the coastal plains, erosion becomes a considerable issue. To counter the erosive forces and to prevent beach erosion, armoring of the beach with revetments and seawalls is a procedure that has been adopted by many coastal regions. Figure 8.20 shows an erosive beach on the coast of Japan facing the Pacific Ocean. A huge number of concrete blocks have been installed to protect the coastline and to gather sand. Figure 8.21 shows soil dumping as a countermeasure for erosion. The



FIGURE 8.20
An erodible coast in Japan facing the Pacific Ocean.

record shows that some period after leveling of the dumped soil, erosion of the slope occurred. To overcome this, geotextile tubes can be used to protect coastline from waves and tides—as has been utilized in some countries. The tubes, which can be installed along the coastline, are a few meters in diameter and a few kilometers in length can be filled with dredged soils (Figure 8.22). They can also serve as a breakwater for man-made islands and wetlands.



FIGURE 8.21
Countermeasure for coastal erosion by dumping and the action of erosion.

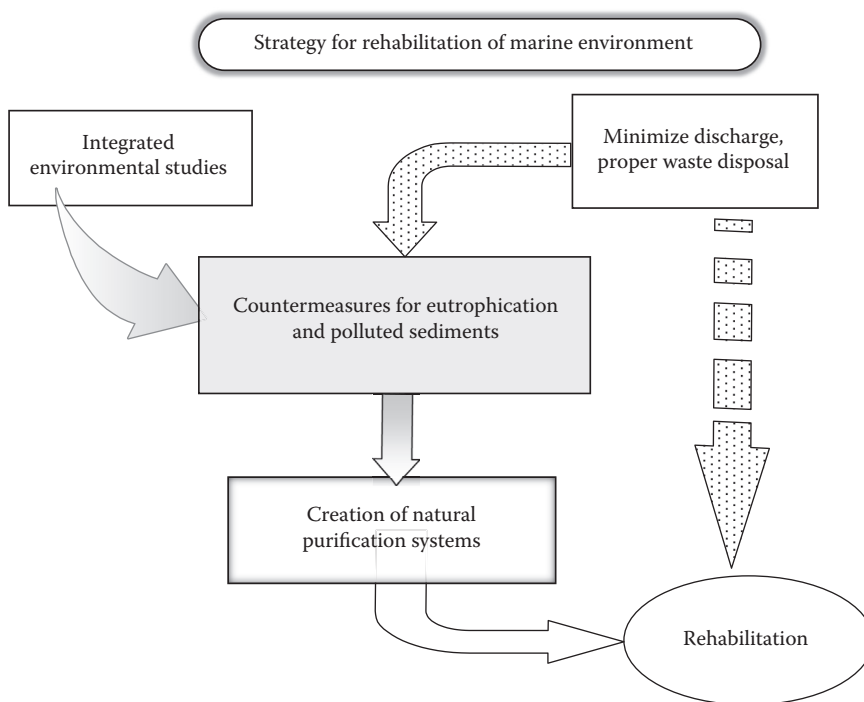
**FIGURE 8.22**

Geotextile tube used for protection and creation of a coast.

8.9 Concluding Remarks

The health of coastal marine environments is vital to the productivity of the marine aquatic resources in the ecosystems within this environment. The oceans and the coastal marine environments are significant resource bases and are essential components of the life-support system for the human population. The two groups of events that pose significant threats to the health of this environment are distinguished on the basis of *natural* and *man-made*. In the first instance, the natural events include phenomena such as coastal erosion resulting from aggressive current, waves, and tidal action. Man-made events result in fouling of the coastal marine environment and of the seas through discharge of wastes from ocean vessels and from land-based industries and activities. It has been argued that coastal erosion is also a victim of man-made events, according to the thesis that *man-generated variations* in sea level contribute to the aggressive actions of the currents, waves, and tidal actions. The thrust of this thesis is that global warming is in part responsible for the variations in sea level not only through ice melting, but also through changes in the seabed levels. Although a discussion on global warming is not within the purview of this book, it is nevertheless important to point out that the many facets of geoenvironmental sustainability are affected by such an event. Some of these issues have been discussed in Section 1.5 in Chapter 1.

Fouling of the coastal marine environment and of the seawater affects both seawater and sediments. Contaminants are accumulated in the sediments, whereas others are put into circulation through the food chain and bioconcentration—ultimately posing health threats to the human population. Two basic problems exist in respect to fouling of the coastal marine environment and the seawater: eutrophication and concentration of toxic and hazardous substances. Figure 8.23 gives an illustration of a simple strategy for rehabilitation of the coastal marine environment. Hazardous substances and nutrients have been discharged into the coastal marine environment for many decades. These have to be collected and removed. A balance in the amount of nutrients removed is needed. On the

**FIGURE 8.23**

A strategy for rehabilitation of the marine environment.

one hand, sufficient removal of excess nutrients is needed to avoid eutrophication, and on the other hand, sufficient nutrients must be available for the aquatic animals that rely on these nutrients for their food supply. A sustainable coastal marine environment requires a natural purification system. Research and development into how this can be achieved would contribute substantially to the goals of a sustainable coastal marine environment. In the final analysis, since fouling of the marine coastal environment and the sea is in large measure attributable to the land-based activities and industries, proper control and management of the land contamination would go a long way towards mitigating fouling.

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9

Contaminants and Land Environment Sustainability Indicators

9.1 Introduction

We use the term *land environment* instead of *geoenvironment* because we do not include the coastal marine environment (considered in the previous chapter) in our discussions in this chapter. As we have seen and discussed in the previous chapters, in respect to the land environment, other than depletion of natural resources and habitat destruction, ground contamination by all kinds of contaminants and pollutants from anthropogenic activities poses one of the greatest threats to the sustainability of the natural capital of the *geoenvironment*. The term *pollutants* is used to remind the reader that these are contaminants that are deemed by Regulatory Agencies to be injurious to human health. In the treatment of the subject of contaminants and pollutants in this chapter, the encompassing term *contaminants* will be used. When emphasis is needed, the term *pollutants* will be used. Within the context of the land environment, the term *natural capital* refers to the land ecosystem, which includes (a) the receiving waters in the land surface environment such as rivers, lakes, ponds, and streams, (b) the solid land surface and the underlying soil–water system, (c) the natural resources such as forests, mineral, and carbon resources, and (d) the various biotic species and the biodiversity of the ecosystem. The presence of contaminants in the ground affects not only soil and water quality, but also those living elements and biota that more or less depend on soil and water for their wellbeing. This would include forests, agricultural production, habitats, and the host of biotic species contributing to the biodiversity of the land ecosystem.

Anthropogenic activities associated with production of goods and services, such as resource exploitation, agricultural production, harvesting of forest and carbon resources, urbanization, industrial production and manufacturing, are by far the greatest contributors to the generation of waste and contaminants that ultimately find their way onto and into the land environment. Sustainability of the land environment natural capital cannot be easily or readily defined for many of the individual components that make up the natural capital of interest because of their dynamic nature. This is particularly true for the *living* components. It is easier to define sustainability goals for the natural capital as part of the life cycle assessment process discussed in Chapter 4. This task is facilitated if one could establish an acceptable natural capital baseline.

9.2 Indicators

The general understanding of sustainability of a natural capital of the land environment can be stated as follows: “To ensure that each natural capital maintains its full and uncompromised functioning capability without loss of growth or replenishment potential.” Clear baseline values for the various components that constitute the land environment natural capital are needed to define or establish sustainability requirements of the natural capital in quantitative terms. Since absolute sustainability is not always attainable, the use of indicators is a means to establish benchmarks or targets that point the way toward sustainability of specific components of the natural capital and of the natural capital itself.

9.2.1 Nature of Indicators

Section 1.4 in Chapter 1 has discussed, very briefly, the nature of indicators. They are essentially “signs” or “markers” used daily by ordinary people and also by professionals. The example cited earlier of vehicular traffic lights at an intersection is a very good example of one’s everyday encounter with indicators. In terms of day-to-day living, personal events such as prolonged headaches, stomach aches, muscle pain, toothaches, etc., are used as indicators of some form of health distress and that one should visit one’s health-care specialist. Numbers, statistical information, events, etc., can all be used as indicators. Unemployment rates, gross domestic product (GDP), and financial indices such as those used for tracking the ups and downs of various equities are all indicators of the health of the economy. In a sense, indicators have been used by humans for as long as there has been human life on the planet.

From the geoenvironmental perspective, the indicators discussed in this chapter are considered to be markers or benchmarks specified or prescribed by individuals and/or organizations interested in tracking: (a) the progress of events, (b) operations and performance of systems, (c) the outcome of actions on something specific, and (d) the status of a particular set of events, actions, process, activity, and situation—all of which are with specific reference to the land environment. Indicators can also be used: (1) for performance assessment of various systems, processes, actions, etc., and (2) to set goals and/or targets for operation and performance of systems, processes, activities, etc. The example of the use of soil functionality indices (*SFIs*) shown in Section 1.4 and Figure 1.7 of Chapter 1 is a good demonstration of the usefulness of indicators for tracking operations of systems.

There are many varieties and types of indicators that can be used to determine or track the sustainability of the geoenvironment. For convenience, we can group all of these into two major groups: (1) system status indicators and (2) material performance indicators. System status indicators refer to the status of a system—an ecosystem, for example, at any time period. They are essentially performance indicators. This is because the system status at any one time period is the result of the performance of the system over the time period under consideration. In that same sense, material performance indicators are designed to provide information on the performance of materials at any specified or required time period—quantitatively or qualitatively. Since material properties and characteristics may be functions of system processes, it follows that material performance indicators are also material properties’ indicators. When the term *indicators* is used, it is understood that this refers to both system status and material performance indicators. The greatest benefit of status indicators comes when they are used in relation to some predetermined or defined criterion, target, or objective.

Not all indicators are sustainability indicators. A good example is the measurement of acid precipitation onto the ground where the sources of SO_x and NO_x are known. The acidity

measurements themselves are material indicators, i.e., they are acidity indicators. This begs the question, “so what?” Four courses of action come to mind: (1) do absolutely nothing, (2) implement a ground surface neutralization program using perhaps a surface spray technique, (3) monitor target components such as soil and water quality, environmental mobility of contaminants in the affected area, and (4) determine the source of the airborne–gaseous discharge and rectify the situation through implementation of better process technology and more effective scrubber systems. Figure 9.1 illustrates this example from a land environment perspective.

Figure 9.1 shows that *indicators* (a) inform us on “where we are” in respect to specific indices and prescribed parameters, (b) provide specific information to be used to compare with (or contrast with) baseline values or other target values, (c) provide monitoring and tracking information for use in determining the transient state of items being monitored, and (d) tell us if we are on target or “off-track.” SO_x , NO_x , PM_{10} , and TOMP as shown in the top right-hand corner of Figure 9.1 are *material indicators*. They provide information on the noxious gases and other airborne contaminants that are responsible for the chemistry of the airborne deposition of contaminants on the land surface. This information gives one the opportunity to exercise any one of four different options—as shown in the diagram. Depending on the nature of the contaminants (chemistry, concentration, distribution, etc.) being deposited on the land surface, the distinct courses of available action are (a) actions undertaken at the industrial plant itself and (b) actions taken to address the impact of the deposition of the airborne discharges. *Action (a)* is essentially *source control*, e.g., improve

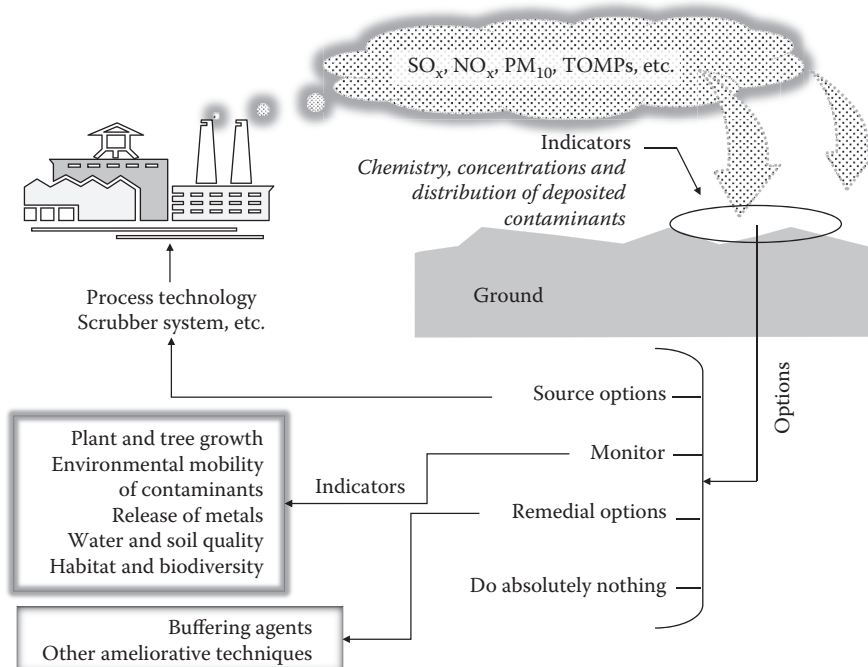


FIGURE 9.1

Illustration of the role of indicators in a typical precipitation situation in an atmosphere with noxious gaseous and other airborne contaminants in the context of impacts on the land surface. The indicators shown do not cover the entire impact problem. Note that changes to process technology and scrubber system do not fall within the purview of this book—and neither do plant-tree growth, habitat, and biodiversity. Note that PM_{10} is particulate matter less than $10\ \mu\text{m}$ in size and TOMP is toxic organic micropollutants such as obtained PAHs, PCBs, dioxins, and furans from incomplete combustion of fuels.

the scrubber system in the industrial plant shown in the top left-hand corner of the diagram, whereas *action (b)* is *contaminant management*.

For the second option, i.e., contaminant management, information from material indicators is required for one to determine the management course of action, as shown in Figure 9.1. The actions are (a) do nothing, (b) monitor, and (c) undertake remedial actions. In the case of the “monitor” option, the associated indicators are *status indicators*. These indicators essentially track the status of the various items such as water and soil quality at various times to determine whether negative changes occur. More importantly, these system status indicators are important markers along the road to sustainability, and where appropriate, they may be called sustainability indicators. *Sustainability indicators* (SIs) are those indicators that point the way toward achievement of the goals and objectives of sustainability. For these indicators to have value and meaning, it is necessary to provide or specify the sustainability goals or objectives. Because true sustainability may never be attained, for example, in the case diminishing nonrenewable natural resources, the sustainability indicators provide us with a measure of nonrenewable natural resource depletion (depletion rate). By targeting a depletion rate that would allow for a longer time before exhaustion of the resource, SIs can alert us as to whether we are on target or whether drastic remedial or corrective steps need to be taken. However, as will be evident in further discussions on indicators, SIs are really a collection of many intermediate indicators situated as markers along the road to sustainability—with the final set of indicators located at the terminal point of the road. The various intermediate indicators should set the requirements and conditions of performance at stages along the way, as shown, for example, in Figure 9.2. The combination of these indicators can be considered as “requirements to satisfy sustainability objectives.”

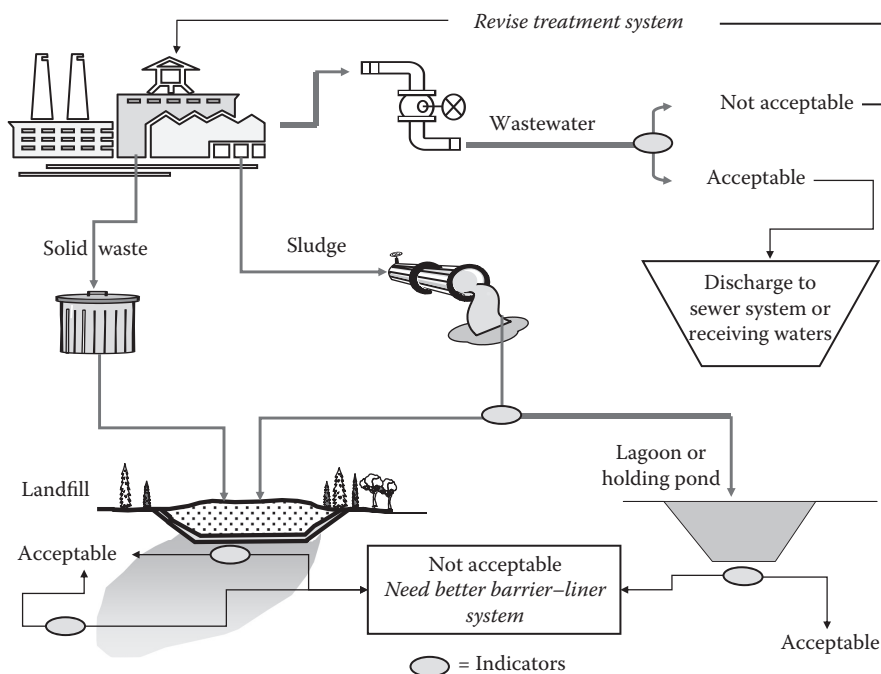


FIGURE 9.2

The role of indicators in assessing status and sustainability of operations in a plant discharging liquid and solid wastes. The indicators in the diagram are shown as shaded ovals.

9.2.2 Contaminants and Geoenvironment Indicators

An example of impacts from the discharge of liquid waste and/or sludge and solid waste is shown in Figure 9.2. Not all the indicators shown in the diagram (depicted by the shaded ovals) are sustainability indicators (SIs). These indicators have several functions. In the top right-hand corner, the various pieces of information from the wastewater discharge from the industrial plant, which are wastewater chemistry indicators, tell us whether the wastewater discharge meets the regulatory requirements permitting discharge into the sewer system or receiving waters. The wastewater chemistry indicators, which are material indicators, could include, for example, suspended solids, alkalinity, metals, fats, oils, grease, organic chemicals, etc. Failure of the wastewater chemistry to meet discharge standards will require a re-engineering of the treatment system.

Information obtained from analyses of the sludge being discharged (from the discharge end of the sludge pipe, i.e., the sludge discharge indicators) can be used to determine whether the toxicity and sludge characteristics meet lagoon (holding pond) capabilities or whether the sludge should be contained in a secure landfill. This assumes that lagoons and holding ponds do not generally have the same type of secure impervious barrier–liner systems that are required for landfills. In this instance, the sludge discharge indicators are not sustainability indicators but are status indicators that provide one with the information required to make the necessary judgment for disposal of the sludge.

The contaminant indicators located below the lagoon and the landfill serve several purposes. In the lagoon case, assuming that the barrier–liner system for the lagoon is not as secure as the landfill system, the contaminant indicators will tell us whether the contaminants escaping from the lagoon are in the range of acceptable concentrations. One needs to rely on the attenuation characteristics and properties of the subsoil strata to further ameliorate the concentration of contaminants as the contaminant plume travels further into the soil substratum. If the contaminant indicators show unacceptably high concentrations of contaminants immediately under the lagoon, regulations would require corrective action to be taken.

The same situation applies to the contaminant indicators immediately adjacent to or under the barrier–liner system of the landfill. Corrective action is needed if the contaminant indicators exceed specified concentration trigger levels. Acceptable concentration levels reported by the contaminant indicators immediately under the barrier–liner system do not mean that the other contaminant indicators located further away from the landfill would report favorably. Much depends on the nature of the contaminants and the transport processes. Contaminant transport modeling, using the information from the first set of indicators under the barrier–liner system, can be useful. Predicted transport values can be used to compare with the second set of contaminant indicators. The contaminant indicators are seen to be markers that show progress of the contaminant front (i.e., trackers of transport), and if design specifications and expectations of attenuation are correct, the indicators should accord well with predictions, provided that the transport models accurately predict performance. The transport of contaminants has been briefly discussed in Chapter 2. A further detailed discussion of these transport and fate processes will be found in Section 9.3.

9.2.3 Prescribing Indicators

Where and how are indicators prescribed? To a large degree, material performance and system status indicators are specified or determined on the basis of how or what one needs

to know and undertake to meet the specific targets identified in *sustainability status indicators*. There are two starting points for delineation of indicators:

1. Starting with the objective itself: In this instance, as an example, we could begin with a particular item in a natural capital component, e.g., maintaining the quality of the soil in a tract of land or a particular site. This is important because of the life-support role of the specific tract of land. In this instance, one begins by (a) defining or establishing what indicators are needed as sustainability status indicators, e.g., specifics of soil quality as shown, for example, in Figure 9.3; (b) determining the sources and nature of interactions with the tract of land and their impacts; and (c) establishing the required actions to ameliorate, mitigate, avoid, and protect the desired soil quality. Material and macrostatus indicators are established to determine and track the results of the corrective and protective measures. Figure 9.3 shows the use of status indicators in tracking anticipated or predicted outcomes from analyses or modeling of the processes initiated by the corrective actions. Failure to meet tracking results from the status indicators requires one to decide (a) to ignore indicators or (b) modify or add or correct the actions previously prescribed to manage the impacts.

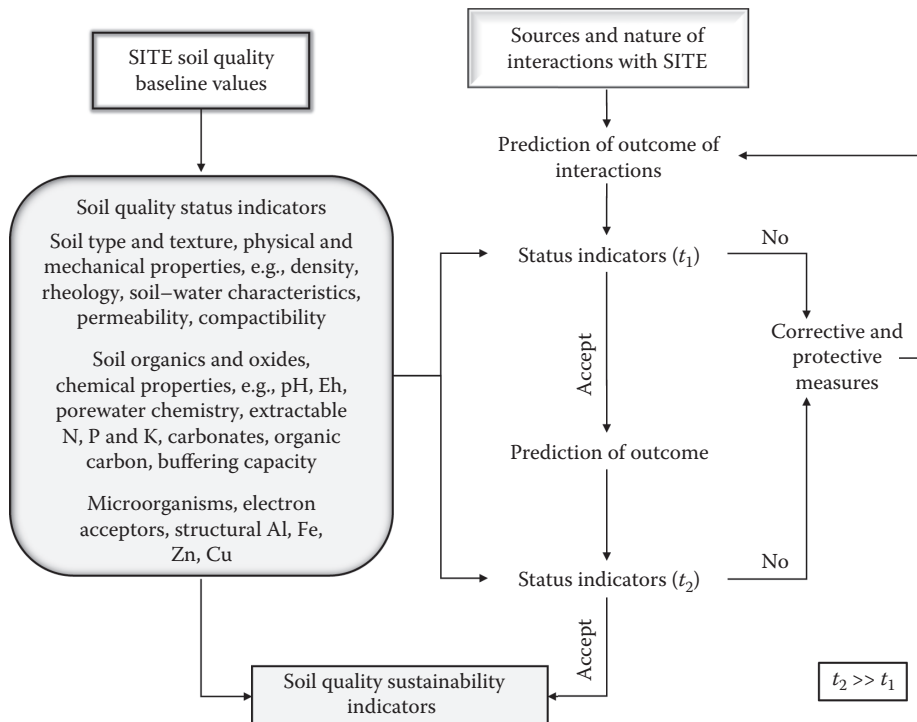


FIGURE 9.3

Example of specification and utilization of system status and material performance (properties) indicators using sustainability of soil quality as a goal. Note that the physical, chemical, and biological indicators listed in the soil quality status indicators are meant to portray the kinds of indicators that might be used. (t_1) and (t_2) indicate two different times.

2. Starting with the external sources of interactions with the land environment itself: With this starting point, one follows a reverse sequence. Figure 9.4 shows a typical protocol to determine or evaluate sustainability capabilities for the actions or impacts resulting from a specific project, activity, or industry. Status indicators (1) and (2) are indicators that may refer to different periods, intervals, circumstances, or locations. Prediction of the outcome of preventative or ameliorative actions (corrective actions) is generally obtained via modeling of the processes involved in the impact and corrective interactions, as also in the case of the actions shown in Figure 9.3.

The importance of system status and material performance indicators is evident in the *soil quality indicators* shown in the left-hand side of Figure 9.3. The list of physical, chemical, and biological indicators shown in the diagram are not meant to be comprehensive. They are prescribed according to the specifics of the natural capital component under consideration. Status indicators (1) and (2) are prescribed in accordance with tracking or monitoring requirements. These are both spatial and temporal in nature and can include more than the numbers shown in the diagrams. Even though true sustainability may not be attained, it is necessary for the objectives and goals for sustainability to be properly articulated. These will serve to establish what, where, how many, and how often status indicators will be used or required.

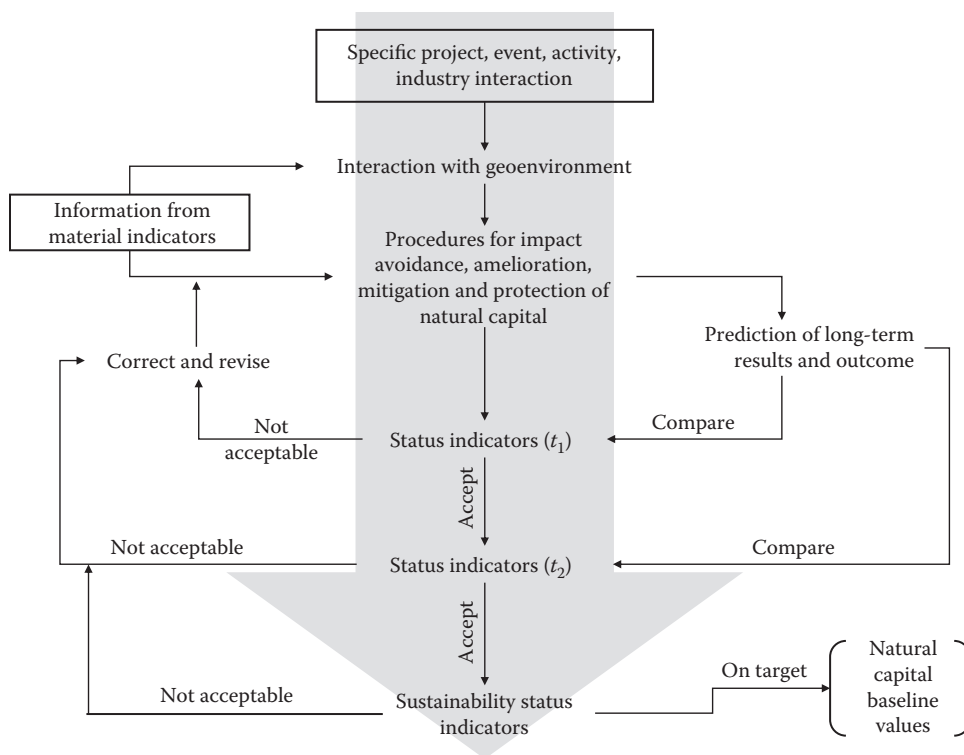
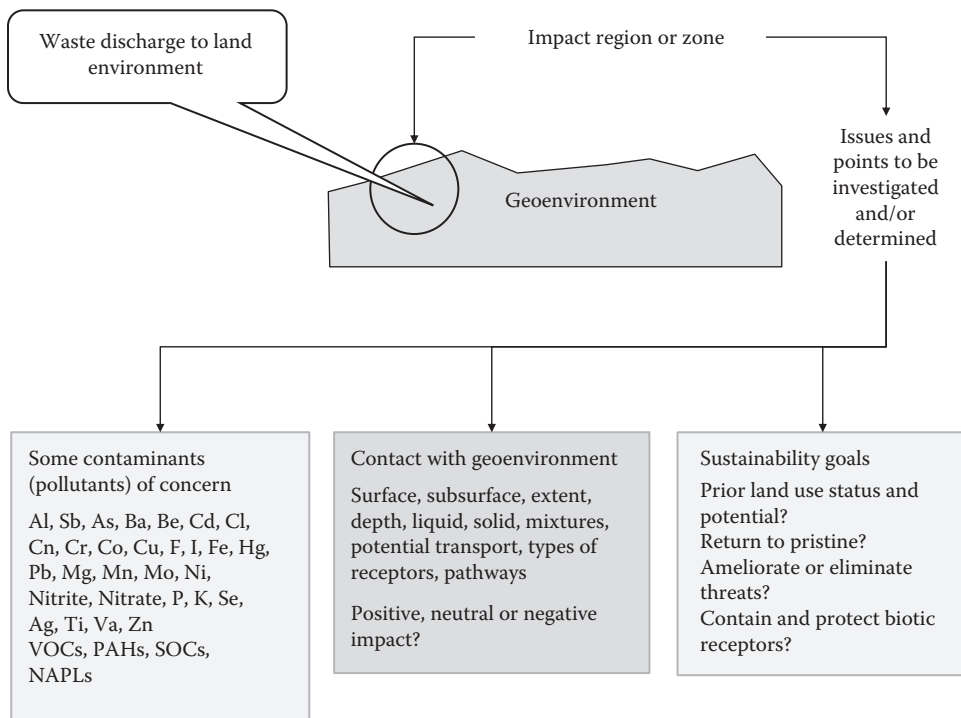


FIGURE 9.4

Prescription of material performance (properties) and system status indicators for determination of procedures for impact avoidance, amelioration, mitigation, and protection of natural capital.

**FIGURE 9.5**

Simple schematic showing first sets of determination for assessment of impact of waste discharge to the land environment.

9.3 Assessment of Interaction Impacts

Figure 9.5 shows many of the pollutants and contaminants found as discharge waste from activities associated with urbanization and industrial manufacturing and production. Knowledge of the geoenvironment impact interactions with specific projects and industrial manufacturing and production processes is required in structuring defensive and mitigation actions. In the case of contaminants in the land compartment of the geoenvironment, this means that knowledge of the transport and fate of contaminants in the subsoil must be obtained. The aim of the outcome of defensive and mitigation actions is to provide the best course of action required to meet the objectives for protection and conservation of the particular natural capital component under consideration. Contaminant fate and transport modeling is a commonly used tool to predict the outcome of these actions. The basic elements of fate and transport processes and modeling have been discussed in Chapter 2. We will continue the discussion in this section.

9.3.1 Sustainability Concerns

All previous chapters have shown that the major sets of interactions between the various external agents (activities, projects, industries, etc.) that have the potential to severely impact the land environment are the liquid and solid discharges (spills and other discharge

forms) from these agents. The necessary pieces of information and knowledge required to generate preventive and mitigation solutions (Figures 9.3 and 9.4) relate to the local geological and hydrogeological settings, the types and nature of spills and discharges, the various environmental and biotic receptors, and most importantly, the status and sustainability indicators. A useful rule-of-thumb in prescribing sustainability status indicators (the last set of indicators shown in Figures 9.3 and 9.4) is to set objectives and targets that do not yield negative impact results; interaction and preventive–mitigation impacts should not diminish the natural capital component under consideration. Although activities associated with upstream and downstream industries may inevitably generate impacts that cannot be fully ameliorated, minimized, avoided, or totally remediated, it is nevertheless necessary to set status indicators that target sustainability of the natural capital of land environment.

9.3.2 Surface Discharge: Hydrological Drainage, Spills, and Dumping

Surface discharge or liquid/solid contaminant loading of land surface occurs under circumstances that include (a) hydrological drainage occurring at a mine site at intersections of mine openings with the water table, (b) percolation from waste rock and mill tailings piles and surface runoffs, (c) inadvertent spills or deliberate dumping, (d) leaking pipelines, (e) deposition of airborne noxious contaminants from rainfall and snow loads, (f) application of agricultural chemicals (including pesticides) and irrigation, and (g) designed land farming treatment of contaminated materials. Figure 9.6 shows a schematic of some of

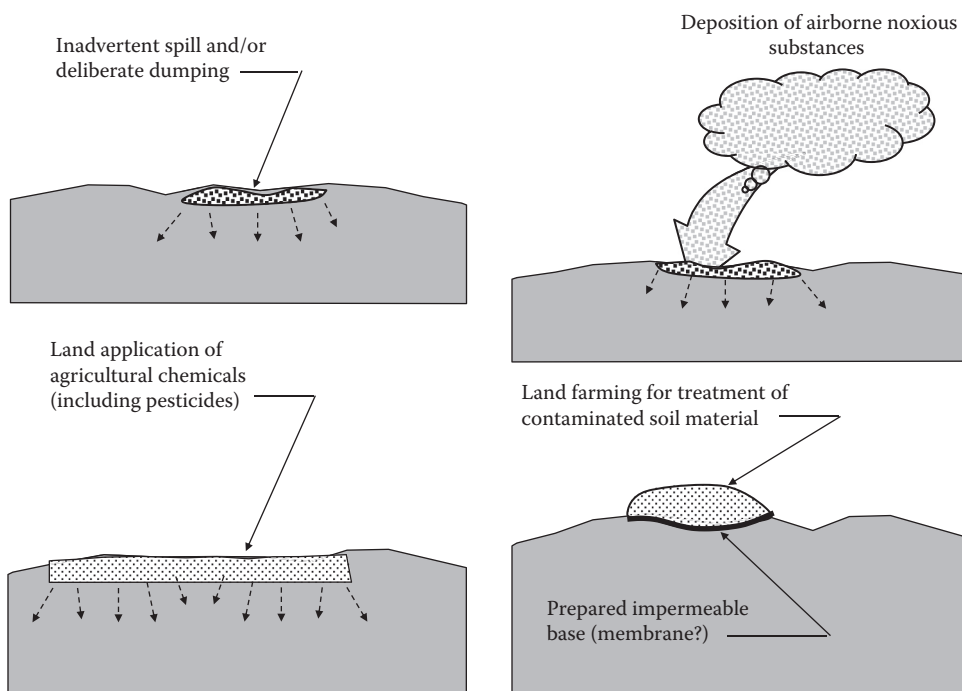


FIGURE 9.6

Scenarios showing contaminant loading on land surface of geoenvironment. For small spills and dumps, point source contamination is assumed. For precipitation and land application of control agents, etc., non-point source contamination is generally assumed.

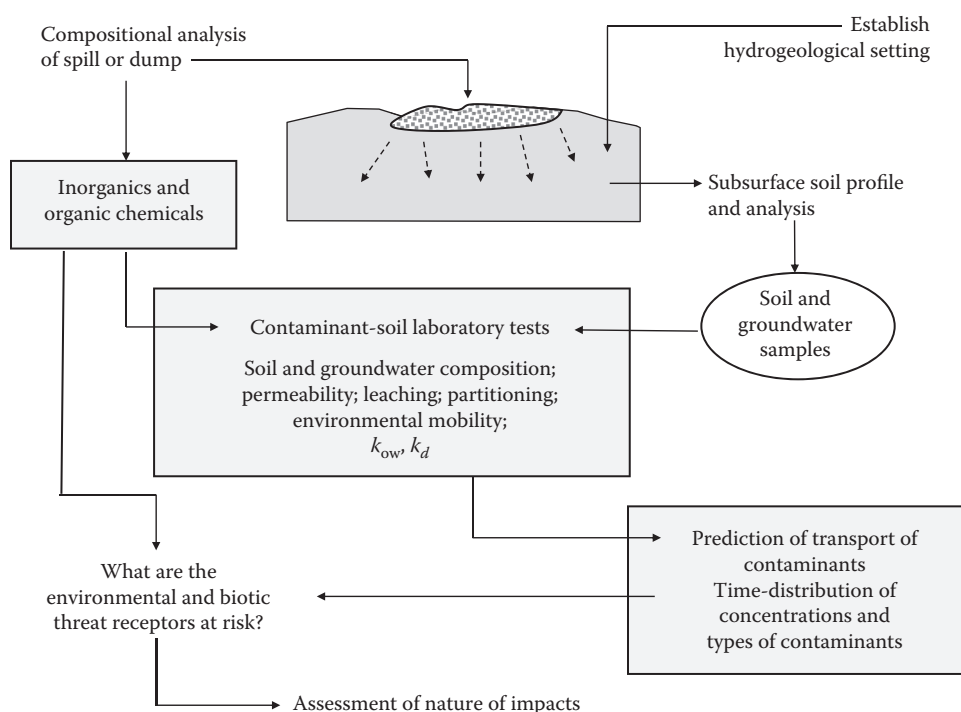
the situations leading to contaminant and contaminant loading of the ground surface. The bottom-left diagram in the figure concerns the problems discussed in Chapter 6. The land farming scheme shown in the bottom right of the diagram assumes that a prepared impermeable base is in place before placement of the material to land farmed. Techniques for land farming will be discussed in a later section when mitigation and treatment alternatives are addressed.

The principal issues for contaminant loading of the land surface relate to the transport of contaminants from the contaminant source. By and large, spills and deliberate dumping of waste materials involve small surficial areas (i.e., small areas on the land surface). These will serve as point sources for transport of contaminants into the ground. Surface runoffs from these regions tend to be small. Meanwhile, surface runoffs for other land application of contaminants resulting from deposition of airborne noxious substances and use of agricultural chemicals (including pesticides) can be serious issues—because of the extent of the land surface affected. The surface runoffs of contaminants arise if rainfall occurs or continues before the noxious substances and agricultural chemicals have a chance to effectively infiltrate or leach into the subsurface. Since the receiving sites for surface runoffs are topographically lower than the source location, these sites will likely be lowlands, wetlands, and receiving waters. Contamination of these regions (from surface runoffs) is commonly identified as *non-point source contamination*.

Contamination of the subsurface material (subsurface geological material) and the underlying aquifers from contaminant sources occurs because of the transport of contaminants in the subsurface material. Laboratory studies on the transport of contaminants in soils have been conducted for a large variety of soil types and contaminants. Field studies have also been performed in support of remediation projects and as due diligence work. Procedures and analytical-computer models have been developed to provide one with the capability to determine and/or predict the movement, distribution, and concentration of contaminants in the subsurface soil. A brief summary of these can be found in Section 2.5.4 in Chapter 2. As also emphasized previously, detailed treatment of these subjects can be found in textbooks dedicated to the study of contaminant fate and transport in soils. The discussion of contaminant transport processes and predictions will be found in the latter portion of this section.

The essential elements required for assessment or evaluation of the impacts from surface discharge phenomena such as spills from industrial operations and systems such as pipelines and vehicular traffic transporting liquid wastes or heavy oils and bitumen, dumping, etc., are shown in Figure 9.7. In addition to determination of the size of affected area and quantity of material spilled, discharged, and/or dumped, one is required to determine the following:

1. Nature and composition of the discharged material
2. Hydrogeological setting in the region
3. Subsoil profile, material composition, and properties
4. Transport processes involving the types of contaminants found in the compositional analyses, from laboratory tests
5. Transport and fate of contaminants (emanating from the surface discharge) in the subsoil, using predictive models and test information on partitioning of contaminants and transmissivity characteristics of the contaminants
6. The environmental and biotic receptors and how they will be impacted
7. Source–path–receptor relationships

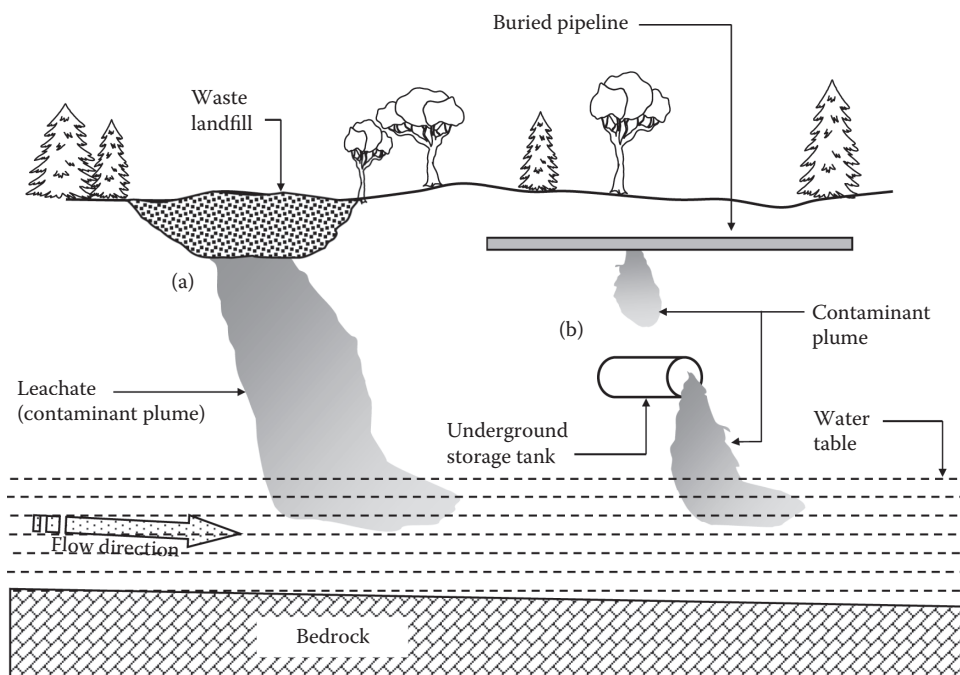
**FIGURE 9.7**

Schematic diagram showing procedures, factors, tests, and analyses required to begin the process for determination of consequence of surface discharge.

9.3.3 Subsurface Discharges

Subsurface discharges of contaminants arise when leaks or breakages in underground liquid/gaseous storage facilities and underground liquid or gaseous pipelines occur. Subsurface discharges of contaminants also occur when leachates escape from waste landfills (Figure 9.8). The left-hand portion of the schematic in Figure 9.8 shows the leachate plume escaping at the bottom of the constructed waste landfill. When properly designed, with adequate barrier and liner systems underlying and surrounding the sides of the landfill, and leachate collection intercepts placed in the bottom barrier system, leakages are not expected. Furthermore, with proper impermeable caps placed on the top of the landfills, water is not permitted to enter into the system. This subject is considered further in the next chapter. A comprehensive discussion of waste landfill barrier systems can be found in textbooks dealing with the subject of landfills and barrier systems (e.g., Yong et al., 2010).

Leachates emanating from landfills result from (a) landfills not properly constructed, (b) breaks in the liner and barrier system, (c) deterioration of barrier system, (d) incompatible interactions between barrier material and leachate chemistry resulting in failure of barrier to perform effectively, and (e) historic (old) landfills built without any real site preparation and therefore not constructed with attention to requirements for proper and secure containment with barrier and liner systems. Typical constituents in municipal solid waste (MSW) leachates consist of various metals and salts such as Cd, Fe, Pb, Zn, Mn, Na, Ca, Mg, K, and other inorganics including Cl and SO_4 . Biological and other parameters characterizing MSW

**FIGURE 9.8**

Schematic showing (a) leachate plume with contaminants and (b) contaminant plumes from a leaking underground storage tank and leaking buried pipeline.

leachates include biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), pH, total nitrogen (N) and total organic carbon (TOC). Typical organics found in MSW leachates include phenols, volatile acids, organic nitrogen, tannins, lignins, oil, and grease, and chlorinated hydrocarbons. One of the many problems encountered when various kinds of organic and inorganic chemicals and elements are combined in a mixture is the reactions that can occur between some of the constituents. For example, reactions between halogenated organics and metals will generate heat in a leachate stream. If this occurs in a relatively dry environment, fire will result. The same occurs when saturated aliphatic hydrocarbons and phenols interact with oxidizing mineral acids.

The constituents of leachate streams in hazardous waste landfills are intimately associated with the composition of the hazardous waste contained in the landfill. The contaminants of concern in the leachate streams are both inorganic and organic in nature. Heavy metals constitute the primary inorganic contaminants whereas the organic contaminants can cover a whole range of organic chemicals, from volatile organic chemicals (VOCs) to synthetic organic chemicals (SOCs). For both the MSW and hazardous waste landfills, the principal sets of problems, outside of the control and remediation-type problems, concern determination of the transport and fate of the contaminants. Knowledge or prediction of where, when, and extent of leachate penetration into the subsurface surroundings will provide one with (a) the requirements for a proper and effective subsurface monitoring program using monitoring wells and other sensing devices and (b) the possible scenarios for various management options and remedial actions. The procedures and requirements shown in Figure 9.7 in respect to surface discharge problems also apply to subsurface discharges. A summary of the various transport processes involving sorption

and partitioning of inorganic and organic contaminants was given in Chapter 2 together with a brief mention of the widely used transport relationship. A detailed treatment of these subjects can be found in Yong (2001) and Yong et al. (2010).

9.4 Contaminant Transport and Fate

Potential sources of contamination of subsurface water or groundwater (porewater and aquifers) other than inadvertent spills and deliberate dumping of hazardous materials, include landfills, underground storage tanks, waste piles and waste sites, underground injection wells, unplugged oil and gas wells, various kinds of surface impoundments and settling ponds, lands treated with pesticides, insecticides, fertilizers, and pipelines transporting carbon resources. Figure 9.8 shows many of these potential sources. The types of contaminants, their concentrations and proportions, and the transport of these in the subsoil and their fate are critical to the structuring of protective measures necessary for the protection of public health and the health of the land environment. The need for predictive tools is obvious.

Questions posed by regulators, investigators, containment facility designers, site remediation technologists, and all others working with containment and remediation of site contamination are summarized as follows:

- Source of contaminants? Nature of contaminant plume?
- Size of contaminant plume? Concentrations and distribution of the various contaminants in contaminant plume? Dominant toxic elements and contaminants in the contaminant plume?
- Where are the receptors? Paths to receptors? Source–pathways–receptors linkage?
- Rate of transport of contaminants? Can we predict its rate and extent of advance?
- Fate and/or persistence of the contaminants in the plume? Can we predict?
- Will contaminant plume threaten or contaminate water resources? Will contaminants pose threats to environment and health of biotic receptors?
- Measures for risk management? Risk tolerance?

9.4.1 Analytical and Predictive Tools

Analytical and predictive tools dealing with the fate and transport of contaminants must account for the following:

- Concentrations of the various target contaminant species
- Hydraulic conductivity of the subsurface material (soil)
- Diffusive capabilities of the target contaminants
- Hydrogeologic setting
- Partitioning potential of the target contaminants
- Solubility of the target contaminants
- Speciation, complexation, and products formed
- Abiotic and biotic reactions and transformations

The factors and elements to be considered fall conveniently into two groups: (1) transport and (2) reactions. Two types of analytical-computer models have been developed: (1) models dealing with fate and transport of contaminants and (2) models that take into account geochemical reactions and their products. By and large, most of the models dealing with fate and transport of contaminants are nonreactive models. This means to say that other than using the partitioning coefficients to account for sorption of contaminants from the porewater, no attempt is made to account for the chemical reactions in the soil-water system or that all reactions are immediate. In particular, speciation and complexations are not included in the structuring of the basic functions. Attempts have been made (and are being made) to develop reactive fate and transport models. In the second type of models, we have geochemical models that pay attention to geochemical speciation equilibria between the various phases (solids, liquid, and gaseous) in the subsurface setting. These include the dissolved and adsorbed elements in the various phases.

Assessment and prediction of the transport and fate of contaminants commonly rely on analytical and/or numerical (computer) models designed to take into account the various processes, site contamination situations, and properties of the contaminants and subsurface materials. These models are useful for regulatory agencies in risk management and performance assessment of target sites and situations, for operators of landfills, and for those involved in site remediation (Figure 9.9). The quality of models—i.e., how accurately their predictions accord with real performance—depends on how well they represent the real problem situation, the material properties, the nature of the contaminants involved, and processes involved. This requires not only proper and accurate problem

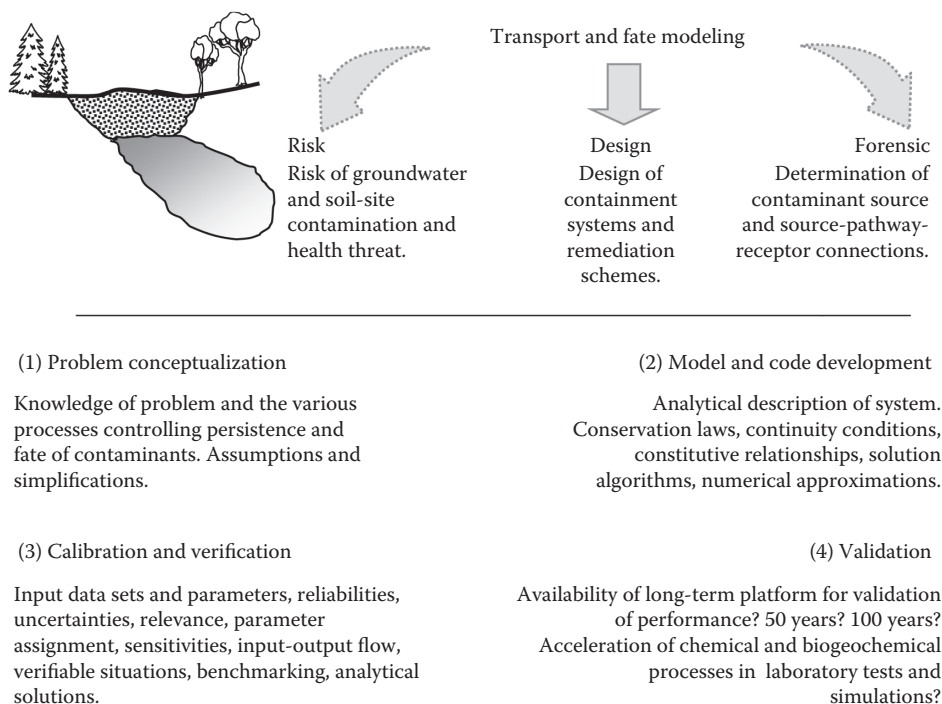


FIGURE 9.9

Principal objectives, issues, and requirements for contaminant transport and fate modeling.

conceptualization, but also the capability to render these into the appropriate mathematical relationships.

Problem conceptualization includes

1. Problem recognition. This encompasses more than an adequate description of the site and interacting elements. To structure the output requirements for the model and the manner in which the results need to be expressed, knowledge of the end purpose (use) of the results is required. The three different areas of application of models shown at the top of the illustration shown in Figure 9.9 (risk, design, forensic) will not have the same input and output requirements inasmuch as the decision-making process and the decisions required are different between them. Taking the problem of the contaminant plume emanating from the landfill, shown in the top left-hand corner of the figure, the differences between the outputs obtained from analysis (or prediction) of plume advance in respect to risk management, design of barrier systems, or determination of source–pathway–receptor are obvious.
2. Elements involved in the total system within the problem domain. In the example shown in Figure 9.10, the contaminant plume emanating from the landfill in Figure 9.10 passes through the capillary fringe before meeting the saturated zone under the water table. The elements involved in the example problem include not only the interacting elements typified by the soil fractions, porewater and contaminants, and microorganisms, but also the problem setting, i.e., the capillary fringe and water-saturated zone.
3. Mechanisms and processes of interactions between participating elements, initial and boundary conditions, and output requirements.

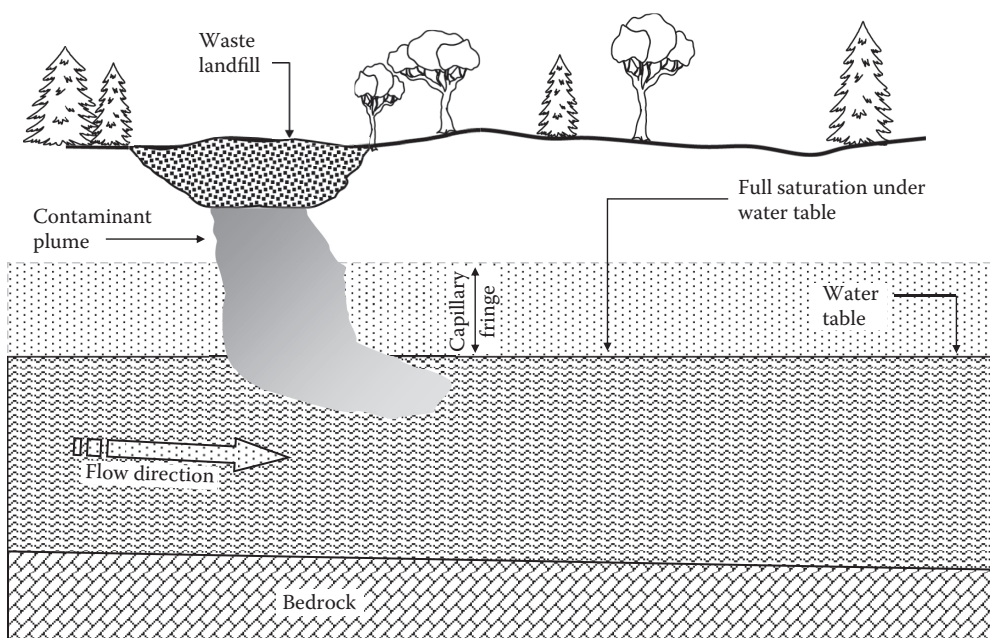


FIGURE 9.10

Schematic showing leachate plume as a contaminant plume spreading downward toward the water table and spreading in the direction of flow of the groundwater.

9.4.2 Basic Elements of Interactions between Dissolved Solutes and Soil Fractions

Interactions occurring between contaminants in the porewater, which are essentially dissolved solutes and reactive soil particle surfaces, are responsible for the transfer of these solutes from the porewater to the soil particle surfaces. These interactions or processes are called *partitioning*. Molecular interactions governing sorption of contaminants are essentially electrostatic in nature. They are coulombic interactions between nuclei and electrons. Of particular importance are the interatomic bonds such as the ionic, covalent, hydrogen, and van der Waals. Ionic forces are coulombic forces. These are forces between positively and negatively charged atoms and the bonds formed are called ionic or electrovalent bonds. The simplest example of ionic bonding is between a sodium atom and a chlorine atom, resulting in the formation of NaCl. The strength of the attractive forces, and hence the strength of the ionic bonds decrease as the square of the distance separating the atoms.

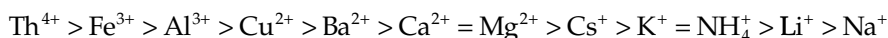
Another example of ionic bonding is the bond established between the oxygen from a water molecule to the oxygen on a clay particle's surface. This is due to the hydrogen atom, which can attract two electronegative atoms, and the ionic bond formed is called the *hydrogen bond*. In comparison to other bonds between neutral molecules, the hydrogen bond is a strong bond. Hydrogen bonding between two oxygen atoms, which are electronegative, is important in bonding layers of clay minerals together, in holding water at the clay surface, and in bonding organic molecules to clay particle surfaces.

Van der Waals forces of attraction can be categorized into three components: (1) Keesom forces developed as a result of dipole orientation, (2) Debye forces developed due to induction, and (3) London dispersion forces. Adsorption of organic anions onto clay particle surfaces can be in the form of (a) anion associated directly with cation or (b) anion associated with cation via a water bridge, referred to as a *cation bridge*. The process consists of replacement of a water molecule from the hydration shell of the exchangeable cation by an oxygen or an anionic group, e.g., carboxylate or phenate of the organic polymer. Hydrogen bonding to the oxygens of siloxane (mica-type) surfaces of clay particles are generally weak bonds. Adsorption of the organic anion is readily reversible by exchange with chloride or nitrate ions.

Cation exchange in soils refers to the exchange of positively charged ions associated with clay particle surfaces. The process is stoichiometric and electroneutrality at the clay particle surfaces must be satisfied. Cations will be attracted to the reactive soil particle surfaces in accordance with the relationship, $M_s/N_s = M_o/N_o = 1$, where M and N represent the cation species and the subscripts s and o represent the surface and the bulk solution, respectively. *Exchangeable cations* are cations that can be readily replaced by other cations of equal valence or by two of one half the valence of the original one. Thus, for example, if a clay containing sodium as an exchangeable cation is washed with a solution of calcium chloride, each calcium ion will replace two sodium ions, and the sodium can be washed out in the solution.

The quantity of exchangeable cations held by the soil is called the *cation exchange capacity* (CEC) of the soil and is expressed as milliequivalents per 100 g of soil (meq/100 g soil). One milliequivalent is equal to 6.023×10^{20} cation exchange sites in the soil. The CEC is a measure of the amount of amount of negatives sites associated with the soil fractions. The predominant exchangeable cations in soils are calcium and magnesium, with smaller amounts of potassium and sodium. The valence of cations plays a significant role in the exchange process. Higher valence cations will show greater replacing power. The higher the charge, the higher is its attraction to exchange sites. The converse also holds true, i.e., higher valence cations at the surfaces of clay particles will be more difficult to replace. The

replacing power or the strength of attraction of cations the soil particle surfaces is given by the lytropic series. An example of some typical cations and the replacing power is given as follows:



Exchange–equilibrium equations can be used to determine the proportion of each exchangeable cation to the total CEC as the outside ion concentration varies. The simplest of these is the Gapon relationship:

$$\frac{M_e^{+m}}{N_e^{+n}} = K \frac{\left[M_o^{+m} \right]^{\frac{1}{m}}}{\left[N_o^{+n} \right]^{\frac{1}{n}}}, \quad (9.1)$$

where m and n refer to the valence of the cations and the subscripts e and o refer to the exchangeable and bulk solution ions, respectively. The constant K is dependent on the effects of specific cation adsorption and the nature of the clay surface. K decreases in value as the surface density of charges increases.

The adsorption of ions due to the mechanism of electrostatic bonding is called *physical adsorption* or *nonspecific adsorption*. The ions involved in this type of process are identified as *indifferent ions*. The other mechanism of ion adsorption is a chemical reaction that involves covalent bonds and activation energy in the process of adsorption. This type of adsorption process is generally identified as *chemisorption* or *specific adsorption* and occurs at specific sites. *Specific cation adsorption* refers to the situation where the ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via the O and OH groups to the structural cations. It is useful to note that when the energy barrier is overcome by the activation energy (in the chemisorption process), desorption of the ions will not be easily accomplished since desorption energy requirements may be prohibitively large. This has considerable significance in the evaluation of contaminant–soil interaction, especially with respect to the environmental mobility of sorbed contaminants. Chemisorption and adsorption on soil particle surfaces involving siloxane cavities are generally confined to the surface layer and the monolayer next to the electrified interface. To obtain a better picture of the adsorption processes at the surface monolayer and beyond, we need to look more closely into the various energies of interaction developed. In short, the net energy of interaction due to adsorption of a solute ion or molecule onto the surfaces of the soil fractions is the result of both short range chemical forces such as covalent bonding, and long range forces such as electrostatic forces. Furthermore, sorption of inorganic contaminant cations is related to their valences, crystallinities, and hydrated radii.

9.4.3 Elements of Abiotic Reactions between Organic Chemicals and Soil Fractions

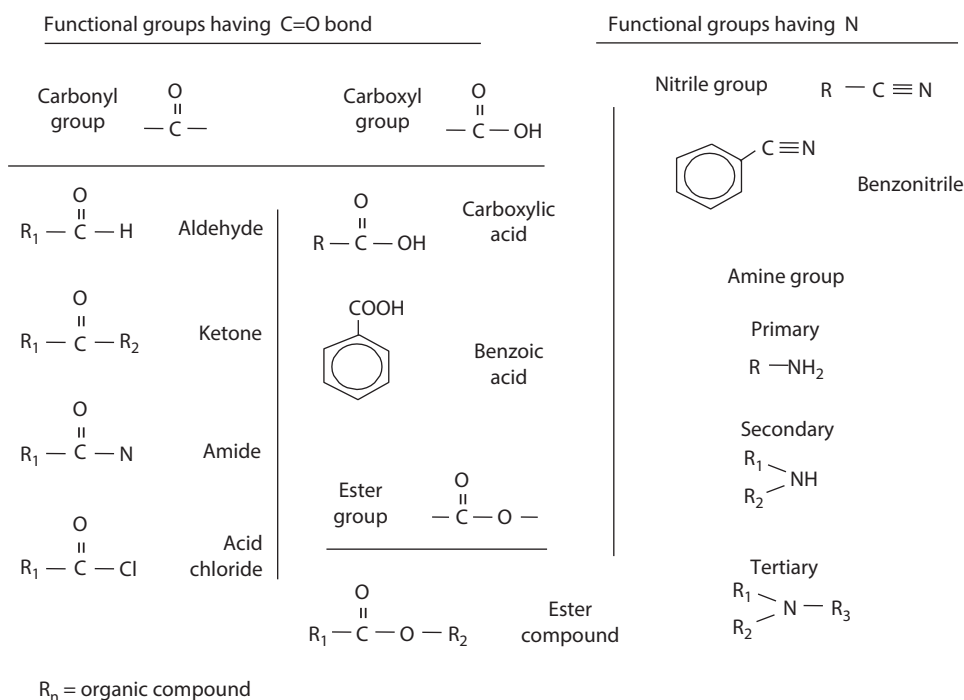
Abiotic adsorption reactions or processes involving organic chemicals and soil fractions are governed by (a) the surface properties of the soil fractions, (b) the chemistry of the pore-water, and (c) the chemistry and physical–chemistry of the contaminants. Mechanisms pertaining to ion exchange involving organic ions are essentially similar to those between inorganic contaminants and soil fractions. The adsorption of the organic cations is related to the molecular weight of the organic cations. Large organic cations are adsorbed more

strongly than inorganic cations by clays because they are longer and have higher molecular weights. Organic chemical compounds develop mechanisms of interactions at the molecular level that include

- *London-van der Waals forces*: These have been described previously and include the three types: Keesom, Deybe, and London dispersion forces.
- *Hydrophobic reactions and bonding*: Organic chemical molecules bond onto hydrophobic soil particle surfaces because this requires the least restructuring of the original water structure in the pore spaces of the soil. For soil organic matter (SOM), the fulvic acids are by and large hydrophilic. These kinds of organic matter have the least influence on the structuring of water. Meanwhile, the SOM humins are highly hydrophobic. These have considerable influence on the restructuring of the water structure.
- *Hydrogen bonding and charge transfer*: hydrogen bonding is a special case of charge transfer complex formation. These are complexes formed between the electron donor and the electron acceptor. The bonding between the aromatic groups in SOM and organic chemicals is an example of charge transfer.
- *Ligand and ion exchange*: The bonding process requires that the organic chemical possesses a higher chelating capacity than the replaced ligand.
- *Chemisorption*: For soils and contaminants, the process of chemical adsorption involves chemical bonding between the contaminant molecule or ion in the pore-water and the reactive soil particle surfaces. The process is sometimes called *specific adsorption* and the bonds are covalent bonds.

The functional groups for organic chemical compounds (organic chemical contaminants) are either acidic or basic. The characteristics and properties of these groups in organic molecules, such as shape, size, configuration, polarity, polarizability, and water solubility are important in the adsorption of the organic chemicals by the soil fractions. The various functional groups associated with organic chemical contaminants have been described in Section 2.5.2 of Chapter 2. A summary of some of these groups is shown in Figure 9.11. These include the hydroxyl group (alcohols and phenols), the carboxyl group (COOH), carbonyl (CO), and the amines (primary, secondary, and tertiary). The carbonyl group technically includes the carboxyl group, and is considered to be the most important functional group in organic chemistry. Most of the organic chemical contaminants found in the ground contain the carbonyl group. These chemicals are associated with production of pharmaceuticals, synthetic chemicals, and synthetic materials.

Not shown in the illustrations in Figure 9.11 are the hydroxy (OH) compounds. These are the compounds that contain the hydroxyl functional group. The two main groups are (1) aliphatic and (2) aromatic. The aliphatic compounds are the alcohols and the aromatics are the phenols. Alcohols are hydroxyl alkyl compounds (R-OH), with a carbon atom bonded to the hydroxyl group. The more familiar ones are CH₃OH (methanol) and C₂H₅OH (ethanol). Adsorption of the hydroxyl groups of alcohol can be obtained through hydrogen bonding and cation–dipole interactions. Most primary aliphatic alcohols form single layer complexes on the negatively charged surfaces of the soil fractions, with their alkyl chain lying parallel to the surfaces of the soil fractions. Phenols, meanwhile, are compounds that possess a hydroxyl group attached directly to an aromatic ring. As with the carbonyl functional group, the various hydroxy compounds are widely used and can be found in the

**FIGURE 9.11**

Some common functional groups for organic chemical contaminants.

manufacture of industrial products and pharmaceutical agents. Both alcohols and phenols can function as weak acids and weak bases.

Functional groups exert considerable influence on the characteristics of organic compounds, and contribute significantly to the processes that control accumulation, persistence, and fate of the organic chemical compounds in soil. Organic chemicals with C=O bond functional groups and nitrogen-bonding functional groups (see Figure 9.11) are fixed or variable-charged organic chemical compounds. They can acquire a positive or negative charge through dissociation of H^+ from or onto the functional groups depending on the dissociation constant of each functional group and the pH of the soil–water system. An increase in the pH of the soil–water system will cause these functional groups (i.e., groups having a C=O bond) to dissociate. The outcome of the release of H^+ is a development of negative charges for the organic chemical compounds. Charge reversal (i.e., from positive to negative charges) could lead to the release of organic chemical contaminants held originally by cation bonding to the negatively charged reactive surfaces of the soil particles. The phenomenon is a particular case of environmental mobility of previously sorbed contaminants.

9.4.4 Reactions in Porewater

Since contaminants consist of both inorganic and organic chemicals, it is more convenient to use the Brønsted-Lowry concept of acids and bases to describe the various reactions, and interactions occurring in a soil–water–contaminant system. In the Brønsted-Lowry

concept, an *acid* is a substance that has a tendency to lose a proton (H^+), and conversely, a *base* is a substance that has a tendency to accept a proton. With this acid–base scheme, an *acid* is a *proton donor*. It is a *protogenic* substance. Similarly, a *base* is a *proton acceptor*, i.e., it is a *protophilic* substance. Water is both a *protophilic* and a *protogenic* solvent, i.e., it is *amphiprotic* in nature. It can act either as an acid or as a base. It can undergo self-ionization, resulting in the production of the conjugate base OH^- and conjugate acid H_3O^+ . The self-ionization of water is called *autoprotolysis*. *Neutralization* is the reverse of autoprotolysis. Substances that have the capability to both donate and accept protons such as water and alcohols are called *amphiprotic* substances.

Chemical reactions in the porewater include (a) acid–base reactions and hydrolysis, (b) oxidation–reduction (redox) reactions, (c) speciation and complexations. Acid–base reactions and equilibrium in the porewater have important consequences on the partitioning and transport of contaminants in the soil. Acid–base reactions are *protolytic* reactions resulting from a process called *protolysis*, i.e., proton transfer between a proton donor (acid) and a proton acceptor (base).

To assess the bonding and partitioning relationships between heavy metals and soil solids, it is useful to use the Lewis (1923) concept of acids and bases. This concept defines an acid as a substance that is capable of accepting a pair of electrons for bonding, and a base as a substance that is capable of donating a pair of electrons. This means that *Lewis acids* are electron acceptors, and *Lewis bases* are electron donors. All metal ions M^{nx} are Lewis acids. The Lewis acid–base concept permits us to treat metal–ligand bonding as acid–base reactions. Hydrated metal cations can act as acids or proton donors, with separate *pk* values for each. The dissociation constant *k* is a measure of the dissociation of a compound. This constant *k* is generally expressed in terms of the negative logarithm (to the base 10) of the dissociation constant, i.e., $pk = -\log(k)$. The smaller the *pk* value, the higher is the degree of ionic dissociation, and the more soluble is the substance. A comparison of the various *pk* values between compounds will tell us which compound would be more or less soluble in comparison to a target compound.

Oxidation–reduction reactions involve the transfer of electrons between the reactants and the activity of the electron e^- in the chemical system plays a significant role. There is a link between redox reactions and acid–base reactions since the transfer of electrons in a redox reaction is accompanied by proton transfer. Redox reactions involving inorganic solutes result in a decrease or increase in the oxidation state of an atom. Organic chemical contaminants, meanwhile, show the effects of redox reactions through the gain or loss of electrons in the chemical. Biotic redox reactions are of greater significance than abiotic redox reactions. These reactions are significant factors in the processes that result in the transformation, persistence, and fate of organic chemical compounds in soils.

The stability of inorganic solutes in the porewater is a function of such factors as pH, the presence of ligands, temperature, concentration of the inorganic solutes, and the *Eh* or *pE* of the porewater. *Eh* is the redox potential and *pE* is a mathematical term that represents the negative logarithm of the electron activity e^- . The redox potential *Eh* is a measure of electron activity in the porewater, and is described by the following relationship:

$$Eh = E^0 + \left(\frac{RT}{nF} \right) \ln \frac{a_{i,ox}}{a_{i,red}}, \quad (9.2)$$

where E^0 is the standard reference potential, *n* is the number of electrons, *R* is the gas constant, *T* is the absolute temperature, *F* is the Faraday constant, a_i is the activity of the *i*th

species, and the subscripts *ox* and *red* refer to the oxidized and reduced *i*th species. At a temperature of 25°C, the relationship between Eh and pE will be obtained as $Eh = 0.0591 pE$. Figure 9.12 (from Yong, 2001) shows the pE – pH diagram for Fe and water with a maximum soluble Fe concentration of 10^{-5} M. As can be seen, the valence state of the reactants is a function of the pH – pE status.

Speciation and complexations are central to the processes that control the fate of heavy metals in soils. Speciation refers to the formation of complexes between heavy metals and ligands in the aqueous phase (porewater). In a soil–water system, speciation provides competition between the ligands and the reactive soil solids for sorption of heavy metals. Various dissolved solutes in the porewater participate in the aqueous and surface complexation that are characteristic of the interactions between the solutes and the reactive soil particles. These interactions impact directly on the predictions of contaminant transport, and especially modeling procedures that rely on the use of simple partition coefficients. For example, Cl^- ions, sulfates, and organics can form complexes with heavy metals. The result of this is seen as a lesser amount sorbed onto the soil particles—i.e., a lower adsorption isotherm performance—and a larger amount of the target heavy metal transported in the porewater. In other words, the environmental mobility of heavy metals is enhanced with speciation and complexation. Studies on Cd adsorption by kaolinite soil particles indicate that the Cd that were not adsorbed by the soil were in the form of $CdCl_2^0$, $CdCl_3^-$ and $CdCl_4^{2-}$ (Yong and Sheremata, 1991). The amount of Cd not adsorbed by the kaolinite soil particles in the presence of Cl^- was due to (a) a decrease in activity due to the presence of NaCl, (b) competition from Na^+ for adsorption sites, and (c) complexation of Cd^{2+} as negative and neutral chloride complexes. With increasing pH values, there is a tendency for Cd to be removed from the porewater as hydroxides, and if the pH is above the precipitation pH of Cd, precipitation of the Cd onto clay particle surfaces is likely. At pH values higher than the isoelectric point (iep), Cd is more likely to remain in solution in the presence

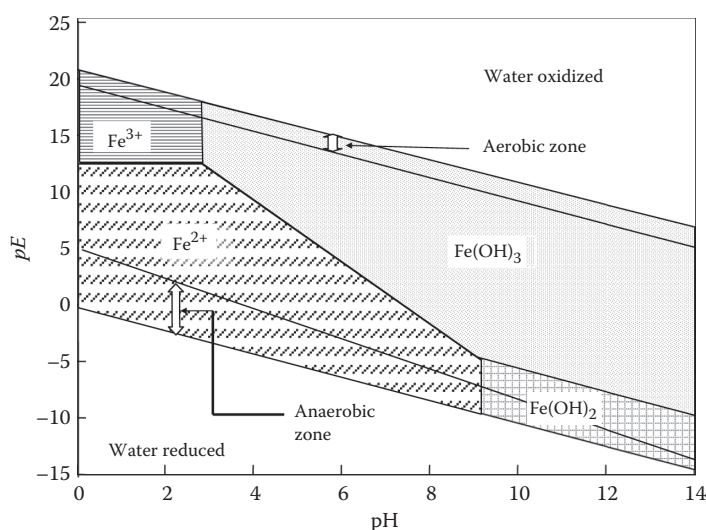


FIGURE 9.12

pE – pH chart for Fe and water with maximum soluble Fe concentrations of 10^{-5} M. The zone sandwiched between the aerobic and the anaerobic zones is the transition zone. (From Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, 307 pp., 2001.)

of Cl^- than in the presence of ClO_4^- . This is the result of competition of Cl^- with OH^- for formation of complexes with the Cd^{2+} that were not sorbed by the kaolinite soil.

9.5 Surface Complexation and Partitioning

As opposed to speciation and complexation in the aqueous phase (porewater), surface complexation refers to the complexes formed by the inorganic contaminants and the reactive sites on the soil particle surfaces. Surface complexation includes several mechanisms of solute–particle surface interaction, described broadly as sorption mechanisms. These have been discussed previously as nonspecific adsorption, specific adsorption, and chemisorption. The processes involved have been described as coulombic molecular interactions, with bonds formed that include ionic, covalent, and van der Waals.

The result of surface complexation is partitioning. We describe *partitioning* of contaminants as the transfer of contaminants in the porewater to the soil solids as a result of sorption mechanisms between the two. This is also called mass transfer (of contaminants). Section 2.5.3 of Chapter 2 has considered the partitioning of contaminants in a very general manner. Partitioning, as a phenomenon, includes the transfer of both inorganic and organic chemical contaminants. This is an important phenomenon since this is the outcome of one of the fundamental processes that determines the persistence and fate of contaminants. In the case of organic chemicals, the processes involved include London-van der Waals forces, hydrophobic reactions, hydrogen bonding and charge transfer, ligand and ion exchange, and chemisorption. In this section, we will be examining partitioning of both inorganic contaminants and organic chemicals in greater detail. Although there may be some similarity in mass transfer mechanisms in the partitioning of inorganic solutes and organic chemicals, it is generally more convenient to consider these separately.

9.5.1 Partitioning of Inorganic Contaminants

A popular measure of partitioning of inorganic and organic chemical contaminants is the partition coefficient k_p . Chapter 2 has given a very brief description of the general types of partition coefficients. In brief, partition coefficients describe the relationship between the amount of contaminants transferred onto soil particles (sorbed by the soil particles) and the equilibrium concentration of the same contaminants remaining in the porewater (Figure 9.13). The popular relationships such as Langmuir and Freundlich are shown in Figure 2.15 in Chapter 2. To distinguish between partition coefficients obtained using different laboratory techniques, the term *distribution coefficient* k_d is often used to denote partitioning of contaminants obtained with batch equilibrium adsorption isotherm procedures. By and large, the distribution coefficient is the partition coefficient most commonly used to describe partitioning of heavy metals and other inorganic solutes.

What is the significance of partitioning? It is necessary to bear in mind that *partitioning* is the result of mass transfer of contaminants from the porewater onto the soil particles. How one determines the results of mass transfer (i.e., partitioning) can be a contentious issue, and can severely affect one's prediction of the transport and fate of contaminants under consideration. A quantitative determination of partitioning, such as the distribution coefficient k_d , is needed in many mathematical relationships structured to evaluate the fate of contaminants transporting in a soil system. For example, Equation 2.2 in Chapter 2 uses

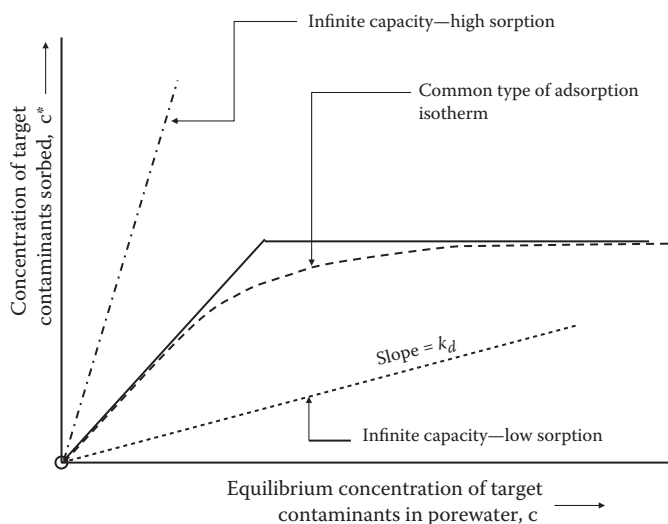
**FIGURE 9.13**

Illustration of partitioning of target contaminants between contaminants in porewater and contaminants sorbed by soil particles. Note that unless limits are placed on the maximum sorption capacity of the soils, specification of constant k_d values means infinite sorption capacity by the soil particles in the soil–water system.

the distribution coefficient k_d as a key parameter in the relationship used to predict the transport of contaminants in a saturated soil.

There are at least two broad issues regarding the determination and use of the distribution coefficient k_d : (1) the types of tests used to provide information for determination of k_d , and (2) range of applicability of k_d in transport and fate predictions. We will discuss the former in this section and leave the latter discussion for a later section where the problem of prediction of transport and fate of contaminants is addressed. Laboratory tests used to provide information on the mass transfer of contaminants from the porewater onto soil solids are the most expedient means to provide one with information on the partitioning of contaminants. By and large, these tests provide only the end result of the mass transfer, and not direct information on the basic mechanisms responsible for partitioning.

The distribution coefficient k_d is determined from information gained using batch equilibrium tests on soil solutions. Ratios of 10 or 20 parts solution to 1 part soil are generally used, and the candidate or target contaminant is part of the aqueous phase of the soil solution. In many laboratory test procedures, the candidate soil is used in the soil solution, and the candidate or target contaminant is generally a laboratory-prepared contaminant, e.g., PbNO_3 for assessment of sorption of Pb as a contaminant heavy metal. Since the soil particles are in a highly dispersed state in the soil solution, one would expect that all the surfaces of all the particles are available for interaction with the target contaminant in the aqueous phase of the soil solution. Using multiple batches of soil solution where the concentration of the target contaminant is varied, and by determining the concentration of contaminants sorbed onto the soil solids and remaining in the aqueous phase, one will obtain characteristic adsorption isotherm curves such as those shown in Figures 9.13 and 2.15. The slope of the adsorption isotherm defines k_d .

Consider the illustration shown in Figure 9.14. This schematic compares the loose structure or dispersed state of soil particles in a soil suspension (bottom illustration) with an aggregation of a multitude of particles constituting a microstructural unit that

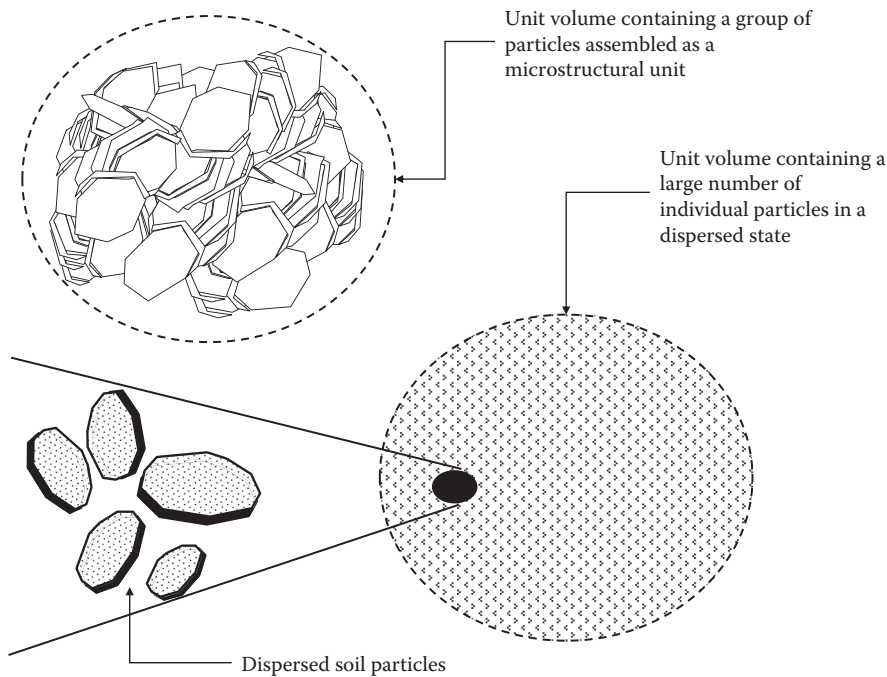
**FIGURE 9.14**

Illustration of influence of soil structure on availability of exposed reactive soil particle surfaces for sorption of contaminants. The dispersed particles are typical of soil suspensions used for batch equilibrium test for determination of adsorption isotherms, whereas the microstructural unit is typical of soil structures in subsurface soils.

is representative of a soil structure in a natural soil subsurface environment (top illustration). The schematic shows that although the two identical unit volumes do not necessarily contain the same number of particles, a relatively small proportion of the reactive particle surfaces in the microstructural unit is available for interaction with the contaminants in the porewater.

Distribution coefficients k_d obtained from adsorption isotherms using the batch equilibrium with soil solutions and prepared target contaminants are very useful in that they define the upper limit of partitioning of the target contaminant. Problems or pitfalls arising from the application of k_d values reported in the literature for use in models to predict actual fate and transport of contaminants in the natural subsoil can be traced to

- Inappropriate use of the coefficient, i.e., using the reported k_d value to represent partitioning effects in a natural compact subsoil. This can arise from a lack of appreciation or knowledge of the particulars of the batch equilibrium tests. If the tests were conducted to provide the upper limit of partitioning, as has been described, the model would overpredict sorption and therefore underpredict transport.
- Major differences in the composition of the leachate and contaminants in the leachate plume being modeled. Unless the batch equilibrium tests were conducted with actual leachates from the site under consideration, it is inappropriate to use results from single-species contaminant tests to represent multispecies behavior. In any

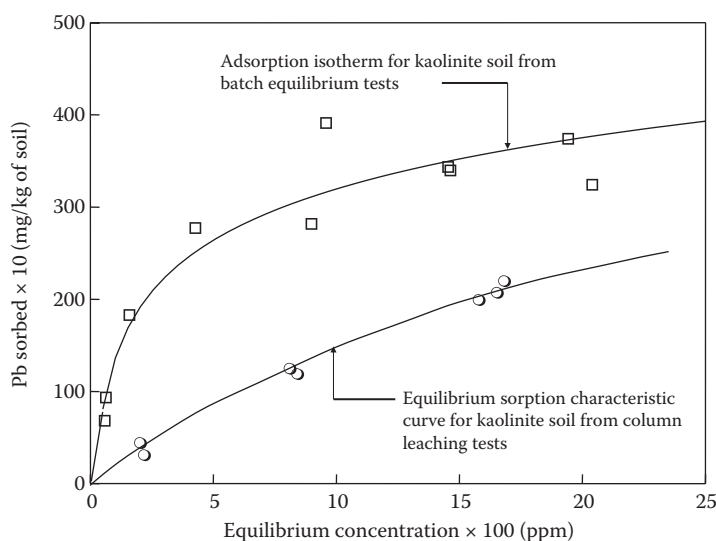


FIGURE 9.15

Comparison of Pb sorption curves obtained from batch equilibrium and column leaching tests for kaolinite soil. (From Yong, R.N., *Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press, Boca Raton, 307 pp., 2001.)

event, it needs to be remembered that the k_d values would be upper limit values. Competition for sorption sites, preferential sorption, and speciation–complexation are some of the major factors that would directly affect the nature of the adsorption isotherm obtained.

For assessment of partitioning using soils in their natural compact state, it is necessary to conduct column leaching or cell diffusion tests. In these kinds of tests, the natural soil is used in the test cell or column, and either laboratory-prepared candidate contaminants or natural leachates are used. The partition coefficient deduced from the test results is not the distribution coefficient identified with the adsorption isotherms obtained from batch equilibrium tests. Instead, the partition coefficients obtained from column leaching or cell diffusion tests need to be properly differentiated from the traditional k_d . Yong (2001) has suggested that these partition coefficients be called *sorption coefficients* to reflect the sorption performance of the soils in their natural state in the column or cell. The disadvantages in conducting column leaching and cell diffusion tests are (a) the greater amount of effort required to conduct the tests, (b) the much greater length of time taken to obtain an entire suite of results, and (c) inability to obtain exact replicate soil structures in the companion columns or cells. The results indicate that the characteristic curves obtained from column leaching tests, for example, are much lower than corresponding adsorption isotherms. Figure 9.15 gives an example.

9.5.2 Organic Chemical Contaminants

The partitioning of organic chemical contaminants is a function of several kinds of interacting mechanisms between the organic chemicals and the soil solids in the natural soil–water system that constitutes the subsoil. A key factor in the development of the kinds

of interaction mechanisms is the type or class of organic chemicals. The degree of water miscibility of the organic chemical appears to be a key element. A good example of this is the difference between nonaqueous phase liquids (NAPLs) and water miscible alcohols. The family of NAPLs include those that are denser and lighter than water. The DNAPLs (dense NAPLs) include the organohalides and oxygen-containing organic compounds, and the LNAPLs (light NAPLs) include gasoline, heating oil, kerosene, and aviation fuel. Most NAPLs are partially miscible in water. Consideration of the transport of NAPLs in the saturated zone requires attention to two classes of substances: (1) miscible or dissolved substances and (2) immiscible substances.

The basic processes involved in transport and fate of NAPLs are demonstrated in Figure 9.16. The chemical properties that affect NAPL transport and fate include (1) volatility, (2) relative polarity, (3) affinity for SOM or organic contaminants, and (4) density and viscosity. The higher the vapor pressure of the substance, the more likely it is to evaporate. Movement in the vapor phase is generally by advection. At equilibrium between NAPLs and the vapor phase, the equilibrium partial pressure of a component is directly related to the mole fraction and the pure constituent vapor pressure, as described by Raoult's law. Designating P_i as the partial pressure of the constituent, x_i as the mole fraction of the constituent, and P_i^0 as the vapor pressure of the pure constituent, Raoult's law states that when equilibrium conditions are obtained, and when the mole fraction of a constituent is greater than 0.9, $P_i = x_i P_i^0$.

As Figure 9.16 shows, an organic chemical compound in the soil may be partitioned between the soil–water, soil–air, and the solid soil constituents. The rate of volatilization of an organic molecule from an adsorption site on the solid phase in the soil (or in solution

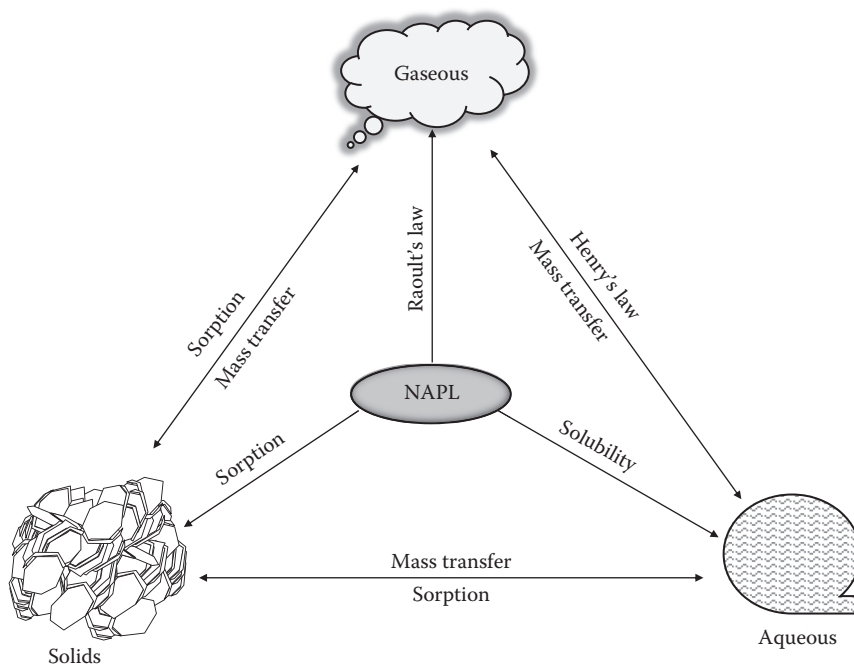


FIGURE 9.16

Processes involved in partitioning and fate of NAPLs.

in the soil water) to the vapor phase in soil air and then to the atmosphere is dependent on many physical and chemical properties of both the chemical and the soil, and on the process involved in moving from one phase to another. The three main distribution or transport processes involved are

1. Compound in soil solids \leftrightarrow compound in solution
2. Compound in solution \leftrightarrow compound in vapor phase in soil air
3. Compound in vapor phase in soil air \rightarrow compound in atmosphere

Partitioning of a chemical among the three phases can be estimated from either vapor or solution phase desorption isotherms. The process by which a compound evaporates in the vapor phase to the atmosphere from another environmental compartment is defined as volatilization. This process is responsible for the loss of chemicals from the soil to the air and is one of the factors involved in the persistence of an organic chemical. Determination of volatilization of a chemical from the soil to the air is most often achieved using theoretical descriptions of the physical process of volatilization based on Raoult's law and Henry's law. The rate at which a chemical volatilizes from soil is affected by soil and chemical properties, and environmental conditions. Some of the properties of a chemical involved in volatilization are its vapor pressure, solubility in water, basic structural type, and the number, nature and position of its basic functional groups. Other factors affecting volatilization rate include adsorption, vapor density, and water content of the soil in the subsurface.

Adsorption impacts directly on the chemical activity by reducing it to values below that of the pure compound. In turn, this affects the vapor density and the volatilization rate since vapor density is directly related to the volatilization rate. Vapor density is the concentration of a chemical in the air, the maximum concentration being a saturated vapor. The role of water content is seen in terms of competition for adsorption sites on the soil. Displacement of nonpolar and weakly polar compounds by water molecules can occur because of preferential sorption (of water). Hydrates—i.e., hydration layer on the soil particle surfaces—will increase the vapor density of weakly polar compounds. If dehydration occurs, the compound sorbs onto the dry soil particles. This means that the chances for volatilization of the organic chemical compound are better when hydrates are present.

When a vapor is in equilibrium with its solution in some other solvent, the equilibrium partial pressure of a constituent is directly related to the mole fraction of the constituent in the aqueous phase. Once again, designating P_i as the partial pressure of the constituent, X_i as the mole fraction of the constituent in the aqueous phase, and H_i as Henry's constant for the constituent, Henry's law states that: $P_i = H_i X_i$. By and large, so long as the activity coefficients remain relatively constant, the concentrations of any single molecular species in two phases in equilibrium with each other will show a constant ratio to each other. This assumes ideal behavior in water and the absence of significant solute-solute interactions and also absence of strong specific solute-solvent interactions.

Partitioning of organic chemicals is most often described by the partition coefficient k_{ow} . This is the octanol-water partition coefficient and has been widely adopted in studies of the environmental fate of organic chemicals. The octanol-water partition coefficient is sometimes known as the *equilibrium partition coefficient*, i.e., coefficient pertaining to the ratio of the concentration of a specific organic contaminant in other solvents to that in water. Results of countless studies have shown that this coefficient is well correlated to water solubilities of most organic chemicals. Since *n*-octanol is part lipophilic and part hydrophilic (i.e., it is amphiphilic), it has the capability to accommodate organic chemicals

with the various kinds of functional groups. The dissolution of *n*-octanol in water is roughly eight octanol molecules to 100,000 water molecules in an aqueous phase. This represents a ratio of about one to twelve thousand (Schwarzenbach et al., 1993). Since water-saturated *n*-octanol has a molar volume of 0.121 L/mol as compared with 0.16 L/mol for pure *n*-octanol, the close similarity permits one to ignore the effect of the water volume on the molar volume of the organic phase in experiments conducted to determine the octanol–water equilibrium partition coefficient. The octanol–water partition coefficient k_{ow} has been found to be sufficiently correlated not only to water solubility, but also to soil sorption coefficients. In the experimental measurements reported, the octanol is considered to be the surrogate for SOM.

Organic chemicals with k_{ow} values less than 10 are considered to be relatively hydrophilic—with high water solubilities and small soil adsorption coefficients. Organic chemicals with k_{ow} values greater than 10^4 are considered to be very hydrophobic and are not very water-soluble. Chiou et al. (1982) has provided a relationship between k_{ow} and water solubility S as follows:

$$\log k_{ow} = 4.5 - 0.75 \log S \text{ (ppm)}.$$

Aqueous concentrations of hydrophobic organics such as polyaromatic hydrocarbons (PAH) in natural soil–water systems are highly dependent on adsorption/desorption equilibrium with sorbents present in the systems. Studies of compounds that included normal PAHs, nitrogen and sulfur heterocyclic PAHs, and some substituted aromatic compounds suggest that the sorption of hydrophobic molecules (benzidine excepted) is governed by the organic content of the substrate. The dominant mechanism of organic adsorption is the hydrophobic bond established between a chemical and natural organic matter in the soil. The extent of sorption can be reasonably estimated if the organic carbon content of the soil is known (Karickhoff, 1984) using the expression: $k_p = k_{oc} f_{oc}$, where f_{oc} is the organic carbon content of the SOM, k_{oc} is the organic content coefficient, and k_p is the linear Freundlich isotherm obtained for the target organic chemical. This approach works reasonably well in the case of high organic contents (e.g., $f_{oc} > 0.001$). Relationships reported in the literature relating k_{ow} to k_{oc} show that these can be grouped into certain types of organic chemicals. For PAHs, the relationship given by Karickhoff et al. (1979) is

$$\log k_{oc} = \log k_{ow} - 0.21.$$

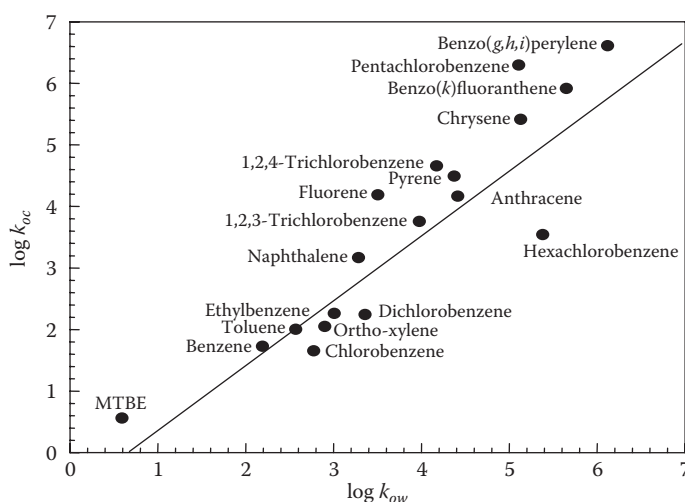
For pesticides, Rao and Davidson (1980) report that

$$\log k_{oc} = 1.029 \log k_{ow} - 0.18.$$

For chlorinated and methylated benzenes, the relationship given by Schwarzenbach and Westall (1981) is

$$\log k_{oc} = 0.72 \log k_{ow} + 0.49.$$

The graphical relationship shown in Figure 9.17 uses some representative values reported in the various handbooks (e.g., Verscheuren, 1983; Montgomery and Welkom, 1991) for $\log k_{ow}$ and $\log k_{oc}$. The values used for $\log k_{ow}$ are essentially midrange results reported in the handbooks and in many studies. Not all $\log k_{oc}$ values are obtained as measured values. Many of these have been obtained through application of the various $\log k_{oc}$ – $\log k_{ow}$

**FIGURE 9.17**

Relationship of $\log k_{oc}$ with $\log k_{ow}$ for several organic compounds. (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

relationships reported in the literature, e.g., Kenaga and Goring (1980), Karickhoff et al. (1979). The linear relationship shown by the solid line in Figure 9.17 is given as

$$\log k_{oc} = 1.06 \log k_{ow} - 0.68.$$

This graphical relationship is useful in the sense of partitioning of the organic chemical compounds shown in the diagram. Yong and Mulligan (2004) have discussed some of the pertinent correlations, stating, for example, in regard to the k_{oc} values shown in Figure 9.17 for dichlorobenzene, that they indicate that it partitions well to sediments, and particularly to the organic fractions (SOM). Because of its resistance to anaerobic degradation, it is very persistent.

9.6 Persistence and Fate

One of the many necessary actions needed along the path toward land environment sustainability is to return contaminated land to its uncontaminated state. This requires one to clean up contaminated sites. The problem of concern in remediation of contaminated sites is the persistence of contaminants in the site. In many instances, natural attenuation can be relied upon as a remediation tool—a sort of natural self-remediation process that is intrinsic to the site properties—as will be discussed in Chapter 10. There exists, however, several kinds of contaminants that are not easily “self-remediated” with natural attenuation processes. These contaminants fall under the general class of persistent pollutants. The term *persistence* has been defined as *the continued presence of a contaminant (pollutant) in the substrate*. The persistence of inorganic and organic contaminants differs in respect to meaning and application. The persistence of heavy metals refers to their continued

presence in the subsurface soil regime in any of their individual oxidation states and in any of the complexes formed. Organic chemical contaminants, meanwhile, can undergo considerable transformations because of microenvironmental factors. We define *transformation* to mean the conversion of the original organic chemical contaminant into one or more resultant products by processes that can be abiotic, biotic, or a combination of these. The intermediate products obtained from transformation of organic chemical compounds by biotic processes along the pathway toward complete mineralization are generally classified as degradation products. Transformed products resulting from abiotic processes in general do not classify as being intermediate products along the path to mineralization. They are, however, not easily distinguished because some of the abiotic transformed products themselves may become more susceptible to biotic transformations. When this occurs, the process is known as a combination transformation process.

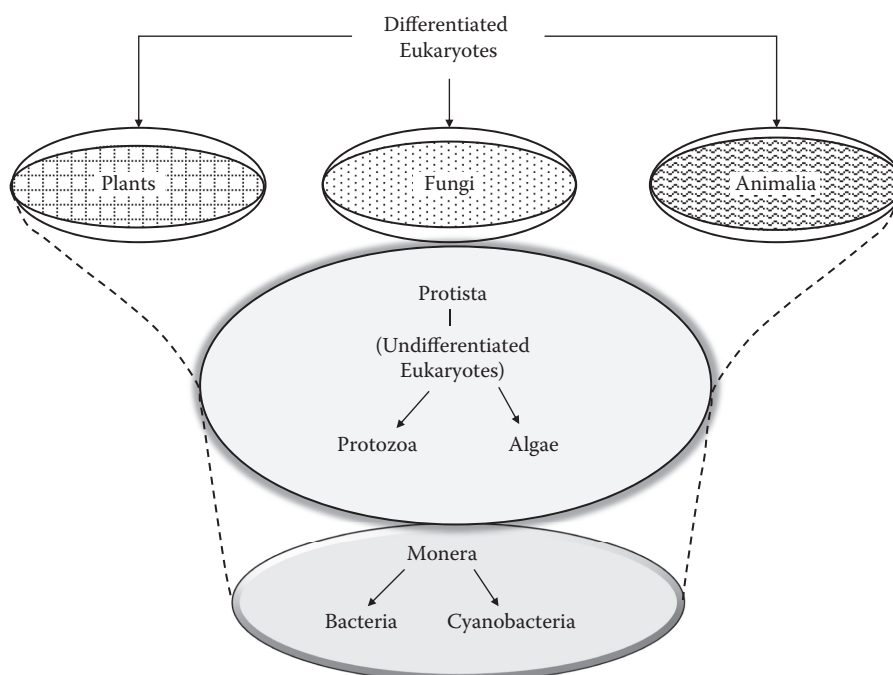
A characteristic term used to describe organic chemicals that persist in their original form or in altered forms is *persistent organic chemical pollutants*, POPs (persistent organic pollutants). These include dioxins, furans, pesticides, and insecticides, polycyclic aromatic hydrocarbons (PAHs), and halogenated hydrocarbons. The persistence of organic chemical contaminants in soils is a function of at least three factors: (1) the physicochemical properties of the organic chemical contaminant itself, (2) the physicochemical properties of the soil, and (3) the microorganisms in the soil. Resultant abiotic reactions and transformations are sensitive to factors (1) and (2), and all factors are important participants in the dynamic processes associated with the activities of the microorganisms in the biologically mediated chemical reactions and transformation processes.

9.6.1 Biotransformation and Degradation of Organic Chemicals and Heavy Metals

The various types of organisms and microorganisms responsible for the biotransformation (including degradation) of organic chemical compounds can be classified under the Whittaker (1969) five-kingdom classification scheme shown in Figure 9.18. The reader should consult the regular textbooks on microbiology for detailed descriptions of these.

The descriptions given by Yong and Mulligan (2004) are summarized as follows:

- Protozoa include pseudopods, flagellates, amoebas, ciliates, and parasitic protozoa. Their sizes can vary from 1 to 2000 μm . They are aerobic, single-celled chemoheterotrophs, and are eukaryotes with no cell walls. They are divided into four main groups: (1) the Mastigophora, which are flagellate protozoans, (2) the Sarcodina, which are amoeboid, (3) the Ciliophora, which are ciliated, and (4) the Sporozoa, which are parasites of vertebrates and invertebrates.
- Fungi are aerobic, multicellular, eukaryotes, and chemoheterotrophs that require organic compounds for energy and carbon. They reproduce by formation of asexual spores. In comparison to bacteria, they (a) do not require as much nitrogen, (b) are more sensitive to changes in moisture levels, (c) are larger, (d) grow more slowly, and (e) can grow in a more acidic pH range (less than pH 5). Fungi mainly live in the soil or on dead plants and are sometimes found in freshwater.
- Algae are single-celled and multicellular microorganisms that are green, greenish tan to golden brown, yellow to golden brown (marine), or red (marine). They grow in the soil and on trees or in fresh or salt water. Those that grow with fungi are called lichens. Seaweeds and kelps are examples of algae. Since they

**FIGURE 9.18**

Organisms and microorganisms participating in natural bioremediation processes grouped according to the Whittaker 5-kingdom hierarchical system. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

are photosynthetic, they can produce oxygen, new cells from carbon dioxide or bicarbonate (HCO_3^-), and dissolved nutrients including nitrogen and phosphorus. They use light of wavelengths between 300 and 700 nm. Red tides are indicative of excessive growth of dinoflagellates in the sea. The green color in a body of lakes and rivers is eutrophication due to the accumulation of nutrients such as fertilizers in the water.

- Although viruses are smaller than bacteria and require a living cell to reproduce, their relationship to other organisms is not clear. For them to replicate, they have to invade various kinds of cells. They consist of one strand of DNA and one strand of ribonucleic acid (RNA) within a protein coat. A virus can only attack a specific host. For example, those that attack bacteria are called bacteriophages.
- The most significant animals in the soil are millimeter-sized worms. Nematodes are cylindrical in shape and are able to move within bacterial flocs. Flatworms such as tapeworms, eel worms, roundworms, and threadworms, which are nematodes, can cause diseases such as roundworm, hookworm, and filaria.
- Bacteria are prokaryotes that reproduce by binary fission by dividing into two cells, in about 20 min. The time it takes for one cell to double, however, depends on the temperature and species. For example, the optimal doubling time for *Bacillus subtilis* (37°C) is 24 min and for *Nitrobacter agilis* (27°C) is 20 h. Classification is by shape, such as the rod-shaped bacillus, the spherical-shaped coccus, and the

spiral-shaped spirillum. Rods usually have diameters of 0.5 to 1 μm and lengths of 3–5 μm . The diameter of spherical cells varies from 0.2 to 2 μm . Spiral-shaped cells range from 0.3 to 5 μm in diameter and 6 to 15 μm in length. The cells grow in clusters, chains, or in single form and may or may not be motile. The substrate of the bacteria must be soluble. In most cases, classification is according to the genus and species (e.g., *Pseudomonas aeruginosa* and *Bacillus subtilis*). Some of the most common species are *Pseudomonas*, *Arthrobacter*, *Bacillus*, *Acinetobacter*, *Micrococcus*, *Vibrio*, *Achromobacter*, *Brevibacterium*, *Flavobacterium*, and *Corynebacterium*. Within each species, we will have various strains. Each of these can behave differently. Some strains can survive in certain conditions that others cannot. The ones that are better adapted will survive. For survival, strains called mutants originate due to problems in the genetic copying mechanisms. Some species are dependent on other species for survival. Degradation of chemicals to an intermediate stage by one species of bacteria may be required for the growth of another species that utilizes the intermediate.

9.6.1.1 Alkanes, Alkenes, and Cycloalkanes

Alkanes, alkenes, and cycloalkanes, among others (PAHs, asphaltenes, etc.), are components of petroleum hydrocarbons (PHCs). Low-molecular-weight alkanes are most easily degraded by microorganisms. As the chain length increases from C_{20} to C_{40} , hydrophobicity increases and both solubility and biodegradation rates decrease. Alkenes with a double bond on the first carbon may be more easily degradable than those alkenes with the double bond at other positions (Pitter and Chudoba, 1990). Cycloalkanes are not as degradable as alkanes due to their cyclic structure, and their biodegradability decreases as the number of rings increase.

9.6.1.2 Polycyclic, Polynuclear Aromatic Hydrocarbons

As with cycloalkanes, the compounds become more difficult to degrade as the number of rings of PAHs increases. This is due to decreasing volatility and solubility and increased sorption properties of these compounds. They are degraded one ring at a time in a manner similar to single ring aromatics.

9.6.1.3 Benzene, Toluene, Ethylbenzene, and Xylene

Benzene, toluene, ethylbenzene, and xylene (BTEX) are volatile, water-soluble components of gasoline. Aromatic compounds with benzene structures are more difficult to degrade than cycloalkanes. Aerobic degradation of all components of BTEX occurs rapidly when oxygen is present. Aromatic compounds can also be degraded under anaerobic conditions to phenols or organic acids to fatty acids to methane and carbon dioxide (Grbic-Galic, 1990). Degradation is less assured and is slower than under aerobic conditions.

9.6.1.4 Methyl Tert-Butyl Ether

Methyl *tert*-butyl ether (MTBE), which is an additive to gasoline, is highly resistant to biodegradation. It is reactive with microbial membranes.

9.6.1.5 Halogenated Aliphatic and Aromatic Compounds

Halogenated aliphatic compounds are pesticides such as ethylene dibromide (DBR) or CHCl_3 , CHCl_2Br , and industrial solvents including methylene chloride and trichloroethylene. Halogenated aromatic compounds are also pesticides, and they include such pesticides as DDT, 2,4-D and 2,4,5-T, plasticizers, pentachlorophenol, and polychlorinated biphenyls. The presence of halogen makes aerobic degradation of the halogenated aliphatic compounds difficult to achieve, due to the lower energy and the higher oxidation state of the compound. Anaerobic biodegradation is easier to achieve. This is particularly true when the number of halogens in the compound increases, making aerobic degradation more difficult. In the case of the halogenated aromatic compounds, the mechanisms of conversions include hydrolysis (replacement of halogen with hydroxyl group), reductive dehalogenation (replacement of halogen with hydrogen), and oxidation (introduction of oxygen into the ring causing removal of halogen).

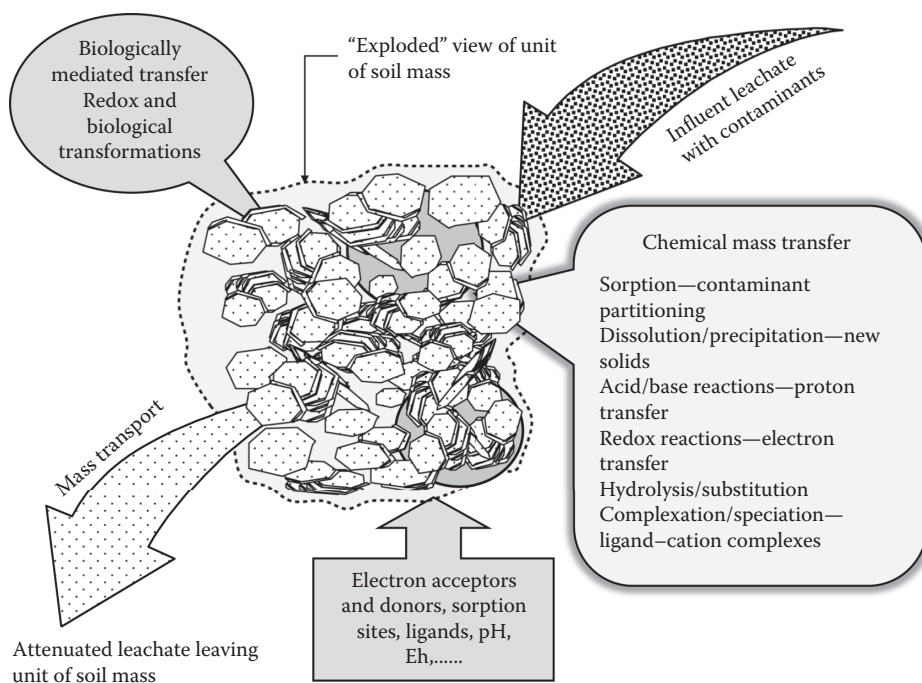
9.6.1.6 Heavy Metals

Microbial cells can accumulate heavy metals through ion exchange, precipitation, and complexation on and within the cell surface containing hydroxyl, carboxyl, and phosphate groups. Processes involving bacterial oxidation–reduction will alter the mobility of the heavy metal contaminants in soil. An example of this is the reduction of Cr(IV) in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) to Cr(III). Conversion can also be indirect by microbial production of Fe(II), sulfide, and other components that reduce chromium. Oxidation of selenium in the four naturally occurring major species of selenium (selenite [SeO_3^{2-} , IV], selenate [SeO_4^{2-} , VI], elemental selenium [Se , 0], and selenide [-II]) can occur under aerobic conditions. Transformation of selenate can occur anaerobically to selenide or elemental selenium, and methylation of selenium detoxifies selenium for the bacteria by removing the selenium from the bacteria.

9.7 Prediction of Transport and Fate of Contaminants

A key factor in the decision-making process in structuring sustainability objectives for the land environment is to have knowledge of the movement and spread (transport) of contaminants in the ground. Apart from procurement of field information required to delineate the parameters of the contamination problem at hand, this requires development of techniques for prediction of the transport and fate of the contaminants in the ground. The main elements in mass transport and mass transfer of contaminants in a soil–water system in the ground are shown in Figure 9.19.

Prediction of the transport and fate of contaminants in the subsoil requires consideration and incorporation of these elements in the analytical and mathematical analyses. Mass transport refers to transport of the dissolved solutes by advective, diffusive, and dispersion forces. Mass transfer of contaminants in the soil refers to chemical mass transfer processes. These have been discussed previously. They include sorption, dissolution, and precipitation, acid–base reactions and hydrolysis, oxidation–reduction (redox) reactions, speciation–complexation, and biologically mediated transfer. For aspects of design, containment of high-level nuclear waste, where prediction of the transport of radionuclides

**FIGURE 9.19**

Elements of basic mass transport and mass transfer in attenuation of contaminants in leachate transport through a soil element.

is of particular concern, radioactive decay is one of the important chemical transfer processes that need to be considered. Finally, biological mediated transfer of contaminants completes the three main categories of contaminant transfer from porewater to soil solids. Transformation and degradation of the organic chemical contaminants require as much attention as sorption and transport of the organic chemicals.

Many of the chemical mass transfer processes are kinetic processes, and reactions are not instantaneous. However, in a majority of the analytical considerations, most of the reactions are considered as instantaneous and chemical equilibrium is immediately obtained. This leads to modeling of transport of contaminants as a nonreactive process, an outcome that is not always appreciated by users of developed models. Consideration of transport and fate as a reactive process requires incorporation of the many transfer mechanisms that are time dependent, and also the transformations and degradations of the chemical. This is not easily accomplished. In the recent attempts to incorporate the reactive processes, incorporation of geochemical models into the “standard” transport models has been attempted, with differing degrees of complexity and success.

9.7.1 Mass Transport

In the conventional treatment of mass transport of contaminants, the three mechanisms for mass transport include advection, diffusion, and dispersion. Advection refers to the flux generated by the hydraulic gradient and is given in terms of the advective velocity v .

Transport of dissolved solutes in the porewater solely by advective means will progress in concert with the advective velocity. In situations where the solutes possess kinetic energy and demonstrate Brownian activity, diffusion of these solutes will occur. Using the porewater as the carrier, the solutes will combine their diffusive capability with advective velocity to produce the combined mass transport. This permits the dissolved solutes to move ahead of the advective front, i.e., the general tendency is for the diffusion front to precede the advection front. In situations where tortuosity and pore size differences combine with pore restrictions to create local mixing in the movement of the dissolved solutes, dispersion results. The degree of dispersion and the resultant effect on mass transport is not readily quantified.

The diffusive movement of a particular solute (contaminant) is characterized by its diffusion coefficient. This diffusion coefficient D_c is most often considered as being equivalent or equal to the effective molecular diffusion coefficient. In dilute solutions of a single ionic species, the diffusion coefficient of that single species is termed as the *infinite solution diffusion coefficient* D_o . The infinite solution diffusion coefficients are dependent on such factors as: ionic radius, absolute mobility of the ion, temperature, viscosity of the fluid medium, valence of the ion, equivalent limiting conductivity of the ion, etc. A useful listing of these coefficients for a range of solutes and for various sets of conditions can be found in many basic handbooks and other references (e.g., Li and Gregory, 1974; Lerman, 1979). From a theoretical point of view, the studies of molecular diffusion by Nernst (1888) and Einstein (1905) show the level of complex interdependencies that combine to produce the resultant coefficient obtained. From studies dealing with the movement of suspended particles controlled by osmotic forces in the solution, the three expressions most often cited, which are

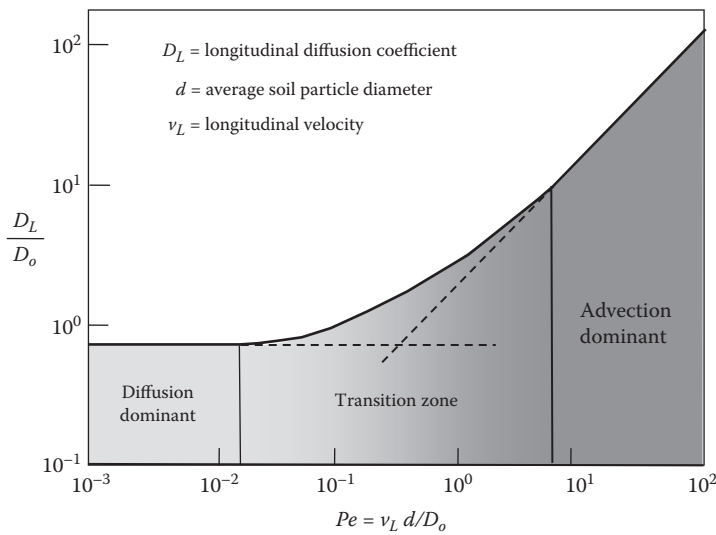
$$\text{Nernst-Einstein} \quad D_o = \frac{uRT}{N} = uk'T \quad (9.3)$$

$$\text{Einstein-Stokes} \quad D_o = \frac{RT}{6\pi N\eta r} = 7.166 \times 10^{-21} \frac{T}{\eta r} \quad (9.4)$$

$$\text{Nernst} \quad D_o = \frac{RT\lambda^\circ}{F^2|z|} = 8.928 \times 10^{-10} \frac{T\lambda^\circ}{|z|} \quad (9.5)$$

where D_o is the diffusion coefficient in an infinite solution, u is the absolute mobility of the solute under consideration, R is the universal gas constant, T is the absolute temperature, N is the Avogadro's number, k' is the Boltzmann's constant, λ° is the conductivity of the target ion or solute, r is the radius of the hydrated ion or solute, η is the absolute viscosity of the fluid, z is the valence of the ion, and F is the Faraday's constant. A large listing of experimental values for λ° for major ions can be found in Robinson and Stokes (1959).

We define a dimensionless Peclet number as $Pe = v_L d / D_o$, where v_L is the longitudinal flow velocity (advective flow). From the information reported by Perkins and Johnston (1963), it is seen that for Peclet numbers less than 1 ($Pe < 1$), diffusive transport of the contaminant solutes in a contaminant plume travels faster than the advective flow of water. For $Pe > 10$, advective flow constitutes the dominant flow mechanism for the movement of solutes. In between the values of 1 and 10, there is a gradual change from diffusion-dominant to

**FIGURE 9.20**

Diffusion and advection dominant flow regions for solutes in relation to Peclet number. (Adapted from Perkins, T.K. and Johnston, O.C., *Journal Society of Petroleum Engineering*, 17, 70–83, 1963.)

advection-dominant transport (Figure 9.20). The longitudinal diffusion coefficient D_L consists of both the molecular diffusion coefficient D_m and the hydrodynamic (mechanical) dispersion coefficient D_h . This is written as

$$D_L = D_m + D_h = D_o \tau + \alpha v,$$

where D_m is the molecular diffusion ($= D_o \tau$; $D_h = \alpha v$), α is the dispersivity parameter, and τ is the tortuosity factor.

The tortuosity factor is introduced to modify the infinite solution diffusion coefficient to acknowledge that we do not have an infinite solution, and that diffusion of a single solute species in a soil–water system is subject to constricting pore volumes and nonlinear paths. Figure 9.20 shows that in the diffusion-dominant transport region, we can safely neglect the v_L term since v_L is vanishingly small. Under those circumstances, the diffusion-dominant transport region, we will have $D_L = D_o \tau$. In the advection-dominant transport region, if we consider that diffusion transport is negligible, then $D_L = v_L$. In the transition region, the relationship for D_L will be given as: $D_L = D_o \tau + \alpha v_L$.

The significance of a correct choice or specification of a diffusion coefficient cannot be overstated. Figure 9.21 is a schematic illustration showing the variation of D (or D_L) coefficients calculated using Equation 2.2 in Section 2.5.4 of Chapter 2, and using the concentration profiles shown at the left-hand side of the diagram in Figure 9.21. The Ogata and Banks (1961) solution of the transport equation, similar to the one shown in Equation 2.2 in Chapter 2 for an initial chloride concentration of 3049 ppm as the input source (Figure 9.22), shows the different chloride concentration profiles obtained in relation to variations in the D value used in the calculations. The differences are not insignificant.

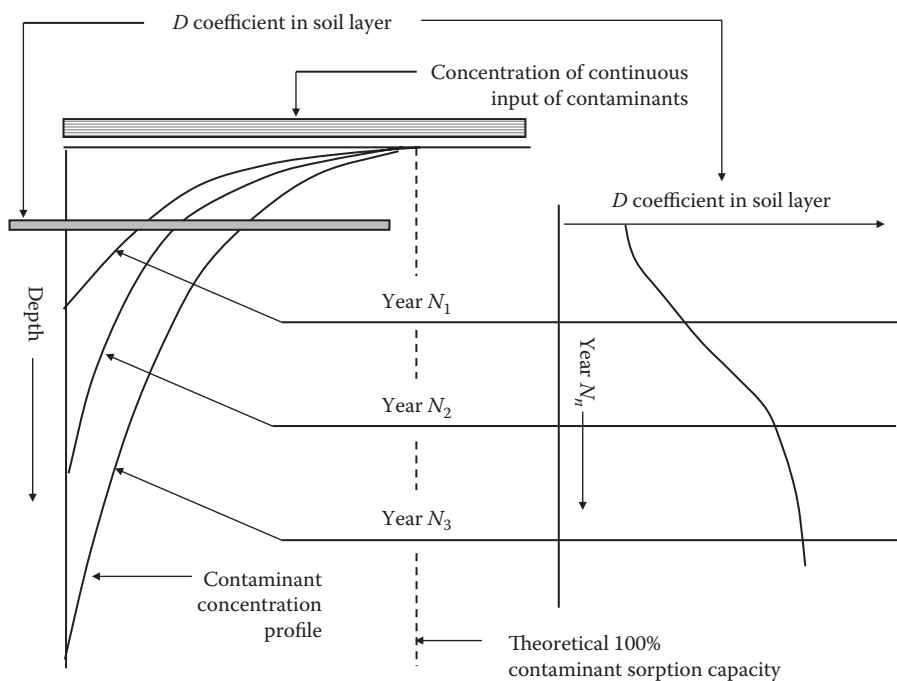
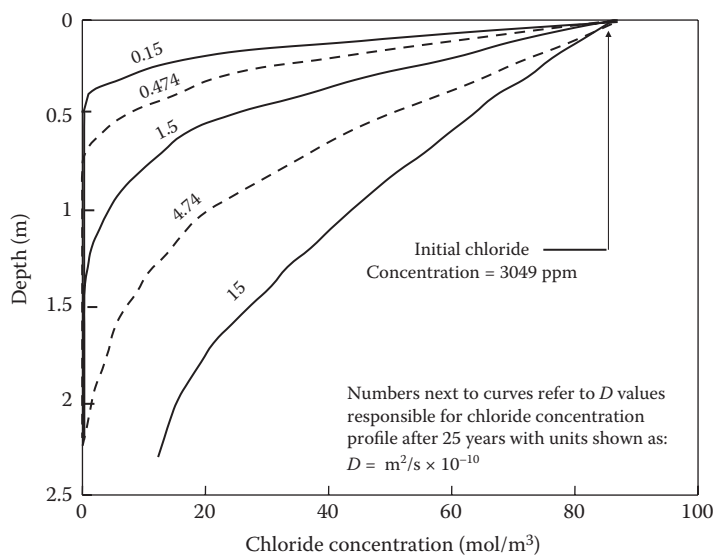
**FIGURE 9.21**

Illustration of contaminant concentration profiles in subsoil in relation to time elapsed given as years N_n . Diffusion coefficient profile (right-hand curve) is obtained from calculations reflecting changes in contaminant concentration with time.

**FIGURE 9.22**

Effect of different values of coefficient of diffusion D on chloride concentration profile after 25 years of continuous input of chloride at 3049 ppm.

9.7.2 Transport Prediction

For contaminants that can be partitioned in the transport process in the subsoil system, it is not uncommon to use the transport relationship given as Equation 2.2 in Chapter 2. For some situations, such as equilibrium-partitioning processes, this is an adequate method for predicting the transport and fate of contaminants that can be partitioned. The assumption is generally made that the rate of reactions is independent of the concentration of contaminants, i.e., a zero-rate reaction process. However, for many other situations relating to contaminants that are partitioned during transport, such as nonequilibrium partitioning, this relationship needs to be knowledgeably applied and perhaps modified to meet the conditions of partitioning. The relationship given as Equation 2.2 in Chapter 2 can be written in its original expanded form as:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\rho}{n\rho_w} \frac{\partial c^*}{\partial t}, \quad (9.6)$$

where c is the concentration of contaminants of concern, t is the time, D_L is the diffusion coefficient, v is the advective velocity, x is the spatial coordinate, ρ is the bulk density of soil media, ρ_w is the density of water, n is the porosity of soil media, and c^* is the concentration of contaminants adsorbed by soil fractions (see ordinate in graph shown in Figure 2.15 in Chapter 2). We recall that the adsorption isotherms portrayed in Figures 2.14 and 2.15 are derived from batch equilibrium tests with soil solutions, and we further recall the discussion in Section 9.5.1 and Figure 9.15 that the distribution coefficient k_d obtained from the adsorption isotherms refers directly to a maximum reactive surface reaction process. Equation 2.2 is obtained when c^* is assumed to be equal to $k_d c$, i.e., if a linear adsorption isotherm is assumed. Substituting for c^* in Equation 9.6 gives us:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\rho}{n\rho_w} \frac{\partial (k_d c)}{\partial t}. \quad (9.7)$$

Collecting terms and defining R as the *retardation* = $\left[1 + \frac{\rho}{n\rho_w} k_d \right]$, the equation previously seen as Equation 2.3 is obtained:

$$R \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}. \quad (9.8)$$

If the partition isotherms obtained from actual laboratory tests do not show linearity, the obvious solution is to use the proper function that describes c^* , e.g., the Freundlich or Langmuir (see Figure 2.15) or some other equivalent relationship. In this instance, the opportunity to properly reflect the partitioning process through a compact soil mass should be taken. Instead of using the nonlinear adsorption isotherm obtained from batch equilibrium tests on soil solutions, the sorption relationship obtained from column leaching tests through compact soil should be used. This has been discussed in Section 9.5.1 and illustrated in terms of adsorption curves' differences in Figure 9.15.

Equations of the type shown as Equation 2.2 or Equation 9.7 have been described as nonreactive transport relationships. This description has been applied to such equations

to reflect the observation that biotic and abiotic chemical reactions in the aqueous phase have not been factored into the structuring of the relationship. The chemical reactions discussed in Section 9.4 cannot be ignored since they not only compete with the soil solids for partitioning of the contaminants, but they may also transform the contaminants—especially the organic chemicals. The reactions and transformations will not only change the character of the contaminants, but they will also change the distribution of contaminants in the zone of interest. The problem is magnified in field situations because of multispecies contaminants and a mixture of both inorganic and organic chemicals. Unlike laboratory leaching column and batch equilibrium tests, real field situations provide one with a complex mix of contaminants transporting through an equally complex subsoil system.

9.7.2.1 Chemical Reactions and Transport Predictions

To meet the objectives of sustainability of the land environment, proper prediction of transport and fate of contaminants requires knowledge of how the abiotic and biotic reactions affect the long-term health of the terrain system—especially the subsoil system. From the myriad of possibilities in handling the complex problem of chemical reactions and reaction rates, and transformations, there exist at least four simple procedures that provide some accounting, to a greater or lesser degree, of the various processes controlling transport. These include (a) the addition of a reaction term r_c in the commonly used advection–diffusion equation given as Equation 2.2 or Equation 9.8, (b) accounting for the contaminant adsorption–desorption process, (c) use of first-, second-, or higher-order reaction rates, and (d) combining transport models with geochemical speciation models. None of these appear to handle biotransformations and their resultant effect on the transport and fate processes.

Addition of a reaction term r_c to Equation 9.8 is perhaps the most common method used to accommodate a kinetic approach to fate and transport modeling. The resultant formulation is a linearly additive term to Equation 9.8 as follows:

$$R \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + r_c. \quad (9.9)$$

The last term in Equation 9.9 can be expressed in the form of a general rate law as follows:

$$r_c = -k |A|^a |B|^b, \quad (9.10)$$

where r_c in this case is the rate of increase in concentration of a contaminant of species A , k is the rate coefficient, ϑ represents the volume of fluid under consideration, A and B are the reactant species, and a and b are the reaction orders.

The use of an adsorption–desorption approach to fate and transport modeling recognizes that in field situations, desorption (or displacement) occurs as part of the ion exchange process. Determination of the transport and fate of contaminants using the partitioning approach typified by the advection–diffusion relationship with adsorption–desorption consideration requires that one can write a relationship for c^* in Equation 9.6. Curve fitting procedures are commonly used to deduce information obtained from batch equilibrium and/or flow-through (leaching column) tests. The Freundlich and Langmuir curves, for example (see Figure 2.15), are specific cases of such procedures.

Prediction and modeling for biotransformation and biodegradation and their effects on fate and transport require a different approach. Yong and Mulligan (2004) have provided an accounting of some of the more popular analytical-computer models used in the application of natural attenuation schemes. These in effect are fate and transport models since biotransformation and biodegradation are the primary attenuation processes—a principal feature in fate and transport of organic chemicals. For example, the analytical model BIOSCREEN (Newell et al., 1996) developed for the Air Forces Center for Environmental Excellence by Groundwater Services (Houston, Texas) assumes a declining source concentration with transport and biodegradation processes for the soluble hydrocarbons that include advection, dispersion, adsorption, aerobic, and anaerobic degradation. Most of the available analytical-computer models developed to handle biotransformation and biodegradation in fate and transport modeling have the essential items contained in BIOSCREEN. The principal distinguishing factors between the available computational packages such as BIOPLUME III (Rifai et al., 1997), MODFLOW and RT3D (Sun et al., 1996), BIOREDOX (Carey et al., 1998), and BIOCHLOR (Aziz et al., 2000), include (a) structure of the outputs, (b) manner in which degradation is handled, such as order of degradation and degradation rates, (c) types of organic chemicals, (d) inclusion of heavy metals and some other inorganics, (e) availability and types of electron acceptors, and (f) adsorption–desorption. There are various versions of the groundwater flow model MODFLOW including MODFLOW-96, MODFLOW-2000, and MODFLOW-2005. The various versions of the solute transport model are MT3DMS (v5.3), MT3D, RT3D (v2.5), and MT3D99 (available from S.S. Papadopoulos & Associates). MT3D (Scientific Software Group, 1998) is a groundwater solute transport model for complex transient and steady-state flows, anisotropic dispersion, first-order decay, and production reactions to include biodegradation and sorption (linear and nonlinear). The newer version, MT3D99, adds the capability for simulating multispecies reactions and simulate or assess natural attenuation within a contaminant plume. MT3D99 works with MODFLOW.

Other models have also been developed according to the Center for Subsurface Modeling Support (USEPA, 2013). Footprint is based on the Domenico model (1987), which was released in 2008 by the EPA (Martin-Hayden and Robbins, 1997). It can be used to estimate the extent of a plume using either a zero- or first-order decay rate or can simulate the biodegradation of BTEX and/or ethanol. The Remediation Evaluation Model for Chlorinated Solvents (REMChlor) released in 2007 is used to simulate the first-order sequential decay and production of several species of chlorinated solvents. It is applicable for simulating contaminants in groundwater source and remediation whereas REMFuel, released in 2012, is applicable for fuel hydrocarbons.

Solution of the transport relationships shown as Equations 9.7 and 9.8 and other similar relationships can be achieved using analytical or numerical techniques. For well-defined geometries, initial and boundary conditions, and processes, analytical techniques provide exact solutions that can further one's insight into the processes involved in the problem under consideration. Numerical techniques such as finite difference, finite element, and boundary element are useful and are perhaps the techniques favored by many because of their capability to handle more complex geometries and variations in material properties and boundary conditions.

9.7.3 Geochemical Speciation and Transport Predictions

Abiotic reactions and transformations, together with the biotic counterparts, form the suite of processes that are involved in the transport and fate of contaminants in the

subsoil. The reactions between the chemical species in the porewater and also with the reactive soil particle surfaces discussed in the previous sections and chapters constitute the basic platform. Because individual chemical species have the ability to participate in several types of reactions, the equations to describe the various equilibrium reactions can become complicated, particularly since one needs to be assured that all the reactions are captured.

Geochemical modeling provides a useful means for handling the many kinds of calculations required to solve the various equilibrium reactions. Specific requirements are a robust thermodynamic database and simultaneous solution of the thermodynamic and mass balance equations. Appelo and Postma (1993) provide a comprehensive treatment of the various processes and reactions, together with a user guide for the geochemical model PHREEQE developed by Parkhurst et al. (1980). As with many of the popular models, the model is an aqueous model based upon ion pairing and includes elements and both aqueous species and mineral phases (fractions).

Other available models include the commonly used MINTEQ (Felmy et al., 1984) and the more recent MINTEQA2 version 4.03 released in 2006 that includes PROFEFA2 (Allison et al., 1991; EPA, 2014), a preprocessing package for developing input files, GEOCHEM (Sposito and Mattigod, 1980), HYDROGEOCHEM (Yeh and Tripathi, 1990), and WATEQF (Plummer et al., 1976). GEOCHEM-EZ is a multifunctional chemical speciation program, designed to replace GEOCHEM-PC, which can only be used on DOS consoles. HYDROGEOCHEM 2 is the newer version of HYDROGEOCHEM V1.0 (Yeh and Tripathi, 1990). The modification includes replacement of the EQMOD chemical equilibrium subroutines by a mixed chemical Kinetic and Equilibrium Model (KEMOD) to deal with species whose concentrations are controlled by either thermodynamics or kinetics. HYDROGEOCHEM 2 is a coupled model of hydrological transport and geochemical reaction in saturated–unsaturated media. The newer version of the chemical speciation program WATEQF is WATEQ4F, which is maintained by the Chemical Modeling and Thermodynamic Data Evaluation Project of the USGS and mainly applicable for large numbers of water analyses (Ball and Nordstrom, 2001).

PHREEQC version 3, which is now available (USGS, 1998) works with various models such as the Lawrence Livermore National Laboratory model and WATEQ4F), a Pitzer specific ion interaction aqueous model, and the SIT (Specific ion Interaction Theory) aqueous model. The PHREEQC model can perform

1. Speciation and saturation index calculations
2. Batch reaction and one-dimensional (1D) transport calculations
3. Inverse modeling

By and large, most of the geochemical codes assume instantaneous equilibrium, i.e., kinetic reactions are not included in the calculations. In part, this is because reactions such as oxidation–reduction, precipitation–dissolution, substitution–hydrolysis, and to some extent, speciation–complexation, can be relatively slow. To overcome this, some of the models have been able to provide analyses that point toward possible trends and final equilibria. The code EQ3/6 (Delaney et al., 1986) does, however, provide for consideration of dissolution–precipitation reactions. Transformations, however, are essentially not handled by most of the codes, although more models are including them.

9.8 Concluding Remarks

1. The concern in this chapter is for land environment sustainability, as it pertains to the effects of anthropogenic discharges of wastes in the land environment. Attention has been focused on developing concepts that consider the natural capital of land environment. The objective for sustainability has been articulated as follows: *To ensure that each natural capital component maintains its full and uncompromised functioning capability without loss of growth potential.*
2. For the objective to be fulfilled, actions, reactions, and management techniques require specification of *indicators* that mark the path toward sustainability of the natural capital. Although we recognize that absolute sustainability is not generally attainable, one should nevertheless adopt and implement strategies and technological/engineering means that point toward sustainability objectives.
3. The first half of this chapter examined the nature of indicators, and has distinguished between system status and material performance indicators. This distinction is necessary since various situations demand a proper accounting of the relationship between the two. Figure 9.4 provides the protocols that assist in this type of accounting.
4. Contaminants from anthropogenic activities are perhaps the largest sources and types of geoenvironment stressors. The manner in which they are handled in respect to land environment impact will, to a large extent, greatly dictate whether sustainability or “near sustainability” of the land environment and/or its natural capital can be achieved. The impact of these (contaminants) and the implementation of indicators as a technique for assessment need proper consideration. Figure 9.5 provides the sustainability goals in respect to waste discharge onto the land environment, and the subsequent figures provide examples. To some extent, we can learn how to prescribe the necessary indicators to achieve the objective. Obviously, real field situations are both site- and industry-specific.
5. In the assessment of waste impacts, it is clear that this cannot be achieved without an understanding of both the interactions with the subsoil system and the goals of sustainability. Central to the various issues is the problem of gaining a proper knowledge of the health status of the subsoil system. This requires one to be able to predict the transport and fate of pollutants in the subsoil system. The problem of prediction is not a simple problem that can be handled with one set of tools. Analytical-computer modeling is perhaps the most common technique used to provide information that allows one to predict system behavior.
6. For pollutants that can partition between the aqueous phase and the soil solids in the subsoil system, we have well-developed advection–diffusion transport models that can address the problem. The pitfalls in implementation of such models include the availability (or lack) of appropriate and realistic input parametric information (especially partition and distribution coefficients) and chemical reactions that affect the status of the contaminants in the system.
7. The use of geochemical speciation modeling allows one to determine these reactions. However, since kinetic reactions are not readily handled in some of the present available geochemical models and since many of these models are not coupled

to the regular transport models, much work remains at hand to obtain a reactive prediction model that can tell us about the fate and transport of contaminants in the subsoil system. Present research into coupling between geochemical models and advection–dispersion models has identified the complex and highly demanding computational requirements for a coupled model. Nevertheless, a realistic reactive coupled model is needed if we are to reach the stage where knowledge of the fate and persistence of contaminants in the subsoil system is to be obtained.

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10

Geoenvironment Impact Mitigation and Management

10.1 Introduction

10.1.1 Geoenvironmental Impacts

As shown in Chapter 1, impacts on the geoenvironment come from stressors whose sources include (a) natural events such as earthquakes, tornadoes, hurricanes, typhoons, floods, drought, etc., (b) activities associated with the procurement of life-support elements for humans, such as mining for resources, drilling and fracking for extraction of oil and gas, farming, and manufacturing, (c) disasters and failures associated with natural landscape features and man-made structures and activities such as collapse of dams and holding ponds, failure of pipelines carrying crude oil and bitumen, derailment of trains carrying dangerous goods, etc., and (d) inadvertent and deliberate stressor impact actions such as application of chemical aids in control of pests and dumping of hazardous wastes. The adverse impacts generated by geoenvironmental stressors result in diminishing the natural capital of the geoenvironment—thereby reducing the capability of the geoenvironment to provide the wherewithal to provide for the future needs of society. This, in essence, is the picture of an unsustainable geoenvironment.

10.1.1.1 Types of Stressors

Chapters 1 and 2 show that regardless of the sources of stressors on the geoenvironment, the stressors generated by the various sources can be grouped or classified according to the type of action or mechanism/process involved. The most useful way of classifying stressors is to group them according to the types of action that would result from the application of the stressor in question. Such a classification of stressors would be as follows: (a) thermal, (b) hydraulic, (c) mechanical, (d) chemical and geochemical, and (e) biological and biological mediated. This kind of classification scheme allows one to examine the processes or actions involved and in conjunction with the appropriate knowledge of the geoenvironment landscape, would permit one to determine the outcome of the impact on the geoenvironment. Since the discussions in this book are directed toward maintaining the health of the soil ecosphere (see Figure 1.1 in Chapter 1), the types of geoenvironment landscape information required refer particularly to soil properties and behavior.

10.1.1.2 Impact Mitigation and Management

Section 2.1.1 in Chapter 2 has provided some detailed information of the kinds of impacts generated from the various types of stressors. One can obviate stressor impacts on the

geoenvironment by eliminating the direct stressor sources associated with the activities, etc., of humans, i.e., exercising source control. Source control is, however, not an option for natural events such as earthquakes, etc. Experience has shown, however, that source control can rarely fully eliminate stressors delivered to the geoenvironment landscape. We need to develop strategies and technologies to mitigate the stressor impacts and to undertake remediation of the impacted sites to maintain the health of the geoenvironment. This holds true for geoenvironment stressors generated from both natural and anthropogenic sources.

We cite two recent examples of “incidents” (or “perceived” incidents) to illustrate the importance of impact mitigation and management. The first example concerns the perceived geoenvironment impact incidents raised in relation to the construction and use of pipelines across virgin terrain carrying bitumen and other similar products. The concerns relate to perceived construction disturbance of sensitive landscape features and expectations of pipeline failures (ruptures, leaks, etc.) discharging large quantities of the product into the geoenvironment (i.e., onto the ground and also into receiving waters). These concerns provide the geoenvironmental engineering profession with a clear set of objectives for management of a sustainable geoenvironment. Other than using more robust materials and prudent and sensible engineering practice designed to protect the sensitive features of the geoenvironment in the construction of the pipeline as source control measures, impact avoidance and mitigation in this case requires one to develop strategies and technologies that would: (a) protect the sensitive geoenvironment landscape features and habitats; (b) minimize or perhaps even eliminate potential pipeline failure events; (c) provide strict monitoring of pipeline integrity through instrumentation that sense pressure drops or other performance factors; and (d) establish a disaster response protocol for effective immediate corrective action in the case of a failure while implementing immediate geoenvironment remediation of the contaminated region.

The second example is one that seeks to develop remediation schemes for an unexpected disaster, namely, the fallout of discharged airborne radioactive cesium from the destruction of the nuclear power plants in Fukushima. The details of contamination of contiguous land surface by radioactive cesium from this unexpected tragedy will be discussed in a later chapter. For now, it is sufficient to point out that implementation of remediation of the land surface to precontamination levels is required, if original land-use activities is to be restored, i.e., if *original site functionality* is to be restored.

10.2 Site Functionality and Restoration

The restoration of sites adversely impacted by natural causes or by anthropogenic activities requires one to establish restoration goals or objectives. The central question to be addressed is “what does one want to have as a restored site”? Two distinct choices are available: (1) restoration of the impacted site to its pre-impacted state or (2) restoration of the site to an altered (i.e., different from pre-impacted) state that meets the requirements of regulatory agencies and stakeholders. Both of these choices require one to establish the functionality of the site, i.e., the functional purpose or purposes that have been served or can be served by the site.

10.2.1 Site Functionality

Much like the concepts of soil quality and soil functionality, introduced in Chapters 1 and 2, we can apply the same conceptual model to a site or even a region (assuming a site to be on a smaller scale than a region) facing the threat of stressors from natural and anthropogenic sources. Site functionality essentially tells one about the capability of the site, i.e., the present site usage and, more importantly, what the usage of the site could be if one makes full use of all the attributes (properties and characteristics) of the site. There are at least three reasons for determining or articulating the functionality of a particular site:

1. *Pre-impact status*—establishing the *initial conditions, status, and usage* of the site
2. *Design status*—stating the type, manner, and usage as the outcome of planned human intervention
3. *Optimum status*—defining the potential (best benefit) usage and status of the site

To establish *pre-impact status* site functionality, one needs to determine the present usage of the site, i.e., present status of the site. Examples of present status would include such landscape or terrain scenarios as: natural virgin land, farmland, pastureland, developed land, natural or cultivated forest, etc. Of the preceding scenarios, except for natural virgin land, all the other land or terrain scenarios are land-use scenarios. This means to say that *natural virgin land* is a category by itself and that all the other “present usage” scenarios fall into the *land-use* category. By definition, *land use* indicates a land status that has had, or does have, human intervention. Farmlands, cultivated forests, developed lands, etc., are all the result of human intervention.

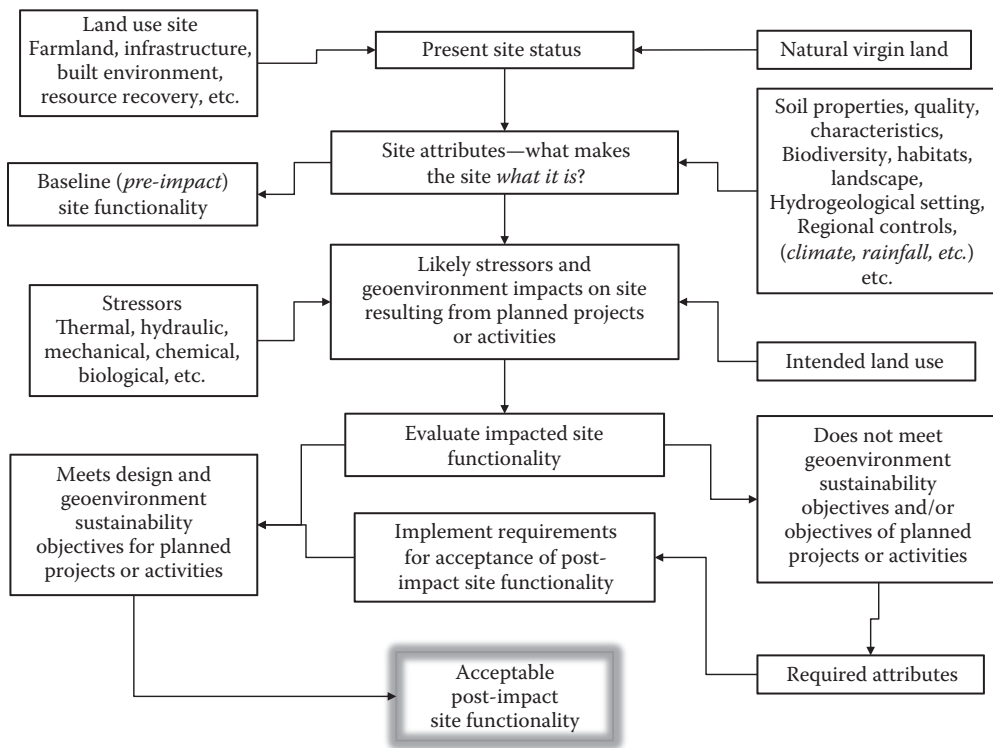
Both *design status* and *optimum status* site functionality options classify under the category of restoration of site to an *altered status*. *Design status* site functionality may or may not coincide with *optimum status* site functionality. Obviously, this depends on whether the planned (design) land use takes advantage of the full potential of the site, i.e., meaning that all the attributes, properties, and site characteristics are exploited at their maximum potential.

10.2.1.1 Choice and Use of Attributes

What are *attributes*? In this particular case, one should ask “what are geoenvironment attributes”? *Attributes* are characteristics of a particular item. In the case of the geoenvironment and in view of the subject of interest in this book, the soil component of the landscape, we are interested in the various elements or parameters that characterize the land or ground. Simply put, the geoenvironment attributes of particular interest and concern are those that govern soil health and behavior. These include soil composition (chemical, mineralogical, biological, etc.), properties and characteristics, and the various factors and elements that constitute a soil and the ground.

The decision on the attributes that need to be determined to characterize site functionality can be simple or arduous, depending on (a) the nature and extent of the geoenvironment impacts involved in the site and (b) the aims or objectives of the planned site restoration, i.e., the land-use plans. In the example of the type of protocols used to assess changes in site functionality in Figure 10.1, we show the importance and use of attributes in assessment process.

The partial list of attributes seen in the second upper-right box of Figure 10.1 is a small example of the kinds of properties, characteristics, data, and settings that one might choose to gather. Obviously, the entire vast array of information is not required for each site or region

**FIGURE 10.1**

Example of protocol used to assess changes in site functionality as a result of planned changes or activities to a specific site.

under consideration. The choice that one makes must take into account the type of planned project or activity contemplated. Also seen in the right-hand group of boxes of Figure 10.1 is the specification of required attributes, i.e., attributes required to meet such requirements as geoenvironment sustainability objectives and design or planned project objectives.

10.2.2 Site Restoration

Site restoration means *restoring the impacted site to pre-impact state*. A good example of site restoration to pre-impact state is the planned rehabilitation of farmlands contaminated by the fallout of radioactive nuclides from the disastrous Fukushima nuclear power plant explosions following the 2011 East Japan earthquake (Nakano and Yong, 2013). Rehabilitation of the contaminated farmlands to precontaminated productive farm status is the present site restoration goal.

There are many cases and reasons why restoration to pre-impact state may not be the prime objective of site restoration. The following considerations are important in arriving at decisions and objectives concerning the technical details and implementation of site restoration plans:

- The pre-impact state of the site may be such that it does not meet the site functionality requirements such as that represented by a derelict site (i.e., a site that has served no useful purpose because of the lack of positive site attributes) and hence would require restoration to some level of positive functionality.

- The objectives for restored site functionality by the stakeholder undertaking the restoration do not coincide with the pre-impact state site functionality—meaning that the stakeholder plans to develop the impacted site and has to remediate the site before implementing site development. A good example of this is the remediation of a brownfield site so as to be able to provide for development of housing projects. (A brownfield site, generally in an urban setting, is one that has been impacted by various kinds of chemical stressors.)
- The extent of site restoration means remediating the impacted site to a state that may or may not meet the pre-impact state level—depending on the interests of the stakeholder conducting the restoration, and more importantly, depending on regulatory acceptance of site restoration plans. This restoration plan assumes that site restoration will be implemented to a level that is on a lower level of site functionality as compared with pre-impact levels. Under such conditions, regulatory permission is the key to implementation of site restoration plans.
- The type of restored site, applied technology, and extent of site restoration plans will be decided in accord with regulatory requirements and public acceptance—with the latter being of utmost importance. In instances where the impacted site directly involves the public at the impacted site, it is not a surprise to expect that the affected public would want to “have a say” in what type of site restoration scheme is being considered, and in particular, how the restored site will impact their daily lives. Under such circumstances, combined regulatory–public hearings are required.

10.3 Stressor Impacts and Mitigation

The nature and types of stressors have been discussed in the previous chapters and have been classified or grouped according to their actions or impacts in the geoenvironment (Section 2.1.1 in Chapter 2), e.g., thermally, hydraulically, mechanically, chemically, geochemically, and biologically mediated. Included in the discussion in Section 2.1.1 in Chapter 2 are some of the main sources of stressors and the encountered impacts from the various kinds of stressors. Mitigation of stressor impacts is a course of action that assumes (expects?) that source control is not available. Such is the case for most, if not all, natural geo-disasters such as earthquakes, tsunamis, tornadoes, hurricanes, etc. For geo-disasters that occur as a result of human activities, source control can minimize the number and intensity (concentration, strength, magnitude, etc.) of stressors from the source.

10.3.1 Geo-Disaster Mitigation and Protection

Disasters occurring in the land compartment of the geoenvironment have often been termed as *geo-disasters*. There are two distinct causative sources for geo-disasters:

1. Naturally occurring events: earthquakes, tornadoes, hurricanes, and drought that result in geo-disasters and
2. Human related: disasters occurring directly and indirectly due to human activities such as failure of embankments and retaining walls, foundation failures due to failure in supporting capacity of the ground, contamination of ground by non-point sources and by fallout from smokestack emissions

Regardless, or independent, of the causative sources, there are many reasons that geo-disasters happen in the constructed environment. One of the main reasons is inadequate consideration or accounting of (a) the nature and intensity of potential geoenvironment stressors, (b) the nature, extent, and magnitude of their impacts on constructed facilities, and (c) the capability of the land compartment to fulfill its design site functionality requirements.

10.3.1.1 Naturally Occurring Events

Naturally occurring events provoking or resulting in geo-disasters fall into two categories: (1) weather-related or weather-provoked and (2) non-weather-related events. Included in the first category of weather-related events are

- Seasonal winter–summer cycles: Stressor impacts include frost heave in winter, ground collapse in summer due to thawing of ice lenses formed in winter, flooding due to melting of snowpacks, avalanches, seasonal drought conditions, etc. By and large, knowledge of these kinds of stressors and their impacts is well established in civil and geotechnical engineering practice, and preventative design and construction procedures have been developed to avoid development or mitigation of geo-disasters resulting from these stressors. Examples of some of these include the use of frost-free soil material underpinning foundations, restricting water inflow to underpinning foundations in frost-susceptible regions, alleviation of excessive pore pressures in slopes to minimize or eliminate slope instability and slope failures due to buildup of excessive porewater pressures, application of avalanche control procedures, construction of flood-protective barriers along river banks, construction of diversion ditches and canals, etc.
- Hurricanes, typhoons, and tornadoes: Although the common feature to these weather-related events is *wind*, the results of the actions represented by these events differ somewhat. The distinguishing feature is *water*. The resultant stressors from hurricanes and typhoons passing over open water are both hydraulic and mechanical—taking the form of flooding of shorelines and low-lying areas and wind forces acting on exposed facilities and objects.

As with the previous naturally occurring seasonal events, knowledge of the extent of the effects of these events are well-appreciated. Predictive analytical-computer models have been developed to forecast the advent and magnitude of such events—to a greater or lesser degree of accuracy depending on the availability of on-site data. Flood control levees and embankments form one of the major mitigating or preventative measures against the hydraulic (water and flooding) stressors and their impacts. Wind-resistant design of structures will minimize damage to structures, and most importantly, the construction and use of robust storm shelters is perhaps the best means for withstanding the impacts from the mechanical (wind force and tornado forces) stressors.

Outside of ensuring robust ground stability and support capability to mitigate the mechanical and hydraulic geoenvironment stressor impacts, mitigation of stressor impacts from the more commonly reported type of naturally occurring events provoking geo-disasters such as earthquakes, hurricanes, tornadoes, and floods are technically not “mitigation” but are “protection” against stressor impacts. Examples of these are storm shelters,

earthquake-resistant design of constructed facilities, flood control dykes and embankments, avoidance of earthquake zones and other natural geo-disaster zones or regions, etc. To be considered a geo-disaster, one needs to make a distinction between (a) a disaster that happens to an above-ground facility due solely to failure of the facility itself as a result of impacts from stressors, and (b) failure of the above-ground facility due to failure of the ground to provide durable support. The latter disaster is considered a geo-disaster. Most of the types of stressors involved in the preceding natural geo-disaster types are generally mechanical and hydraulic. Civil (structural, hydraulic, and geotechnical) engineering capabilities have developed technology that will respond to the need for protection against these types of geo-disasters.

Ground improvement is one of the techniques used to provide stable supporting platforms and competent soil capable of resisting excessive ground motion under mechanical and hydraulic stressors. In addition to the more traditional geotechnical engineering methods for ground improvement, a new innovative and sustainable method for ground improvement has recently been developed. This will be discussed in detail in Chapter 12.

10.3.1.2 Anthropogenic Actions

A major group of geo-disasters occurring as a result of anthropogenic actions are chemical in nature, as has been demonstrated in the previous chapters, more often than not resulting in threats to the health of biotic receptors. Inadequate or deficient foundation or subgrade or soil stability considerations under mechanical and/or hydraulic stressors, leading to ground failure, constitute another group. The means for mitigating or counteracting stressor impacts for this second group are similar to those mentioned in the previous subsection discussion relating to *natural events*.

By and large, a significant proportion of geo-disasters of a chemical nature are really geo-hazards, i.e., they present threats to the health of biotic receptors and also to the geoenvironment. In most instances, the line separating *geo-hazards* from *geo-disasters* is a function of several factors: (a) a matter of scale (size and intensity), (b) direct consequence and level of threat (toxicity, lethality, harm, exposure), (c) magnitude of physical and geoenvironmental damage, and (d) economic consequence. Geo-hazards and/or geo-disasters involving chemicals, in one form or another, occur as a result of

- *Source control*: Inadequate or insufficient measures of control of plant operations involving fugitive and planned discharges in operational processes. Mitigation of stressor impacts consist of corrective action by management to reduce or eliminate chemical stressors and their sources and to install or implement *capture and treat* systems, i.e., systems to capture fugitive and planned discharges for treatment prior to final discharge from the plant.
- *Direct application of chemical aids*: Use of chemical aids (a) for control of pests and unwanted plant species (e.g., pesticides, herbicides, fungicides, insecticides, etc.) and (b) as soil amendments (fertilizers) or as control agents (e.g., deicing compounds). These direct actions give rise to non-point source contamination of the soil and receiving waters. Mitigation of stressor impacts for contaminants in the soil consists of reduction or elimination of chemical stressor toxicity (concentration and toxic level) before the contaminant reaches any biotic receptor. This is the subject of discussion in the rest of this chapter and the next chapter.

- *Consequence of industrial operations:* Resource extraction (minerals, hydrocarbons, aggregates, etc.) and farming (cattle and other livestock) provide the major sources for chemical stressors. The discussions on the types of stressors and their sources have been reported in the previous chapters. Mitigation of stressor impacts begin with source control and implementation of “collect and treat” systems. For chemical stressors (contaminants) that find their way into the subsoil, the techniques for mitigation will be discussed in this and the next chapter.
- *Leachates, spills, accidents during hazardous material transport, illegal dumping, etc.:* Leachates leaking from containment systems, spills, accidents of trains during transport resulting in fires or leakage of hazardous materials and illegal dumping of chemical-type liquid and solid wastes are some of the major sources of chemical stressors found in the subsurface soil. These are, by and large, point source chemical stressors.

The discussion on procedures for mitigating the impacts from the stressors will be found in the rest of this chapter and continued in the next chapter as options in remediation.

10.4 Chemical Stressors: Contaminants

Regardless of the cause of the geo-disaster, the primary concern arising therefrom is in respect to the health of the geoenvironment and the biotic receptors in the presence of contaminants in the subsoil. Contaminants are chemical stressors that can severely affect the quality of water and groundwater resources, and soil quality. These (contaminants) include non-point source contaminants such as herbicides, pesticides, fungicides, etc., spread over large land surface areas, and point source contaminants from effluents, waste treatment plants, and liquid discharges as wastes and spills from industrial plants (e.g., heavy metals, organic chemicals). The previous chapters dealing with urbanization and industries have shown that liquid and solid waste discharges, together with rejects, debris, and inadvertent spills in the plants, all combine to create significant threats to the health of biotic receptors and also the environment. To demonstrate the magnitude of the problem, we can cite the example of sites contaminated with hazardous wastes and other material discards. In the U.S. Environmental Protection Agency (USEPA) (2004) report on the status of the future of site remediation, it is estimated that up to 350,000 contaminated sites would need to be cleaned up over the next 30 year at a cost of \$250 billion.

The impact from the presence of contaminants in the ground needs to be mitigated and managed, as a beginning step toward protection of the resources and the natural capital in the geoenvironment. This is a necessary step toward achievement of a sustainable geoenvironment. The emphasis should be placed on using the properties and characteristics of the natural soil–water system as the primary agent for such purposes. The motivation for this is not because of the high expenditures incurred with the use of various technological remediation schemes and processes, but because it allows one to address contaminant sources that encompass the range from point-source to non-point source. Managing the impact from non-point source contamination with technological

solutions can be prohibitive because of the extent of the source (if such is known), and the extent of contamination resulting from such a source. A good example of this is the transport of contaminants in the ground and on the ground surface in conjunction with pesticides and herbicides use. One needs to pay more attention to the impacts, from both atmospheric- and land-based non-point sources of contamination, on the health of both soil and water resources. If transport of contaminants is to receiving waters such as streams and rivers, how does one use technological aids and engineered systems to manage and control the advance of the contaminants? Erecting barriers that run a certain length of the stream can be prohibitively costly. A good practical solution is to invoke the properties of the natural soil system as a partner in mitigation–management. Amending and enhancing the properties to make it more effective as a control tool would also be a good tactic since this allows the subsoil to remain in place as a mitigation–management tool. This tactic is now being used in a limited way in passive remediation–treatment of contaminated sites.

10.5 Soils for Contaminant Impact Mitigation and Management

We use the term *contaminant* as a more encompassing term that includes both contaminants and pollutants. This means to say that the interactions and relationships established between contaminants and soil particles pay no attention to whether the contaminating substance is a contaminant or a pollutant. The designation of *pollutant* is a “human thing,” made necessary to ensure protection of public health from contaminants that threaten the well-being of humans if and when they are exposed to such contaminants, by direct contact, inhalation, ingestion, etc. The definitions for both contaminants and pollutants have been given in the earlier part of this book.

The latter part of Chapter 2 dealt with the nature and basic properties of soils as they relate to the transport and fate of contaminants in soil. To be factually correct, we will use the term *contaminant* in all the discussions to follow and reserve the use of the term *pollutant* when this is factually required. In this section, we will be dealing with the aspects of soils for mitigation of impacts from containments. The role of soil as a resource material for management of contaminants is due to its physical, mechanical, chemical, and biological properties. These properties constitute the basic tools for the many different strategies and measures available for passive and aggressive management of the land and water resources in the geoenvironment. The short discussions of these tools in previous chapters referred to the total actions of the various soil properties in management of contaminant waste streams as the *natural attenuation* process of soils. In this section, we will examine the basic properties and attributes of soils in respect to “why and how” they can function as tools for mitigation and management of contaminant waste streams in soils.

The properties of soil directly involved as a contaminant mitigation and control tool are

- a. Those that refer directly to the soil solids themselves. These are primarily the physical and mechanical properties of the soil, and also the surface properties of the soil solids responsible for sorption of contaminants. These include the density, macrostructure and microstructure, porosity and continuity of void spaces,

permeability, exposed surface areas in the void channels, specific surface area (SSA), cation exchange capacity (CEC), and surface functional groups associated with the soil solids.

- b. Those that depend on the interactions between the contaminants and the soil solids and the chemical constituents in the porewater. In this respect, the properties of the complete soil–water system become more important. These would be the chemistry of the porewater, the presence and types of inorganic and organic ligands in the porewater, pH and Eh or pE , exchangeable ions, SSA, and CEC. All these properties, together with the biological properties of the soil–water system will define the initial state of the soil–water system and hence the capability of the soil to react with incoming waste leachate streams and contaminants.

10.5.1 Physical and Mechanical Properties

In Chapter 2, we pointed out that the two primary types of interactions between the soil particles (soil solids) and liquid waste streams and contaminants in transport in the soil subsurface are physical and chemical in nature. For soil conditions both in the *in situ* state and in the prepared state (i.e., engineered soil barriers), we need to have good mechanical and hydraulic performance characteristics from the soil. The physical, hydraulic, and mechanical properties useful for mitigation and control of liquid and solid waste substances and contaminants are those that impede and/or prevent the flow or passage of liquid and solid substances. We need to distinguish between (a) the natural *in situ* soil condition where the soil is in the landscape as a surface and subsurface soil, and (b) the situation where human intervention and manipulation of the soil is possible, i.e., placement of a prepared soil in the ground as an active mitigation and/or treatment tool. In the case of natural soils in the landscape and subsurface, transport of liquid waste streams, leachates, and contaminants are controlled by the *in situ* physical properties of the subsurface soil. Without human intervention, it becomes a case of “getting what the natural situation dictates.” Changes in the physical hydraulic, and mechanical properties of the subsoil that will likely occur because of chemical and physico-chemical interactions with contaminants will be discussed in the next subsection.

In the case where prepared soil is used as a sole treatment tool or as one of the tools in a designed mitigation treatment process, control on the soil physical, hydraulic, and mechanical properties can be exercised. At this stage, the design physical, hydraulic, and mechanical properties of the soil to be used are important factors in the mitigation and prevention of contaminant transport. The soil properties of significance include physical and hydraulic properties such as density, permeability, porosity, and mechanical properties such as compactibility, compressibility, consolidation, and strength. All of these properties depend on the texture, grain (particle) morphology, particle size distribution, and composition. These all combine to control the packing of the particles and density of the compacted material. Figure 10.2 shows the relationship between all of these and the physical, hydraulic, and mechanical properties obtained in relation to the compactibility of the soil material. The mechanical properties are of importance in liner, buffer, and barrier systems and the physical and hydraulic properties feature prominently in fluid and gas transport through the soil. The common assumption that transport of contaminants is halted when fluid transport is stopped is wrong since transport mechanisms for contaminants and pollutants are via diffusive processes. So long as there is water in the soil barrier system, diffusive transport will occur. The water in the soil, even if it is immobile, serves as the carrier for the contaminants.

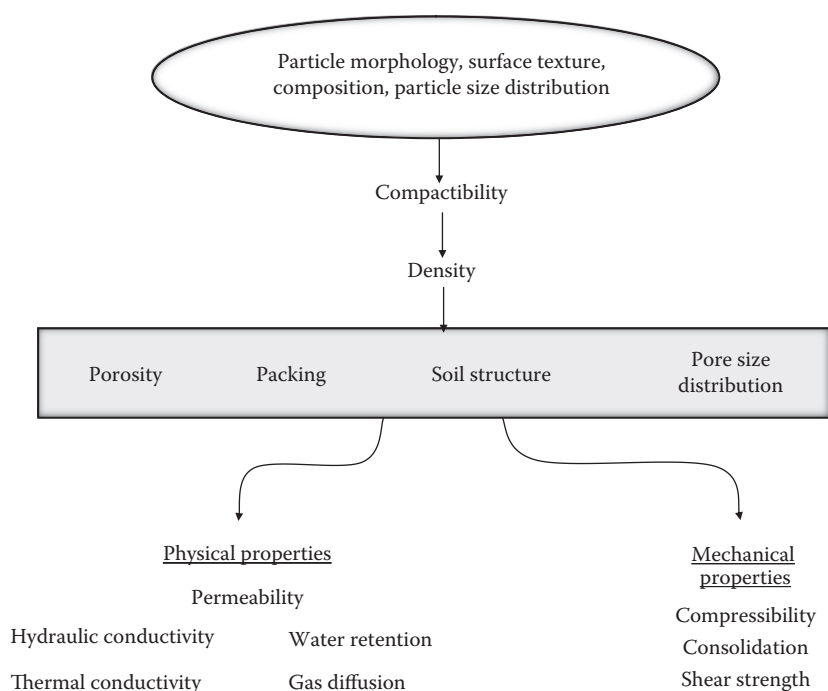
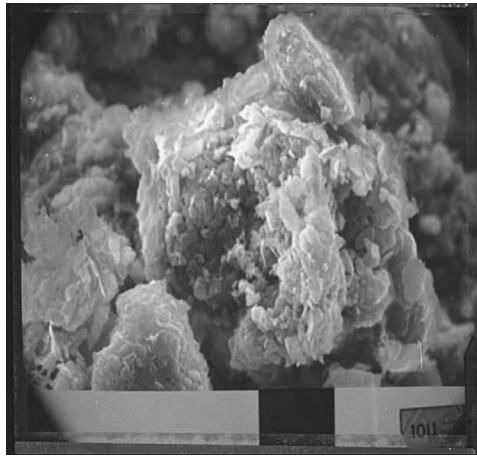


FIGURE 10.2
Control of physical and mechanical properties by soil composition and particle properties and characteristics.

10.5.1.1 Soil Microstructure Controls on Hydraulic Transmission

Figure 2.11 in Chapter 2 illustrates the main points of physical interactions between a liquid waste stream permeating among the soil particles. The physical and hydraulic properties of the soil immediately involved in defining the nature of the fluid permeation are known as the transmission properties of the soil. These are essentially linked to the permeability of the soil to aqueous and gaseous phases, as shown in the bottom left compartment in Figure 10.2. Considering only fluid flow, the factors that affect hydraulic conductivity can be conveniently divided into three distinct categories: (1) external environmental factors such as hydraulic head and temperature, (2) fluid phase factors, and (3) soil structural factors. The fluid phase factors of significance in the rate of fluid movement in the soil include the density, viscosity, and chemistry of the solutes contained in the fluid phase. Soil structural features are very influential in controlling flow rate and partitioning of contaminants. These include the microstructure and the micropores in the soil, the pore size distribution, and the continuity of pores. All of these are functions of the macrostructure and density (packing) of the soil.

For any given density of soil, there is an almost infinite number of arrangements of soil particles in a typical unit volume of soil. The sketches shown in Figures 2.9 and 2.10 in Chapter 2 indicate that individual particles acting as single units are rarely found, except for granular soils. Figure 10.3 shows a scanning electron microscopy (SEM) picture of a typical clay soil unit composed of aggregate groups of clay particles, and depending on the sizes of these groups, they are generally called domains, clusters, peds, or microstructural

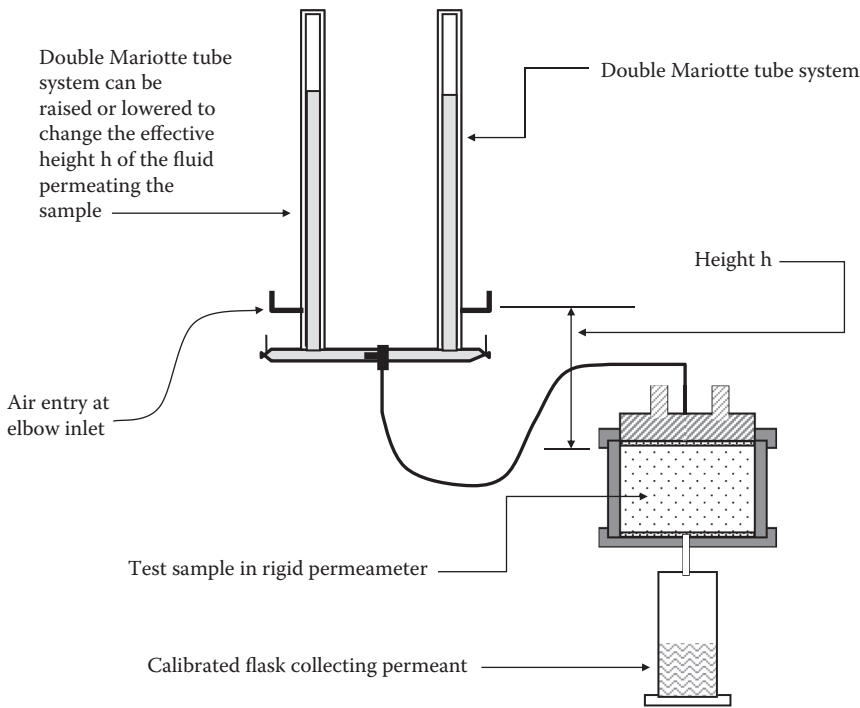
**FIGURE 10.3**

SEM picture showing typical aggregate grouping of particles forming the structure of a clay soil. The black section of the band in the bottom center of the picture represents a scale of 10 μm . Note the variety and sizes of voids, ranging from microvoids in the aggregate group (cluster, ped) to the macro voids between aggregate groups of particles.

units. Because of the variety in sizes, we will use the general term *microstructural units* in our discussion of the aggregate groups that make up the microstructure of the soils. The importance of soil structure in defining flow through a soil is evident from Figure 10.3.

Since flow occurs through void spaces that are connected, the nature of the void spaces and how these spaces are connected will be influential in determining the flow rate of the liquid waste and contaminants. Greater densities of soil will show smaller void spaces. Note that the micropores in the microstructural units will not show the same characteristics of flow as found in the macropores, i.e., the pores between peds. Because of the infinite variations in sizes and types of microstructural units and their distribution, it would not be surprising to find that soils with similar compositions can have different densities and correspondingly different hydraulic conductivities. If soil is to be used as a tool to control flow and distribution of contaminants—i.e., to mitigate contamination—it is important to determine what key factors are involved in controlling contaminant partitioning and distribution in the soil.

Soil permeability to liquids is determined as the hydraulic conductivity of a soil. This holds true for saturated soils. However, for unsaturated soils, movement of liquids is generally identified as diffusive flow, even though this may not be exactly correct. The permeability of a soil is generally expressed in terms of a permeability coefficient, k . The common technique is to perform laboratory permeability tests, as shown, for example, in Figure 10.4, which depicts a constant head permeability test. Procedures for conducting permeability tests using constant head and falling head techniques, and also with flexible wall permeameters have been written as Standards, e.g., ASTM D5084-03 (2003). Although the double Mariotte tube system shown in Figure 10.4 is not the prescribed or specified system for administering the constant hydraulic head for permeameter tests, it is nevertheless a proper and useful system to use. It permits flexibility in adjusting the hydraulic head required for constant head permeation. The Darcy coefficient of permeability k is obtained from the relationship: $Q = kiA = k(\Delta h/\Delta L)A$. The hydraulic gradient i is the ratio of the hydraulic head Δh and ΔL , the spatial distance, and A is the cross-sectional area of the test sample.


FIGURE 10.4

Water entry experiment with constant hydraulic head h for permeating fluid in a rigid permeameter.

Since the Darcy model for determination of the permeability coefficient k from experiments such as those shown in Figure 10.4 does not consider the properties of the permeant and the microstructure of the soil, Yong and Mulligan (2004) have proposed a relationship that uses a modification of the combined form of the Poiseuille and Kozeny-Carman relationships. This takes into account the influence of the properties of pore channels defined by the structure of a soil, and the fact that the wetted soil particles' surface area is controlled by the microstructure of the soil. The relationship obtained is shown as:

$$v = k^* i = \frac{C_s n^3 \gamma}{\eta T^2 S_w^2} \frac{\Delta \psi}{\Delta l} \quad (10.1)$$

where k^* is the PKC (Poiseuille-Kozeny-Carman) permeability coefficient, which considers permeant and soil microstructure properties ($= C_s n^3 \gamma / \eta T^2 S_w^2$), C_s is the shape factor, with values ranging from 0.33 for a strip cross-sectional face to 0.56 for a square face (Yong and Warkentin (1975) have suggested that a value of 0.4 for C_s may be used as a standard value, with a possible error of less than 25% in the calculations for an applicable value of k^*), i is the hydraulic gradient, which is the ratio of the potential or hydraulic head difference $\Delta \psi$ between the entry and exit points of the permeant, and the direct path length Δl of the soil mass being tested, T is the tortuosity, which is the ratio of effective flow path Δl_e to thickness of test sample Δl and which is quite often taken to be $\approx \sqrt{2}$, γ and η are the density and viscosity of the permeating fluid, respectively, n is the porosity of the unit soil mass, and S_w is the wetted surface area per unit volume of soil particles.

Equation 10.1 uses the soil property parameters C_s , T , and S_w in structuring the relationship that describes permeability of a soil. These soil property parameters are dependent on soil composition and soil structure. Assuming that the physical properties of a leachate permeant are not too far distant from that of water at about 20°C, and further assuming a tortuosity T value of $\sqrt{2}$, and $C_s = 0.4$, the graphical relationships shown in Figures 10.5 and 10.6 will be obtained. These graphs show the relationship between the PKC permeability coefficient k^* and the amount of surface area wetted in fluid flow through the soil. A comparison of the

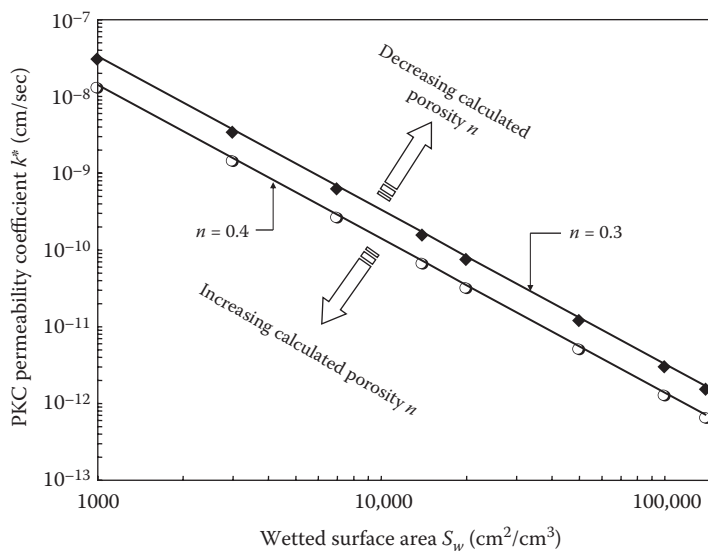


FIGURE 10.5

Variation of PKC permeability coefficient k^* with wetted surface area S_w and calculated porosity n .

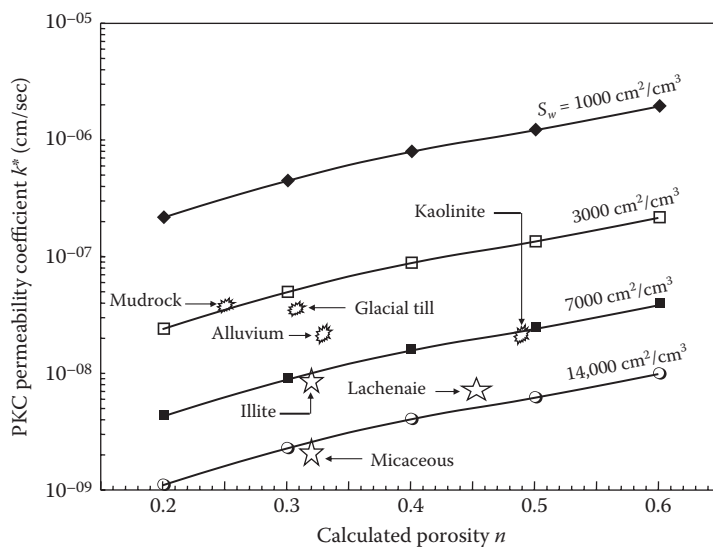


FIGURE 10.6

Variation of PKC permeability coefficient k^* with calculated porosity in relation to wetted surface area S_w .

calculated wetted surface areas S_w for the soils shown in Figure 10.6 show that the wetted surface areas vary from about 3% to 7% of the specific surface area of the soils. This indicates that microstructural units such as those shown in Figure 10.3 encompass a large number of soil particles, to the extent that the effective surface areas presented to a contaminant leachate stream represents only a small fraction of surface areas present. For soils that are prepared for use as barriers and liners, the sizes and distribution of microstructures are significant factors in determining the effectiveness of the barriers and liners.

10.5.1.2 Microstructure, Wetted Surfaces, and Transport Properties

Hydraulic conductivity through a soil engineered barrier is greatly facilitated when interconnected voids and their connecting channels are large. Large voids in a compact soil generally mean large grain sizes and/or large microstructural units. In addition to the advantage of larger flow paths, large interconnected voids generally mean that the surfaces presented as the surrounding surfaces in the void spaces are lesser than if the void volumes were smaller. The surrounding flow path contact surfaces are important factors because they (a) offer drag or boundary resistance to flow, and more importantly (b) provide the surface areas and corresponding functional groups for chemical reactions that include sorption, ion exchange, and complexation. We will discuss this latter aspect in detail in the next section.

Figure 10.7 shows two scanning electron micrographs of the same clay soil. The clay soil was obtained as a core sample from a recently cut slope in northern Québec, Canada,

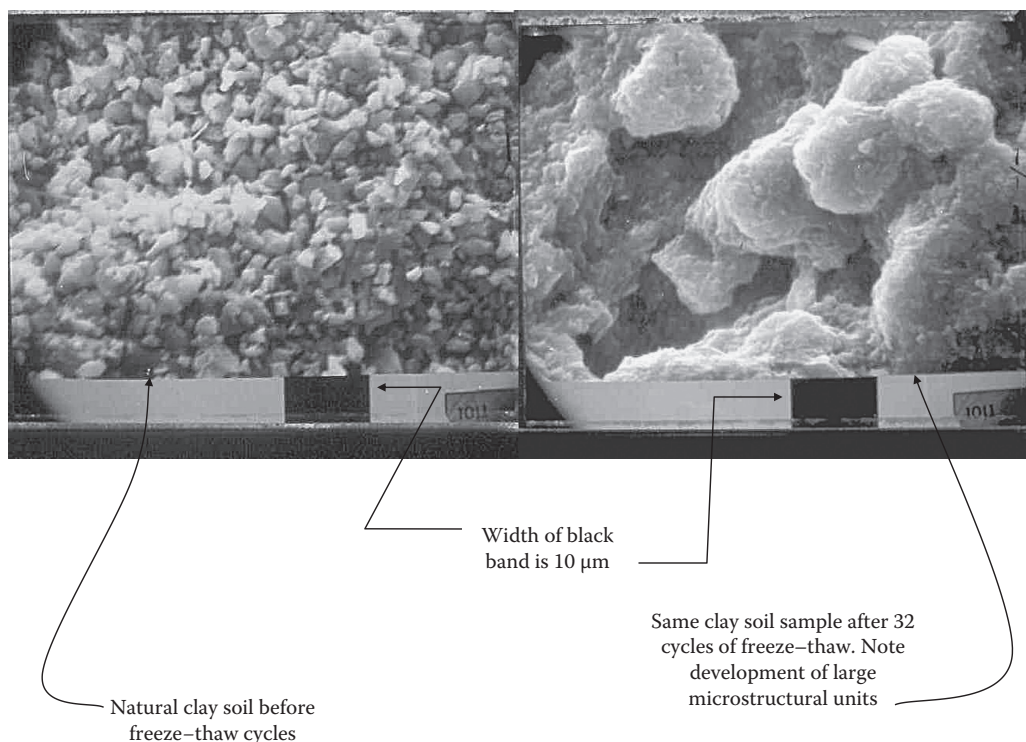


FIGURE 10.7

SEM picture showing formation of large microstructural units in a natural clay soil after 32 cycles of freezing and thawing.

where the winters can be cold and harsh. The picture on the left shows the structure of the soil obtained from a core sample to consist of small microstructural units apparently uniformly distributed in the cross section. The right-hand picture shows the same soil in the thawed state after 32 cycles of freezing and thawing (Yong et al., 1984). The dramatic increase in sizes of the microstructural units is obvious, testifying to the marked decrease in surface areas presented to a permeating fluid and also testifying to the significant increase in void spaces. Transmission or transport through the soil material shown on the right-hand side will be considerably facilitated by the freeze–thaw effect. The lesson to be learned from the pictures in Figure 10.7 is that environmental effects can alter the initial conditions to such an extent that design of mitigation and treatment procedures must anticipate such events.

10.5.2 Chemical Properties

The chemical properties of significance include those that promote ion exchange, sorption, and precipitation of solutes in the fluid phase (including porewater) in the soil, and complexation. These are properties that are more appropriately defined as soil–water system properties. These have been discussed briefly in Chapters 2 and 9 in respect to partitioning processes involving heavy metals. To fully utilize soil as a resource material for management of waste leachate streams and contaminants, a broader discussion of the important chemical properties, and interactions between contaminants and soil particles or fractions is needed.

10.5.2.1 Sorption

As discussed in the previous chapter, sorption processes involving molecular interactions are (a) coulombic in nature, (b) interactions between nuclei and electrons, and (c) essentially electrostatic in nature. The major types of interatomic bonds are ionic, covalent, hydrogen, and van der Waals. Ionic forces hold together the atoms in a crystal. The various types of bonds formed from various types of forces of attraction include (a) ionic bonds, i.e., electron transfer between the atoms that are subsequently held together by the opposite charge attraction of the ions formed, (b) covalent bonds developed as a result of electron sharing between two or more atomic nuclei, and (c) coulombic bonds developed from ion–ion interaction.

For interactions between instantaneous dipoles, we have the three types of *van der Waals* forces: Keesom, Debye, and London dispersion forces. Bonding developed by van der Waals forces is, by and large, the most common type of bonding between organic chemicals and mineral soil fractions. Electrical bonds can be formed between negatively charged organic acids and positively charged clay mineral edges. Sorption of organic anions can occur if polyvalent exchangeable cations are present. The polyvalent bridges formed will be due to (a) anion associated directly with cation or (b) anion associated with cation in the form of a cation bridge (water bridge).

10.5.2.2 Cation Exchange

Cation exchange involves those cations associated with the negative charge sites on the soil solids, largely through electrostatic forces. Ion-exchange reactions occur with the various soil fractions, i.e., clay minerals and non-clay minerals. This process, which has been discussed in detail in Chapter 9, is set in motion because of the need to satisfy

electroneutrality and is stoichiometric. Calculations or determinations of the proportion of each type of exchangeable cation to the total cation exchange capacity of the soil can be made using exchange equilibrium equations such as the Gapon relationship shown in Equation 9.1.

From the electrostatic point of view, physical adsorption (or sorption) of contaminants in the porewater (or from incoming leachate) by soil fractions is due to the attraction of positively charged contaminants such as the heavy metals to the negatively charged surfaces of the soil fractions. This type of adsorption is called nonspecific adsorption. By definition, we can refer to *nonspecific adsorption* when ions are held by the soil particles primarily by electrostatic forces. This distinguishes it from *specific adsorption*, which is another way of identifying *chemisorption*, a process that involves covalent bonding between the contaminant and the soil particle (generally mineral) surface. Examples of nonspecific adsorption are the adsorption of alkali and alkaline earth cations by the clay minerals. By and large, cations with smaller hydrated size or large crystalline size would be preferentially adsorbed.

10.5.2.3 Solubility and Precipitation

The contaminants affected by solubility and precipitation processes are mostly heavy metals. The pH of the soil–water system plays a significant role in the fate of heavy metal contaminants because of the influence of pH on the solubility of the heavy metal complexes. According to Nyffeler et al. (1984), the pH at which maximum adsorption of metals occurs varies according to the first hydrolysis constant of the metal (cationic) ions. When the ionic activities of heavy metal solutes in the porewater of a soil exceed their respective solubility products, precipitation of heavy metals as hydroxides and carbonates can occur. The two stages in precipitation are nucleation and particle growth. This will generally be under slightly alkaline conditions. The precipitate will either form a new separate substances in the porewater or will be attached to the soil solids. Gibbs phase rule restricts the number of solid phases that can be formed.

Factors involved in formation of precipitates include soil–water system pH, type and concentration of heavy metals, presence of inorganic and organic ligands, and the individual precipitation pH of heavy metal contaminants. In the solubility–precipitation diagram shown in Figure 10.8 for a metal hydroxide complex, the left-shaded area marked as *soluble* identifies the zone where the metals are in soluble form with positively charged complexes formed with inorganic ligands. The right-shaded *soluble* area contains the metals in soluble form with negatively charged compounds. The *precipitation region* in-between the two shaded areas contains various metal hydroxide species.

Figure 10.9 shows heavy metal precipitation information using data reported by MacDonald (1994). Transition from soluble forms to precipitate forms occurs over a range of pH values for the three heavy metals. The onset of precipitation can be as early as a pH of about 3.2 in the case of the single heavy metal species (Pb). The process of precipitation is a continuous process that begins with onset at some early pH and finally concludes at somewhat higher pH value, generally around pH 7 for most metals. The influence of other metal species in the precipitation process is felt not only in terms of when onset pH occurs, but also in the rate of precipitation in relation to pH change. Figure 10.9 shows that the onset of precipitation of Zn as a single species is about pH 6.4 and that reduces to about pH 4.4 when other metals are present. Given that the experiments were conducted with equal amounts of each of the three heavy metals, it is expected that the concentrations of the other metals would also have an effect on modification of the onset pH. Precipitation

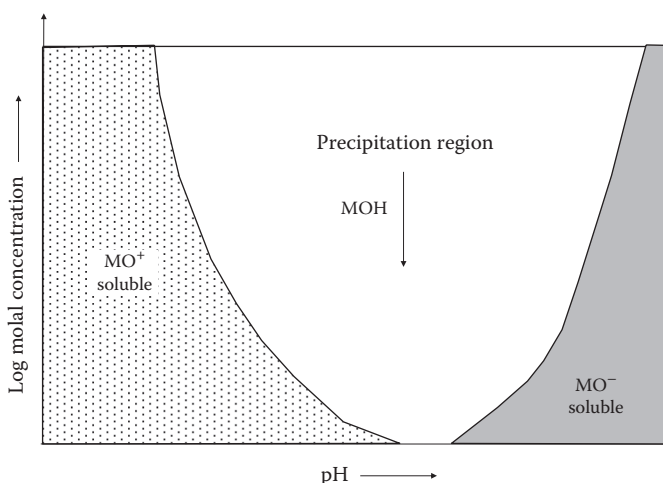


FIGURE 10.8
Solubility-precipitation chart for a metal hydroxide complex.

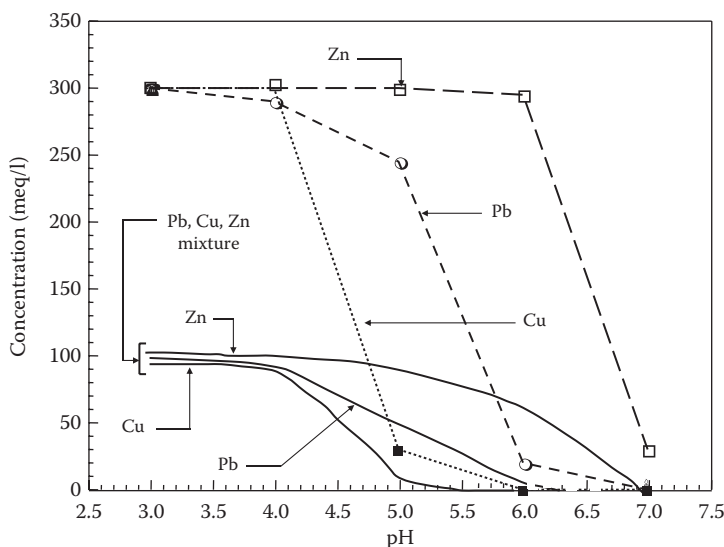


FIGURE 10.9
Precipitation of heavy metals Pb, Cu, and Zn in aqueous solution. Bottom curves are precipitation of individual metal from a mixture of Pb, Cu, and Zn in equal proportions of metal nitrate solution (100 meq each). Top curves are for single solutions of individual metals at 300 meq/l concentration. (Data from MacDonald, E., *Aspects of Competitive Adsorption and Precipitation of Heavy Metals by a Clay Soil*, MEng thesis, McGill University, Montreal, Canada, 1994.)

boundaries are not distinct separation lines, and that transition between the two regions or zones occurs near the boundaries throughout the entire pH range.

The role of pH in the soil-water system is important because of the various complexes formed in relation to pH. For example, when a heavy metal contaminant solution such as a PbCl_2 salt enters a soil-water system at pH values below the precipitation pH of Pb, a portion of the metals will be adsorbed by the soil particles. The ions remaining in solution

would either be hydrated or would form complexes such as Pb^{2+} , PbOH^+ , and PbCl^+ . These would be contained in the left-shaded area of Figure 10.8. When the pH is raised to the pH levels shown in the right-shaded area of Figure 10.8, one would form complexes such as PbO_2H^- and PbO_2^{2-} that would reside in the right-shaded area.

10.5.2.4 Speciation and Complexation

The processes associated with speciation and complexation apply primarily to inorganic contaminants in the liquid waste streams, particularly the heavy metals. The term *speciation* refers to the formation of complexes between heavy metals and ligands in the aqueous phase. Ligands are defined as anions that can form coordinating compounds with metal ions. Inorganic and organic ligands include, for example, CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , OH^- , Si_3^{2-} , PO_4^{3-} , and humic and fulvic acids. For the complexes formed between heavy metals and humic and fulvic acids, these would generally be chelated compounds. From the preceding, we note that the chemistry of the porewater in the soil–water system is an important factor in mitigation and control of contaminant transport in the soil–water system—through competition between the ligands and the soil solids for sorption of the heavy metals.

10.5.3 Biological Properties

Biological properties of soils (soil–water systems) are very important factors in the passive and aggressive treatment and management of organic chemical contaminants in the subsurface soil regime. These properties are determined by the large variety of microorganisms that reside in the soil–water system. These microorganisms consist of viruses, bacteria, protozoa, fungi, and algae. Microorganisms are the key to biological treatment and management of contaminants and contaminants.

10.5.3.1 Protozoa

Protozoa are aerobic, single-celled chemoheterotrophs. They are classified as eukaryotes with no cell walls and with sizes that vary from one to a few hundred micrometers. They include pseudopods, flagellates, amoebas, ciliates, and parasitic protozoa. The four primary groups of protozoa are (1) Mastigophora—flagellate, (2) Sarcodina—amoeboid, (3) Ciliophora—ciliated, and (4) Sporozoa—parasites of vertebrates and invertebrates. Protozoa are found in water and soil and feed on bacteria and need water in order to move. Although they do not generally biodegrade contaminants, they are useful in reducing bacterial numbers near injection wells that become clogged due to excessive growth. Soil protozoa are heterotrophic, and although their general food source is bacteria, they are known to feed on soluble and even insoluble organic material. They mineralize nutrients and release excess nitrogen as NH_4^+ , which is beneficial to plants and others on the food web.

10.5.3.2 Fungi

Fungi include slime molds (filamentous fungus), yeasts, and mushroom and are aerobic, multicellular, eukaryotes, and chemoheterotrophs that require organic compounds for energy and carbon. They are larger than bacteria, and do not require as much nitrogen. They grow more slowly and in a more acidic pH range than bacteria, and are more sensitive to changes in moisture levels. Yeasts are unicellular organisms that are larger than bacteria, and are shaped like eggs, spheres, or ellipsoids.

10.5.3.3 Algae

Algae are single-celled and multicellular microorganisms and are considered to be the abundant photosynthetic microorganisms in soils. According to Martin and Focht (1977), (a) the availability of inorganic nutrients such as C, N, P, K, Fe, Mg, and Ca are said to be responsible for their (soil algae) abundance, and (b) their principal functions in soil are nitrogen fixation, colonization of new rock and barren surfaces, supplying organic matter and nitrogen for humus formation, weathering of rocks and minerals, and binding of soil particles through surface bonding.

10.5.3.4 Viruses

Viruses are the smallest type of microbe and can be 10,000 times smaller than bacteria. They require a living cell to reproduce. It is said that their primary function is to reproduce, and they do it well by taking over a host cell. They have a direct influence on bacterial abundance, and through lysis (cell destruction) and transduction—i.e., transfer of viral DNA from one cell to another through viruses that attack bacteria (bacteriophages)—they can alter bacterial genetic diversity. Beyond their direct attack on the various microbial cells and their influence on community composition, their other functions in soil are not too well known or established.

10.5.3.5 Bacteria

Bacteria are single-celled microorganisms that vary in size and shape from very small spheres to rods that can vary from 1 μm to a few micrometers in length and width. There are literally many thousands of different bacterial species coexisting in the soil. With favorable conditions of temperature and nutrient availability, it is reported that bacterial population in soil can be in the order of 10^8 to 10^{10} /g of soil. They are both autotrophic and heterotrophic. Most bacteria used for bioremediation—treatment of organic chemicals are chemoorganotrophs and heterotrophs. Those requiring organic substrates for energy are called chemoorganotrophs and those using organics as a carbon source are called heterotrophs. Those that use inorganic compounds as an energy source are named chemolithotrophs. Nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*) that use carbon dioxide as a carbon source instead of organic compounds are called autotrophs. Nitrifying bacteria produce nitrite from ammonium ion, which is then followed by conversion to nitrate.

10.6 Natural Attenuation Capability of Soils

By definition, the reduction of toxicity and concentration of contaminants in a contaminant plume during transport in the subsurface soil is called *contaminant attenuation*. We use the general term contaminants to include pollutants and all other kinds of hazardous substances in the fluid phase of the soil–water system. If the various processes responsible for contaminant attenuation are naturally occurring, the attenuation process is said to be the result of the *natural attenuation capability* (i.e., assimilative capacity) of the subsurface soil. What are these naturally occurring attenuation processes? These are the physical, chemical, and biological properties discussed in the previous section. They all contribute to the assimilative capacity of soil, i.e., the capacity of the soil to “cleanse itself” through

attenuation of the flux of contaminants by means of processes that include physical, chemical, and biologically mediated mass transfer, and biological transformation.

The American Society for Testing and Materials (ASTM) (1998) defines *natural attenuation* as the “reduction in mass or concentration of a compound in groundwater over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as; biodegradation, dispersion, dilution, adsorption, and volatilization.” The USEPA (1999), meanwhile, considers natural attenuation specifically in the context of a monitored scheme for treatment of polluted sites. Accordingly, the USEPA use the term *monitored natural attenuation* and define it as:

The reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The ‘natural attenuation processes’ that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. (USEPA 1999)

In the specific context of contaminants and transport of liquid wastes, leachates, etc., in the subsoil, the reduction and detoxification of all of these contaminants from processes associated with natural attenuation is termed *intrinsic remediation*. More specifically, reduction in concentration of contaminants is by processes of partitioning and dilution, and reduction in toxicity of the contaminants is generally achieved by biological transformation (of organic chemicals) and sequestering of the toxic inorganic contaminants. The test results reported by Coles and Yong (2004) in Figure 10.10 show the importance of soil

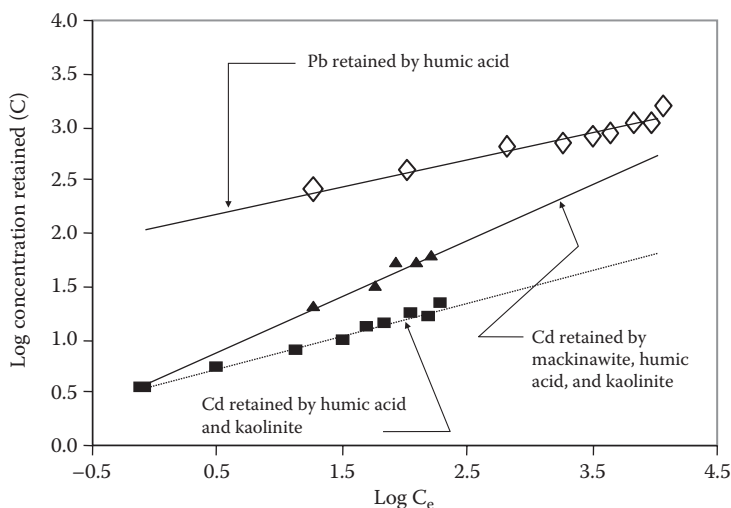


FIGURE 10.10

Freundlich-type adsorption isotherms are showing the retention of Pb humic acid, and Cd by kaolinite and humic acid, and mackinawite ($(\text{Fe,Ni})_9\text{S}_8$, humic acid, and kaolinite. Solutions of Pb and Cd at pH 4.3 were obtained as PbCl_2 and CdCl_2 , respectively. (Data from Coles, C.A. and Yong, R.N., Use of equilibrium and initial metal concentrations in determining Freundlich isotherms for soils and sediments. In R.N. Yong and H.R. Thomas (eds.), *Geoenvironmental Engineering: Integrated Management of Groundwater and Contaminated Land*, Thomas Telford, pp. 20–28, 2004.)

composition on the retention of lead (Pb) and cadmium (Cd). In the particular case shown in Figure 10.10, humic matter in the form of fulvic acid, a sulfide mineral called mackinawite ($(\text{Fe,Ni})_9\text{S}_8$) and kaolinite were used as control soil material.

One speaks of the natural attenuation of contaminants as being a set of positive processes that mitigates the impact of contaminants in the ground through a reduction of their intensity—as measured in terms of concentration and toxicity of the contaminants. In the past, the use of natural attenuation processes had been considered almost exclusively in connection with remediation of contaminated sites—and more specifically with sites contaminated with organic chemical contaminants, as shown, for example, in the definition provided by the USEPA. Little distinction was made between intrinsic remediation and intrinsic bioremediation. More recently, with a better appreciation of the assimilative capacity of soils and especially in view of a growing body of research information on contaminant–soil interactions, more attention is being paid to the use of natural attenuation as a tool for mitigating and managing the transport and fate of contaminants in the ground. A contributing factor has also been the accelerating costs for application of aggressive remediation techniques to treat contaminated sites. The reader is reminded that *contaminants* include all the polluting and health-threatening elements entering into the ground, such as contaminants, toxicants, leachates, liquid wastes, hazardous substances, etc.

10.6.1 Natural Attenuation by Dilution and Retention

We have, up to now, considered natural attenuation of contaminants as being due to the processes associated with physical, chemical, and biological properties of soil. We have considered that these properties contribute directly to the partitioning of contaminants, i.e., the transfer of contaminants in the porewater to the surfaces of the soil solids. Strictly speaking, there is another set of processes that arguably can be considered as part of the natural attenuation capacity of soils—except that we would now have to refer to this as the natural attenuation capacity of soil–water systems. Although the groundwater and porewater aspects of the soil–water system have heretofore been considered only in respect to their physical and chemical interactions with the soil solids and contaminants, they attenuate contaminants through processes of dilution. Thus, in addition to the processes previously described, reduction in concentrations of contaminants can be accomplished by dilution through mixing of the contaminants with uncontaminated or less contaminated groundwater. In total, natural attenuation of contaminants in soils includes (a) dilution, (b) interactions and reactions between contaminants and soil solids resulting in partitioning of the contaminants between the soil solids and porewater, and (c) transformations that reduce the toxicity threat posed by the original polluting contaminants (contaminants). The likelihood of only one mechanism being solely responsible for attenuation of contaminants in transport in the soil is very remote. In all probability, all the various processes or mechanisms will participate to varying degrees in the attenuation of contaminants—with perhaps partitioning being by far the most significant factor in attenuation of contaminants.

10.6.1.1 Dilution and Retention

In the context of contaminant transport in soils, *dilution* refers to the reduction in concentration of contaminants in a unit volume as a result of a reduction of the ratio of number of contaminants n_c to the volume V of the host fluid. An example of this would be when the original contaminant load is given as 100 ppm, and dilution with groundwater reduces this to 50 ppm, the singular process responsible for the decrease or reduction in

concentration is dilution, and transport in the subsoil will likely be consistent with the advective velocity of the groundwater. Except for physical controls on groundwater flow, no other soil properties are involved in the dilution process.

Retention refers to the retention of contaminants by the soil solids through partitioning processes that involve physicochemical and chemical mass transfer. The result of retention is a decrease in the concentration of contaminants in a leachate plume or liquid waste stream as one progress away from the source. Using the same numerical example as above, one would see a reduction from 100 ppm to 50 ppm in a contaminant transport stream at a point further downstream from the contaminant source. The difference between this and the previous example is that when reduction of concentration is obtained through retention processes, the contaminants retained will not be readily available for transport. In the case of dilution as a means for reduction in concentration of contaminants, there are no contaminants held by the soil particles. All the contaminants will be delivered downstream in due time. Figure 10.11 illustrates the differences using assumed ideal bell-shaped concentration distribution pulses. In the case of dilution, the diagram shows that eventually, the total contaminant load will be delivered downstream. The areas of the assumed bell-shaped dilution pulses are all constant and equal to the original rectangular distribution shown on the ordinate. In contrast, the assumed bell-shaped retention pulses will show decreasing areas. These retention pulses will diminish to zero so long as the assimilative capacity of the soil is not exceeded. This is a significant point of consideration in the use of the natural attention capacity of soils for mitigation and management of impacts from liquid waste and contaminant discharges.

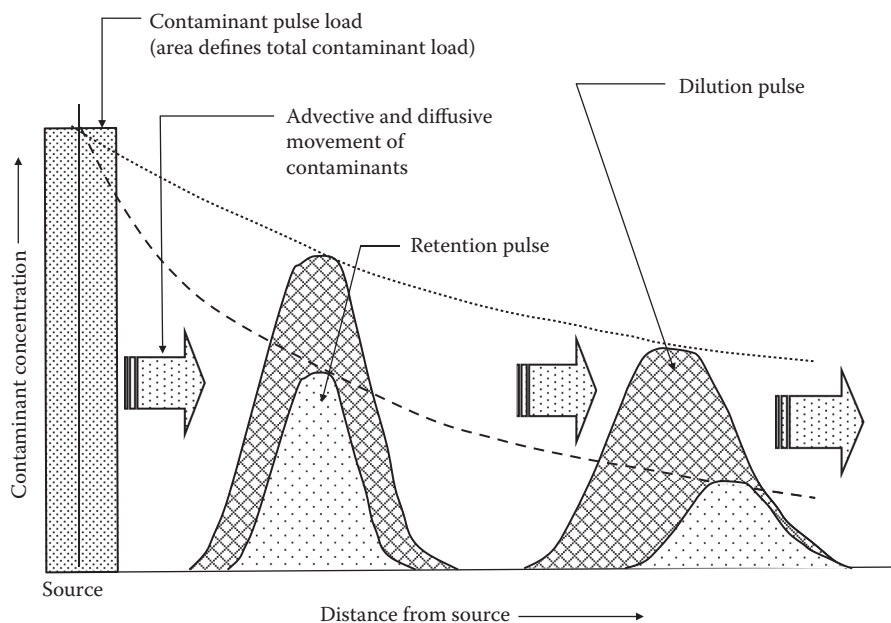


FIGURE 10.11

Illustration of difference between retardation and retention of contaminants during transport of a contaminant pulse load. Note that the areas of the assumed bell-shaped dilution pulses are constant and that they are equal to the original contaminant pulse load. The areas of the assumed bell-shaped retention pulses diminish as one progresses further away from the source.

10.6.2 Biodegradation and Biotransformation

The common perception is that biological activities in the subsoil will degrade organic chemical compounds. Not always understood or perceived is whether this does in fact contribute to attenuation of the concentration and toxicity of the contaminants in the subsoil. Figure 10.12 provides the overall view of various attenuating mechanisms in the soil. The top left-hand corner of the diagram shows the biologically mediated transfer mechanisms participating in the attenuation process. Not well illustrated or sometimes not fully acknowledged are the redox reactions (this includes both abiotic and biotic redox reactions) listed under the *Chemical Mass Transfer* box in the bottom right corner of the diagram.

The discussions in the latter sections of this chapter will provide case histories dealing with treatments using various procedures and techniques. Among these will be the use of intrinsic bioremediation in management of contaminant transport. Before embarking on these discussions, it is useful to clarify the use of the term *substrate* in the discussions to follow. In the context of biological activities in the subsoil, the term *substrate* is used to mean the food source for microorganisms. This term should not be confused with the term *substrate* used in some soil mechanics and geotechnical engineering literature to mean subsurface soil stratum. The use of *substrate* as a term here is consistent with usage in microbiology, and is meant to indicate that it (*substrate*) serves as a nutrient source and also a carbon or energy source for microorganisms.

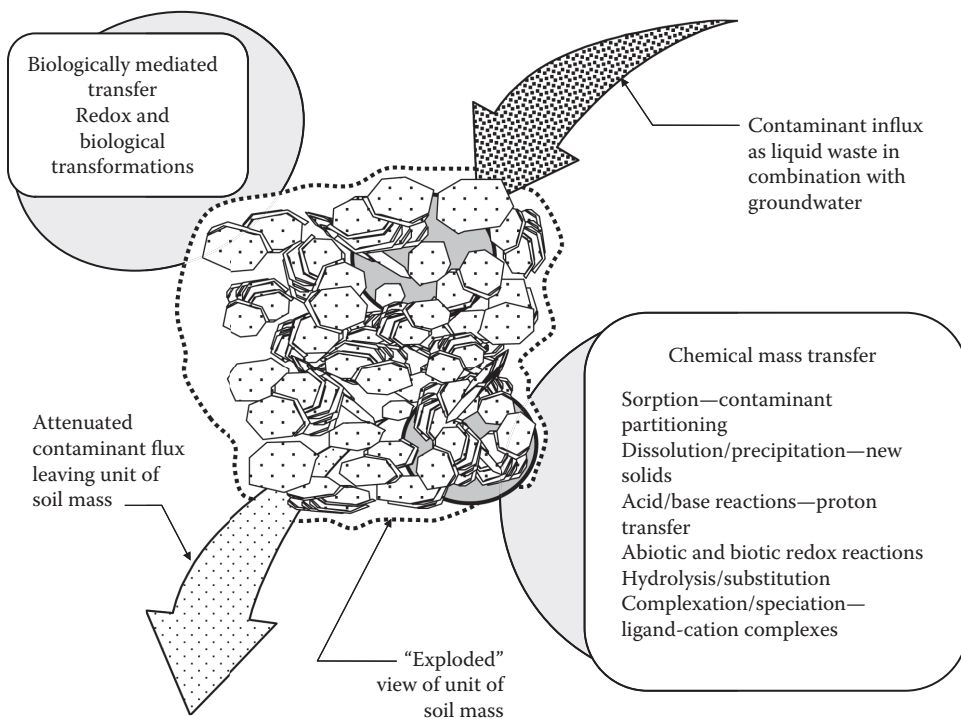


FIGURE 10.12

Processes involved in attenuation of contaminants in leachate transport through a soil element. Dilution of contaminants is not included in the schematic illustration. (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

By definition, *biodegradation* refers to the decomposition of organic matter by microorganisms. The end result of the metabolic and enzymatic processes is seen in terms of smaller compounds, and in respect to organic contaminant remediation goals, ultimately as CO_2 , CH_4 , and H_2O . The organic wastes and chemicals of interest in this book are contaminants such as organic compounds that contain carbon, and organic waste matter. Strictly speaking, biodegradation is a particular form of biotransformation, since *biotransformation* (or biological transformation) means the conversion of a chemical substance into another chemical substance (generally a metabolite) by enzymatic action or other biological processes. The use of the term *biodegradation* implies that the biological transformation process reduces the original organic chemical compound into smaller fragments, with the presumed conclusion that these smaller fragments are less toxic or less threatening to the receptors. To some extent, this is probably valid. However, the well-documented and well-reported example of anaerobic “degradation” of C_2Cl_4 (perchloroethylene, PCE) to $\text{C}_2\text{H}_3\text{Cl}$ (vinyl chloride) shows that the latter “degraded” compound is more of a threat than the original, because $\text{C}_2\text{H}_3\text{Cl}$ is more toxic and volatile than PCE, and does not partition well in the soil. In any event, the transformation of original organic chemical compounds in the subsurface soil into smaller units occurs by oxidation and reduction mechanisms (redox reactions) resulting from the metabolic activities of the microorganisms in the soil. In the next few subsections, we will show examples from Yong and Mulligan (2004) of biotransformation and biodegradation of some organic chemical compounds. Greater details of the many kinds of transformations and conversions can be found in specialized texts dealing with bioremediation.

10.6.2.1 Petroleum Hydrocarbons: Alkanes, Alkenes, and Cycloalkanes

Petroleum hydrocarbon consists of various compounds such as alkanes, cycloalkanes, aromatics, polycyclic aromatic hydrocarbons, asphaltenes, and resins. Their biodegradability in the subsoil range from very biodegradable to recalcitrant. This is because of the varying degrees of branching, chain lengths, molecular sizes, substitution with nitrogen, oxygen, or sulfur atoms. Many of the alkanes found in petroleum are branched.

Alkanes ($\text{C}_n\text{H}_{2n+2}$) are aliphatic compounds. Low molecular weight alkanes are the most easily degraded by microorganisms. However, as the chain length increases from C_{20} to C_{40} , hydrophobicity increases, whereas solubility and biodegradation rates decrease. Conversion of alkanes leads to the formation of an alcohol using a monooxygenase enzyme. This is followed by oxidation to an aldehyde and then to a fatty acid (Pitter and Chudoba, 1990). Further oxidation (β -oxidation) of the fatty acid yields products less volatile than the original contaminants. Anaerobic bacteria such as sulfate-reducing bacteria are capable of degrading fatty acids via this step (Widdel, 1988). Although bacteria that are capable of degrading *n*-alkanes cannot degrade branched ones (Higgins and Gilbert, 1978), *Brevibacterium ethrogenes*, *Corynebacteria* sp., *Mycobacterium fortuitum*, *Mycobacterium smegmatis*, and *Nocardia* sp. have been shown to grow on branched alkanes. The first degradation step is the same as for the unbranched alkanes. However, the β -oxidation is more difficult and less efficient (Pirnik, 1977). In addition, in the presence of *n*-alkanes, the metabolism of the branched alkanes will be repressed, which will cause difficulties during the degradation of mixtures such as petroleum.

Alkenes with a double bond between carbons and have not been extensively studied for biodegradation. Those containing the double bond on the first carbon may be more easily degradable than those alkenes with the double bond at other positions (Pitter and Chudoba, 1990). The products of oxidation of 1-alkenes can be either diols or the methyl group.

Because of their cyclic structure, cycloalkanes are not as degradable as alkanes, and they become less degradable as their number of rings increases. Pitter and Chudoba (1990) attribute some of this to their decreasing solubility. Species of *Nocardia* and *Pseudomonas* are able to use cyclohexane as a carbon source. Oxidation of the cycloalkanes with the oxidase enzyme leads to production of a cyclic alcohol and then a ketone (Bartha, 1986).

10.6.2.2 Gasoline Components BTEX and MTBE

Benzene, toluene, ethylbenzene, and xylene (BTEX) are volatile, water-soluble, hazardous components of gasoline. Aerobic degradation of all components of BTEX occurs rapidly with available oxygen. Under anaerobic conditions, degradation is less reliable and is slower than under aerobic conditions. Bacterial metabolism proceeds through a series of steps depending on the availability of electron acceptors.

The gasoline additive methyl *tert*-butyl ether (MTBE) is believed to be highly resistant to biodegradation since it is reactive with microbial membranes. Some believe that it is slowly biodegraded (Borden et al., 1997), whereas others believe that it partially degrades to *tert*-butyl alcohol (TBA), a health hazard (Landmeyer et al., 1998). More recently, it has become generally accepted that MNA of MTBE is an acceptable remediation scheme. Sorption and volatilization are limited. However, mechanisms such as uptake by plants, and abiotic degradation by oxidation and hydrolysis are likely. In addition biodegradation and its by-products are biodegradable under aerobic and anaerobic conditions (Bradley et al., 2001). Guidance documents have been prepared by the API for the natural attenuation of MTBE (Zeeb and Wiedemeier, 2007).

10.6.2.3 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs, $C_{4n+2}H_{2n+4}$), are components of creosote. As with cycloalkanes, they are difficult to degrade and as the number of rings increases, the compounds become more difficult to degrade—a result of their decreasing volatility and solubility, and increased sorption. They are degraded one ring at a time. As an example, the pathway for biodegradation of anthracene is from anthracene *cis*-1,2-dihydrodiol to salicylate with at least six intermediates beginning with 1,2-dihydroxy anthracene onward to 1-hydroxy-2-naphthoic acid as the last intermediate before salicylate.

10.6.2.4 Halogenated Aliphatic and Aromatic Compounds

Halogenated aliphatic compounds include (a) pesticides such as ethylene dibromide (DBR) or $CHCl_3$, $CHCl_2Br$ and (b) industrial solvents such as methylene chloride and trichloroethylene. Because of the presence of halogen, the lower energy and higher oxidation state make aerobic degradation more difficult to achieve than anaerobic biodegradation. Methylene chloride, chlorophenol, and chlorobenzoate are the most aerobically biodegradable. Removal of the halogen and replacement by a hydroxide group is often the first step of the degradation process, particularly when the carbon chain length is short. An example of this is methylene chloride, with formaldehyde, 2-chloroethanol, and 1,2-ethanediol as intermediates and carbon dioxide as the final product (Pitter and Chudoba, 1990).

Biodegradation of chlorinated ethenes involves formation of an epoxide and hydrolysis to carbon dioxide and hydrochloric acid. Reductive dehalogenation can occur anaerobically and involves replacement of the halogen with hydrogen or formation of a double bond when two adjacent halogens are removed (dihalo-elimination). This is the particular

case for PCE. As discussed previously, perchloroethylene (PCE) and TCE can be reduced to form vinylidene and vinyl chloride (VC) that are more toxic and volatile than the original compound. Oxidation of vinyl chloride to carbon dioxide and water occurs under aerobic conditions. Induction of monooxygenase or dioxygenase enzymes can lead to the co-metabolism of TCE by methanotrophs (Alvarez-Cohen and McCarty, 1991). However, molecular oxygen and a primary substrate (methane, ethene, phenol, toluene, or other compounds) must be available for natural attenuation by this mechanism.

Halogenated aromatic compounds include pesticides such as DDT, 2,4-D, and 2,4,5-T, plasticizers, pentachlorophenol, polychlorinated biphenyls. Although PCBs have been banned since the 1970s, the record shows that they are still found in aqueous and sediment systems. Congeners containing fewer chlorines are degraded more quickly than those with more than four chlorine atoms (Harkness et al., 1993). Soluble forms are much more likely to biodegrade through natural attenuation than those sorbed to solids or entrapped in NAPLs. Mechanisms involved in transformations and conversions of halogenated aromatic compounds include biodegradation, hydrolysis (replacement of halogen with hydroxyl group), reductive dehalogenation (replacement of halogen with hydrogen), and oxidation (introduction of oxygen into the ring causing removal of halogen). As the number of halogens rise, reductive dehalogenation will occur. In addition, ring cleavage could occur before oxidation, reduction, or substitution of the halogen.

Bacterial strains of *Pseudomonas* sp., *Acinetobacter calcoaceticus*, and *Alkaligenes eutrophus* have been able to degrade aromatic halogenated compounds by oxidizing them to halocatechols followed by ring cleavage (Reineke and Knackmuss, 1988). Cleavage for chlorobenzene, for example, can occur either at the *ortho* position to form chloromuconic acid or at the *meta* position to form chlorohydroxymuconic semialdehyde. Subsequent dehalogenation can be spontaneous (Reineke and Knackmuss, 1988). As reported by Yong and Mulligan (2004), chlorinated benzoates (Suflita et al., 1983), 2,4,5-T pesticides, PCBs (Thayer, 1991), 1,2,4-trichlorobenzenes (Reineke and Knackmuss, 1988) are known to undergo reductive dehalogenation under anaerobic conditions. *Rhodococcus chlorophenolicus* (Apajalahti and Salkinoja-Salonen, 1987), and *Flavobacterium* sp. (Steiert and Crawford, 1986) can aerobically biodegrade pentachlorophenol, whereas anaerobic degradation of 3-chlorobenzoate and PCBs has been identified by methanogenic consortia (Nies and Vogel, 1990).

10.6.2.5 Metals

It has long been assumed that biological transformation and degradation applied primarily to organic chemical compounds. More recently, however, research has shown that microbial conversion of metals occurs. The following short account summarizes the discussion from Yong and Mulligan (2004). Microbial conversion includes bioaccumulation, biological oxidation/reduction, and biomethylation (Soesilo and Wilson, 1997). Microbial cells can accumulate heavy metals through ion exchange, precipitation, and complexation on and within the cell surface containing hydroxyl, carboxyl, and phosphate groups. Bacterial oxidation/reduction could be used to alter the mobility of the metals. For example, some bacteria can reduce Cr(IV) in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) to Cr(III), which is less toxic and mobile due to precipitation above pH 5 (Bader et al., 1996).

The use of rhamnolipid biosurfactant has been demonstrated for the removal and reduction of hexavalent chromium from contaminated soil and water in batch experiments (Ara and Mulligan, 2008). A sequential extraction study was used on soil before and after washing to determine from what fraction the rhamnolipid removed the chromium. The exchangeable and carbonate fractions accounted for 24% and 10% of the total chromium, respectively. The oxide

and hydroxide portions bound 44% of the total chromium in the soil. Meanwhile, 10% and 12% of the chromium was associated with the organic and residual fractions. Rhamnolipid was able to remove most of the exchangeable (96%) and carbonate (90%) portions and some of the oxide and hydroxide portion (22%) but from the other fractions. This information is important in designing the appropriate conditions for soil washing and for potential aspects of natural attenuation in the presence of biosurfactant producing microorganisms.

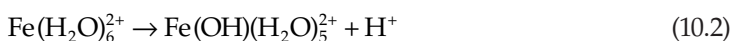
Mercury can be found as Hg(II), volatile elemental mercury (Hg(0)), methyl, and dimethyl forms. Metabolism occurs through aerobic and anaerobic mechanisms through uptake, conversion of Hg(II) to Hg(0), methyl and dimethylmercury or to insoluble Hg(II) sulfide precipitates. Although volatilization or reduction during natural attenuation would still render mercury mobile, Hg(II) sulfides are immobile if sufficient levels of sulfate and electron donors are available.

Arsenic can be found as the valence states As(0), As(II), As(III), and As(V). Forms in the environment include As₂S₃, elemental As, arsenate (AsO₄³⁻), arsenite (AsO₃²⁻), and other organic forms such as trimethyl arsine and methylated arsenates. The anionic forms are mobile and highly toxic. Microbial transformation under aerobic conditions produces energy through oxidation of arsenite. Other mechanisms include methylation, oxidation, and reduction under anaerobic or aerobic conditions.

Selenium, which is a micronutrient for animals, humans, plants, and some microorganisms can be found naturally in four major species, selenite (SeO₃²⁻, IV), selenate (SeO₄²⁻, VI), elemental selenium (Se(0)), and selenide (-II) (Frankenberger and Losi, 1995; Ehrlich, 1996). Oxidation of selenium can occur under aerobic conditions, whereas selenate can be transformed anaerobically to selenide or elemental selenium. Methylation of selenium detoxifies selenium for the bacteria by removing the selenium from the bacteria. Immobilization of selenate and selenite is accomplished via conversion to insoluble selenium. Due to the many forms of selenium, selenium decontamination by microorganisms is not promising.

10.6.2.6 Oxidation–Reduction Reactions

It is useful to recall that (a) the chemical reaction process defined as *oxidation* refers to a removal of electrons from the subject of interest and (b) *reduction* refers to the process where the “subject (electron acceptor or *oxidant*)” gains electrons from an electron donor (*reductant*). By gaining electrons, a loss in positive valence by the subject of interest results and the process is called a reduction. Oxidation–reduction (redox) reactions have been briefly discussed in Chapter 9. Biological transformation of organic chemical compounds results from biologically mediated redox reactions. Bacteria in the soil utilize redox reactions as a means to extract the energy required for growth. They are the catalysts for reactions involving molecular oxygen and organic chemicals (and also soil organic matter) in the ground. Redox reactions involve the transfer of electrons between the reactants. The activity of the electron e⁻ in the chemical system plays a significant role. Reactions are directed toward establishing a greater stability of the outermost electrons of the reactants, i.e., electrons in the outermost shell of the substances involved. The link between redox reactions and acid–base reactions is evidenced by the proton transfer that accompanies the transfer of electrons in a redox reaction. Manahan (1990) gives the example of the loss of three hydrogen ions that accompanies the loss of an electron by Fe(II) at pH 7 resulting in the formation of a highly insoluble ferric hydroxide, as indicated by the following:



It is not easy to distinguish between abiotic and biotic (biologically mediated) redox reactions. To a large extent, it is not always possible to eliminate or rule out involvement of microbial activity in abiotic redox reactions. There does not appear to be a critical need to distinguish between the two in reactions that concern organic chemical contaminants, since it is almost certain that with all the microorganisms in the subsoil, some measure of microbial activity would be involved. In any event, the number of functional groups of organic chemical contaminants that can be oxidized or reduced under abiotic conditions is considerably smaller than those under biotic conditions (Schwarzenbach et al., 1993).

The two classes of electron donors of organic chemical contaminants are (1) electron-rich B-cloud donors, which include alkenes, alkynes, and the aromatics, and (2) lone-pair electron donors, which include the alcohols, ethers, amines, and alkyl iodides. Similarly, in the case of electron acceptors, we have (1) electron-deficient π -electron cloud acceptors, which include the π -acids, and (2) weakly acidic hydrogens such as *s*-triazine herbicides and some pesticides.

A measure of the electron activity in the porewater of a soil–water system is the *redox potential* Eh . It provides us with a means for determining the potential for redox reactions in the contaminant–soil–water system under consideration and is given as

$$Eh = pE \left(\frac{2.3RT}{F} \right) \quad (10.3)$$

where E is the electrode potential, R is the gas constant, T is the absolute temperature, and F is the Faraday constant. The electrode potential E is given in terms of the half reaction



When the activity of $H^+ = 1$ and the pressure H_2 (gas) = 1 atmosphere, we obtain $E = 0$.

10.7 Natural Attenuation and Impact Management

The natural attenuation capacity of soils in the substratum has long been recognized and described by soil scientists as the assimilative capacity of soils. The discussions at the beginning of the previous section and in the earlier chapters of this book show that this is now a tool that can be used as a passive treatment process in the remediation and management of sites contaminated by organic chemicals. The USEPA has wisely coupled the requirement for continuous on-site monitoring of contaminant presence whenever natural attenuation is to be used as a tool for site remediation—as seen in the definition provided in the first part of Section 10.4. The procedure for application of this attenuation process is called *monitored natural attenuation* (MNA). Guidelines and protocols for application of MNA as a treatment procedure in remediation of contaminated sites have been issued. Since site specificities differ from site to site, the prudent course of action is to adapt the guidelines and protocols for site-specific use. A general protocol, from Yong and Mulligan (2004) for considering MNA as a remediation tool is shown in Figure 10.13. A very critical step in the application of MNA as a site remediation tool is to have proper knowledge of (a) *lines of evidence* indicating natural or intrinsic remediation, (b) contaminants, soil

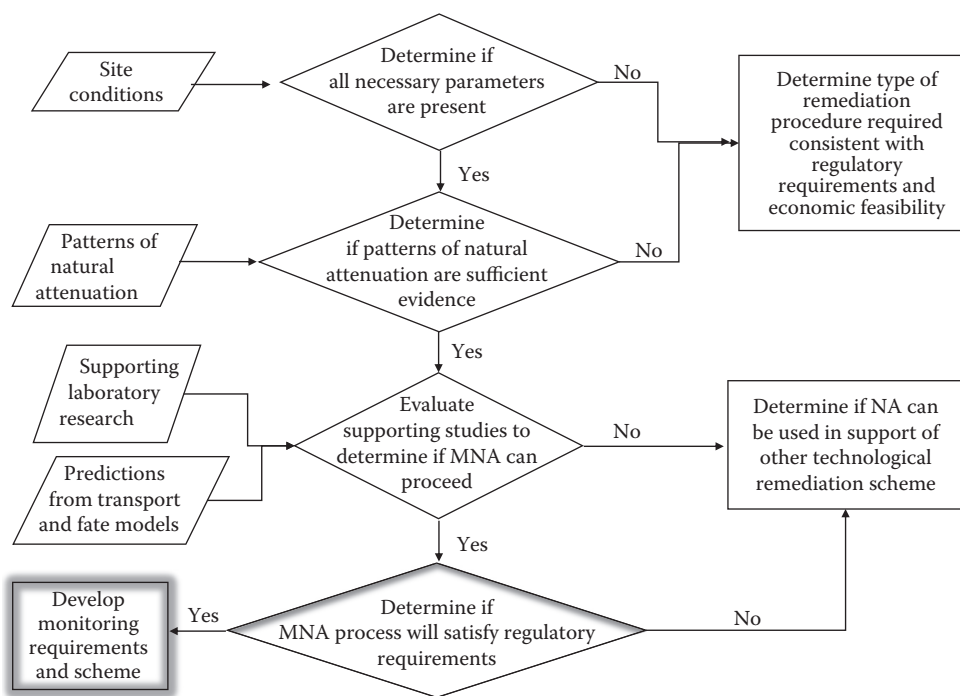


FIGURE 10.13

General protocol for considering MNA as a remediation tool. (From Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

properties, and hydrogeology, and (c) regulatory requirements governing *evidence of success* of the MNA remediation project. Lines of evidence and evidence of success will be discussed in the latter portion of this section.

The data and information inputs shown on the left-hand side of the diagram in Figure 10.13 tell us what is required to satisfy site-specific conditions, and whether the *indicators* for natural bioremediation are sufficient to proceed with further examination to satisfy that the use of MNA is a viable treatment option. Negative responses from the first two decision steps will trigger technological and/or engineered solutions to the remediation problem. As will be seen, laboratory research and transport and fate modeling are needed to inform one about the ability of the site materials and conditions to attenuate the contaminants.

Adoption of natural attenuation (NA) as an active tool in the management of contaminant impact and transport, as opposed to the use of MNA as a passive tool, has been hampered because of insufficient knowledge of the many processes that contribute to the natural attenuation process. The designation of MNA as more of a passive tool as opposed to an active tool is based on the fact that except for the monitoring requirement, the use of natural attenuation processes as existent in situ is essentially a “do-nothing” solution. The do-nothing part refers to human contribution to the processes resulting in natural attenuation of contaminants. As a clarification, we should point out that the acronym NA is used to denote natural attenuation as a process tool. When we wish to discuss the processes that result in the natural attenuation of contaminants, we will use the complete term *natural attenuation*. To make NA an active tool, we can (a) enhance the processes that

contribute to natural attenuation capability and (b) incorporate NA as part of a scheme to mitigate and manage the geoenvironmental impacts from discharge and/or containment of waste products and contaminants.

10.7.1 Enhancement of Natural Attenuation Capability

Successful application of waste discharge and ground contamination impact mitigation procedures reduces and/or minimizes the damage done to the land environment and its inhabitants. The main objective of such procedures is to achieve reduction or elimination of health threats to the biotic receptors through elimination or minimization of ground contamination, and prevention of contamination of receiving waters and groundwater. The objectives or desired end points sought in contaminant impact mitigation fit very well with the capabilities of the processes in soils that contribute to natural attenuation. Accordingly, natural attenuation can be used as tool to provide impact mitigation and management since the basic processes involved in natural attenuation result in reduction of concentration of contaminants and toxicity. To increase the capability of natural attenuation as a process tool—i.e., the process tool NA—one can consider enhancement of the natural assimilative capacity of the soil–water system. These can take the form of geochemical and biogeochemical aids, bioaugmentation, and biostimulation. Successful enhancement of NA as a process tool will produce a subsoil with properties that can be considered as *enhanced NA capability*.

10.7.1.1 Soil Buffering Capacity Manipulation

The capability of a soil to accept and retain inorganic and some organic contaminants can, in some instances, be assessed by determining its chemical buffering potential—particularly if the reactions in the soil–water system result in changes in the pH of the system. The chemical buffering system contributes significantly to the carrying capability of the soil, i.e., the capability of the soil barrier or subsoil to accept and retain contaminants. The main issue is the ability of the soil–water system to maintain a natural pH level (within acceptable limits) despite the input of acidic or alkaline contaminant leachates. In situ soil pH manipulation for the purpose of contaminant impact mitigation requires introduction of buffering agents generally through leaching methods or via injection. In contaminant–soil interaction, the chemical buffering system describes the capability of the system to act as chemical barrier against the transport of contaminants.

The buffering capacity of a soil determines the potential of a soil for effective interaction with leachate contaminants and is more appropriate for inorganic soils and inorganic contaminant leachates. The principal features that establish the usefulness of buffering capacity assessment center around the “acidity” or “alkalinity” of the initial soil–water system and the solutes in the leachate. Soil conditioning in respect to changes in the natural soil buffering capacity is usually considered in terms of addition of buffering agents, much in the same manner as solution chemistry. In the in situ soil conditioning case, however, addition of buffering agents needs to be effectuated through injection wells or through leaching, for example, by adding lime to the surface as the leach source to increase the pH of the soil. In a site contaminated with heavy metals, raising the pH of the soil–water system would precipitate the heavy metal contaminants and thus make them less environmentally mobile and less bioavailable. However, we must recognize that this is not a permanent solution because if the pH of the system is subsequently reduced by environmental forces or external events, the same heavy metals will become mobile again. To

avoid subsequent solubilization, the precipitated heavy metals should be removed from the contaminated site.

10.7.1.2 *Biostimulation and Bioaugmentation*

Chapter 3 introduced the use of biological aids, *biostimulation* and *bioaugmentation*, as part of the available tools for groundwater management. *Biostimulation* occurs when stimuli such as nutrients and other growth substrates are introduced into the ground to promote increased microbial activity of the microorganisms existent in the site. The intent is to obtain improved capabilities of the microorganisms to more effectively degrade the organic chemical contaminants in the soil. The addition of nitrates, Fe(III) oxides, Mn(IV) oxides, sulfates, and CO₂, for example, will allow for anaerobic degradation to proceed. Biostimulation is perhaps one of the least intrusive of the methods of enhancement of the natural attenuation capacity soils.

Bioaugmentation denotes the process whereby exogenous microorganisms are introduced in situ to aid the native or indigenous microbial population in degrading the organic chemicals in the soil. The reason one would use bioaugmentation is presumably because the microorganisms in the soil are not performing up to expectations. This could be because the concentrations of microorganisms are insufficient, or maybe because of inappropriate consortia. The function of the exogenous microorganisms is to augment the indigenous microbial population such that effective degradative capability can be obtained. Frequently, biostimulation is used in conjunction with bioaugmentation. There is the risk that (a) the use of microorganisms grown in uncharacterized consortia, which include bacteria, fungi, and viruses, can produce toxic metabolites (Strauss, 1991) and (b) the interaction of chemicals with microorganisms may result in mutations in the microorganisms themselves and/or microbial adaptations.

10.7.1.3 *Biochemical and Biogeochemical Aids*

Introduction of geochemical aids in situ utilizes the same techniques employed to introduce the various kinds of growth substrate, nutrients, and exogenous microorganisms for biostimulation and bioaugmentation. Manipulations of pH and *pE* or *Eh* using geochemical aids can increase the capability of the soil to mitigate the impact of some toxic contaminants. A good case in point is the changes in toxicity for chromium and arsenic because of changes in their oxidation state. Chromium (Cr) as Cr(III) is an essential nutrient that helps the body use sugar, protein, and fat. Meanwhile, chromium as Cr(VI) has been determined by the World Health Organization (WHO) to be a human carcinogen. Cr(III) can be oxidized to Cr(VI) by dissolved oxygen and quite possibly with manganese dioxides. If such a possibility exists in a field situation, management of the potential impact can take the form of in situ geochemical and/or biogeochemical intervention to create a reducing environment in the subsurface. A useful procedure would be to deplete the oxygen in the subsurface to create a reduced condition in the soil. The danger or risk of manipulation of the *Eh* of the soil–water regime is incomplete knowledge of all the elements in the subsoil that are vulnerable to such manipulation. The case of arsenic in the ground is a good example. It is known that arsenic (As), as As(III) is more toxic than As(V). If ground conditions show that arsenic is present as As(V), creating a reducing environment to prevent oxidation of chromium to the more toxic oxidation state would create the reverse effect on As(V). Reduction of As(V) to As(III) would increase the toxicity of arsenic.

Manipulation of pH can change the nature of the assimilative capacity soils, as stated previously. It addresses the precipitation of heavy metals in solution (porewater) or dissolution of precipitated heavy metals. Changes in pH of the soil–water system will produce changes in the sign of surface electrostatic charges for those soil materials with amphoteric surfaces, i.e., surfaces that show pH-dependency charge characterization. Subsoils containing oxides, hydrous oxides, and kaolinites are good candidates for pH-dependent charge manipulation. Changes in surface charge characterization can result in increased bonding of metals or release of heavy metals from disruption of bonds. Both pH and *Eh* changes will have considerable influence also on acid–base reactions and on abiotic and biotic electron transfer mechanisms. Abiotic transformations of organic chemical contaminants due to acid–base and redox reactions are minor in comparison to biotic transformations.

10.7.2 NA Treatment Zones for Impact Mitigation

Treatment zones are regions in the subsoil that utilize the NA process tool, and more specifically, enhanced NA, to attenuate the impact of contaminants during transport in the subsoil. Since it is rare to find source discharges conveniently located directly in a region where the various elements contributing to natural attenuation capabilities are available, the usual procedure is to provide a treatment zone that would capture the contaminant plume during transport. A good knowledge of site hydrogeology is essential for this type of mitigation procedure to function properly. Figure 10.14 shows

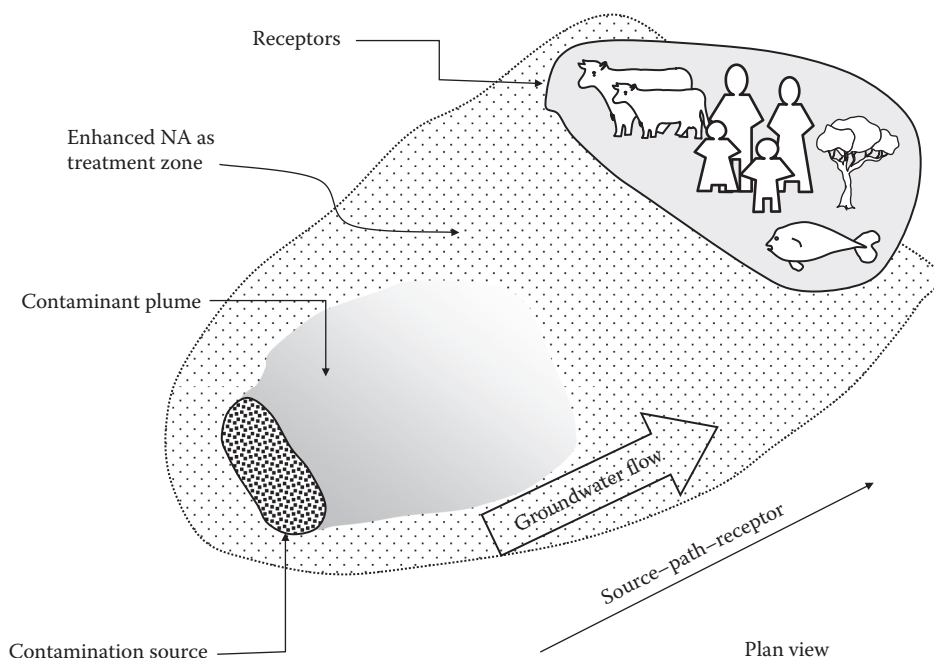
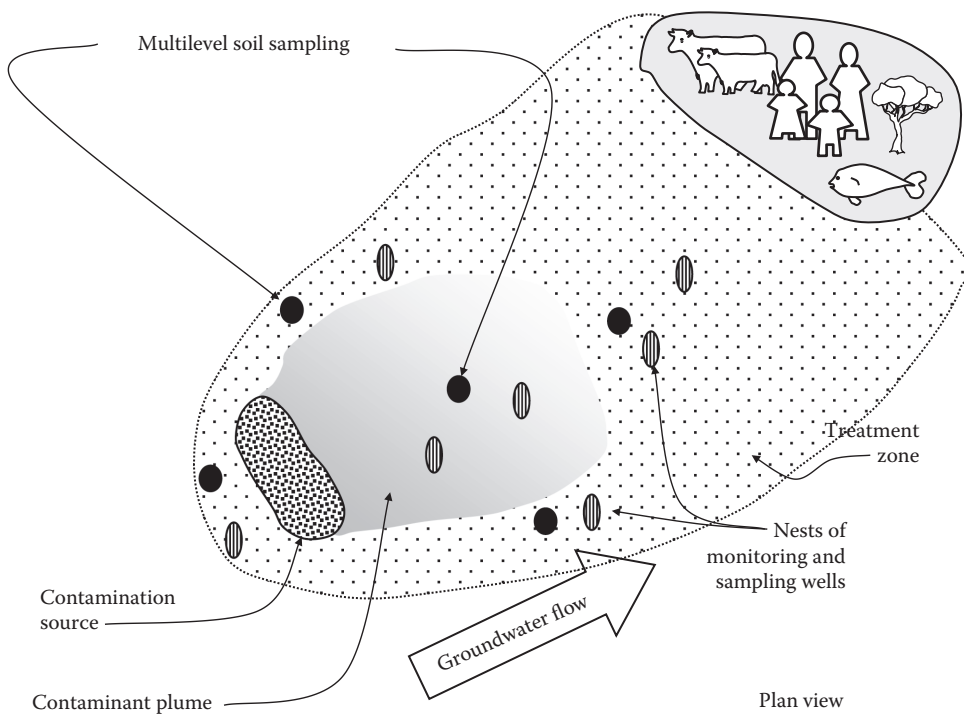


FIGURE 10.14

Simplified plan view of a treatment zone established with enhancement of the natural attenuation capability of the site subsoil to mitigate impact of contaminants on land environment and to protect receptors.

**FIGURE 10.15**

Plan view of distribution of monitoring wells and soil sampling boreholes for verification monitoring of treatment zone effectiveness and long-term conformance monitoring.

a simple SPR (source–pathway–receptor) problem that uses a treatment zone to mitigate the impact of the contaminant plume generated by the contamination source shown at the bottom left of the diagram. To determine if the treatment zone is effective in mitigating the impact of the generated contaminant, the monitoring scheme shown in Figure 10.15 is recommended. By this means, determination of reduction in concentration and toxicity of the contaminants can be obtained. This procedure also allows one to establish evidence of success of the treatment zone. It can be argued that one should remove the contaminant source as part of the mitigation procedure. Assuming that the source is an industrial facility, the obvious course of action is to (a) implement operational procedures in the facility that will reduce output of contaminating items and (b) establish or improve treatment of discharges to capture all the noxious substances discharged into the land environment. The combination of the treatment zone with removal of contaminant source will ensure short-term mitigation and longer-term elimination of the threats posed by the contamination plume—a positive step toward geoenvironmental sustainability.

10.7.2.1 Permeable Reactive Barriers and NA

Permeable reactive barriers (PRBs) are engineered material-barriers constructed and placed in the ground to intercept contaminant plumes. The material in these barriers

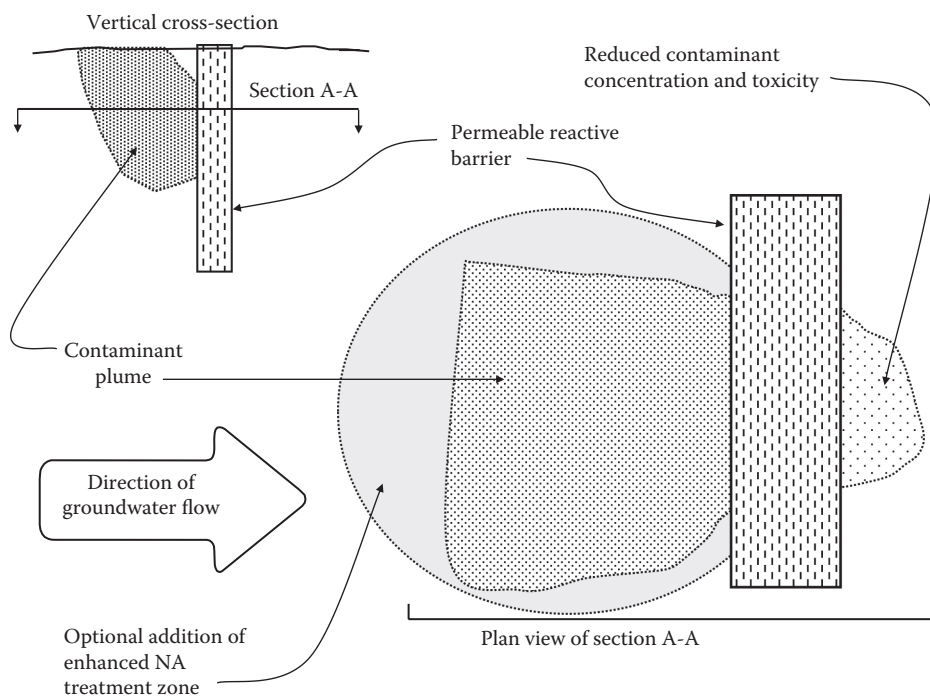
generally consists of permeable soil material containing various elements designed to react with the kinds of contaminants entering the barrier. The whole intent of PRBs is to provide a chemical–physical sieve or filter that would capture the contaminants as they pass through the barrier. In a sense therefore, PRBs are barriers with highly engineered and efficient attenuation properties and characteristics. They are sometimes also known as treatment walls.

The major contaminant capture and immobilization processes needed for the engineered materials in the PRBs to function effectively include (a) sorption, precipitation, substitution, transformation, complexation, oxidation, and reduction for inorganic contaminants and (b) sorption, biotic and abiotic transformations, and degradation for organic chemical contaminants. The types of reagents, compounds, and microenvironment in the PRBs include a range of oxidants and reductants, chelating agents, catalysts, microorganisms, zero-valent metals, zeolite, reactive clays, ferrous hydroxides, carbonates and sulfates, ferric oxides and oxyhydroxides, activated carbon and alumina, nutrients, phosphates, soil organic materials. The selection of engineered materials in the PRBs, such as reagents and compounds, and the manipulation of the pH–*pE* microenvironment in the treatment walls will need to be made on the basis of site-specific knowledge of the nature of the contaminants.

The success of PRBs in mitigating contaminant impacts depends on

1. Effectiveness of types of engineered material in the PRB: This depends on a proper knowledge of the contaminants, barrier material, and the kinds of processes (interactions and bonding mechanisms) resulting from contaminant–barrier material interactions.
2. Sufficient residence time of the contaminant plume in the PRB: There must be sufficient residence time in the PRB for contaminant–material interactions and reactions to be fully realized. This is a function of both the permeability of the barrier itself and the kinds of reaction times needed between contaminants and the barrier material. It would be useless if the contaminant passed through the barrier at high rates—rates that would not permit reactions to be completed. Conversely, it would be useless if the contaminant would not penetrate the barrier, hence denying any opportunity for reactions to occur.
3. Proper intercept of contaminant plume advance: A thorough knowledge of site hydrogeology is required to allow one to place the barrier for optimum intercept of the contaminant plume. A knowledge also of the advective velocity is also required.

For more effective use of PRBs, an enhanced NA treatment zone can be used and placed ahead of the PRB. Such a case has been shown in Figure 3.11 in Chapter 3. The treatment zone in the diagram is shown as an optional tool. Contaminant plumes can be channeled to flow through reactive walls by shepherding the plume with a “funnel-gate” technique. In this technique, the plume is essentially guided to the intercepting reactive wall by a funnel constructed of impermeable material such as sheet-pile walls, and placed in the contaminated ground to channel the plume to the PRB (Figure 10.16). Other variations of the funnel-gate technique exist—obviously in accordance with site geometry and site specificities.

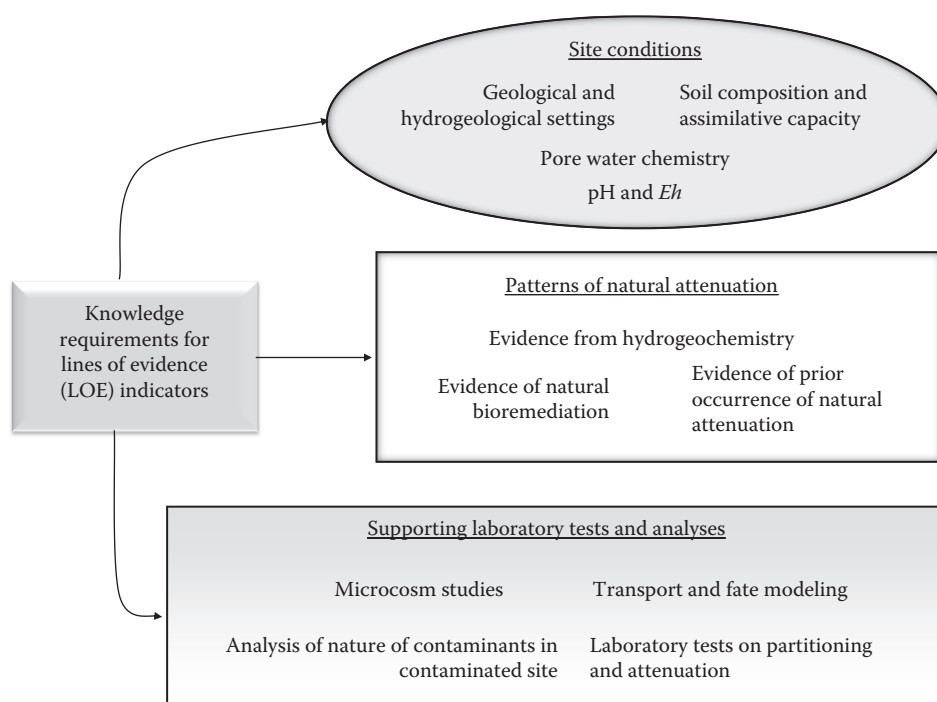
**FIGURE 10.16**

Cross-sectional and plan view of PRB. Plan view shows leachate plume entering the PRB with contaminants and leaving the PRB with reduced contaminant concentration and toxicity. If required, an enhanced NA treatment zone can be situated in front of the PRB to increase the effectiveness of the contaminant impact mitigation scheme. (Adapted from Yong, R.N. and Mulligan, C.N., *Natural Attenuation of Contaminants in Soils*, CRC Press, Boca Raton, FL, 310 pp., 2004.)

10.8 Lines of Evidence

Lines of evidence (LOE) is a term that is associated with the use of NA as a tool for mitigation and management of impacts from waste and contaminant discharges to the land environment. LOE refers to the requirement to determine whether a soil has capabilities for in situ attenuation of contaminants. This requirement originates from procedures associated with the use of monitored natural attenuation (MNA) as a treatment procedure. This is a prudent course of action since there is need to determine how effective a particular soil will be in attenuating contaminants. The types of information and analyses required for LOE indicators are shown in Figure 10.17. Site and problem specificities will dictate how many pieces of information and what specific kinds of analyses will be needed. The type of information needed to define the site characteristics is shown in the top right-hand corner of the diagram. The physical (geological and hydrogeologic) setting sets the parameters of the problem to be resolved. Whether the natural attenuation capability of the subsoil is capable of mitigating and managing the contaminant plume anticipated within the site boundaries will be established by the other two categories; patterns of natural attenuation and supporting laboratory tests and analyses.

Knowledge of the patterns of natural attenuation identified in the central box is essential. What is sought in this category is evidence of previous natural (intrinsic) remediation


FIGURE 10.17

Required information and analyses for LOE indicators.

of contaminants. To determine this, it is necessary to recall the various mechanisms and processes that establish retention and transformation of the various kinds of contaminants generally found in the subsoil. In addition, one needs to determine or assess the environmental mobility of the contaminants in the site under consideration. These are necessary pieces of information for prescription of *indicators* for the lines of evidence (LOE).

10.8.1 Organic Chemical Compounds

The previous chapters have shown that organic chemicals such as organic solvents, paints, pesticides, oils, gasoline, creosotes, greases, etc., are responsible for many of the chemicals found in contaminated sites. These chemicals are known generally as xenobiotic compounds. It is not possible to categorize them all in respect to how they would interact in a soil–water system. The more common organic chemicals found in contaminated sites can be grouped into three broad groups:

- *Hydrocarbons*, including the PHCs (petroleum hydrocarbons), the various alkanes, and alkenes, and aromatic hydrocarbons such as benzene, MAHs (multicyclic aromatic hydrocarbons), e.g., naphthalene, and PAHs (polycyclic aromatic hydrocarbons), e.g., benzopyrene
- *Organohalide compounds*, of which the chlorinated hydrocarbons are perhaps the best known. These include TCE (trichloroethylene), carbon tetrachloride, vinyl chloride, hexachlorobutadiene, polychlorinated biphenyls (PCBs), and polybrominated biphenyls (PBBs)

- *Miscellaneous compounds*, including oxygen-containing organic compounds such as phenol and methanol and nitrogen-containing organic compounds such as TNT (trinitrotoluene)

As shown in Chapter 2, the density of these compounds in comparison to that of water has direct control on their transport in the subsoil. We classify nonaqueous phase liquids (NAPL) into the light NAPLs identified as LNAPLs, and the dense ones called the DNAPLs. LNAPLs include gasoline, heating oil, kerosene, and aviation gas. DNAPLs include the organohalide and oxygen-containing organic compounds such as 1,1,1-trichloroethane, chlorinated solvents such as tetrachloroethylene (PCE), trichloroethylene (TCE) and carbon tetrachloride (CT), PCBs, PCPs (pentachlorophenols) and TCPs (tetrachlorophenols). As shown in Figure 2.7 in Chapter 2, since LNAPLs are lighter than water and the DNAPLs are heavier than water, NAPLs will likely stay above the water table, and DNAPLs tend to sink through the water table and come to rest at an impermeable bottom (bedrock).

The various results of transformations and biodegradation of organic chemicals have been discussed in various forms in the earlier part of this chapter. The significant outcome of NA as a tool for mitigation of impact is the evidence of occurrence of biodegradation and transformation of the target organic chemicals in the NA process. The *indicators* that need to be prescribed in the LOE relate to specific decreases in concentration of the contaminants and transformations (conversions and biodegradation) of organic chemical contaminants. Determination of the nature and composition of the transformed products of the original organic chemical contaminants is required. Knowledge of the products obtained via abiotic and biotic processes is essential. A good example of this is, for example, recognizing that abiotic transformation products are generally other kinds of organic chemical compounds, whereas transformation products resulting from biotic processes are mostly seen as stages (intermediate products) toward mineralization of organic chemical compounds. Procedures for the identification and characterization of abiotic processes for chlorinated hydrocarbons have been reviewed by the USEPA (2009). Biologically mediated transformation processes are the only types of processes that can lead to mineralization of the subject organic chemical compound. Complete conversion to CO_2 and H_2O (i.e., mineralization) does not always occur. However, intermediate products can be formed during the mineralization. New techniques are being developed to study the sources of the contaminants and the biodegradation process such as Compound Specific Isotope Analysis (CSIA) on dissolved organic contaminants such as chlorinated solvents, aromatic petroleum hydrocarbons, and fuel oxygenates isotope (USEPA 2008b).

10.8.2 Metals

At the very least, prescription of the indicators for the lines of evidence in respect to heavy metals requires determination of (a) the nature and concentration of sorbed metal ions, (b) porewater chemistry including pH and Eh , and (c) the environmental mobility of heavy metals. The environmental mobility of heavy metals is dependent to a very large extent upon whether they are in the porewater as free ions, complexed ions, or sorbed onto the soil particles. Prescription of *indicators* for LOE should take into account the assimilative capacity of the subsoil and the nature and fate of the heavy metals in the subsoil. So long as the full assimilative potential of the soil for HM is not reached, attenuation of the HMs will continue. Metals that are sorbed onto the soil particles are held by different sets of

forces—determined to a large extent by the soil fractions and the pH of the soil–water system. The various types of soils and their different soil fractions have different sorption capacities, dependent on the nature and distribution of the HMs and pH of the system.

A four-tiered approach has been developed by the USEPA (2007a) for inorganic contaminants as follows:

1. It must be demonstrated that the groundwater plume is not enlarging and that if immobilization is a dominant attenuation process, then sorption of the contaminant onto aquifer solids is occurring.
2. Both the *rate* and *mechanism* of the attenuation process must be determined.
3. The capacity of the aquifer to attenuate the contaminant within the plume and the irreversibility of the immobilization must be determined.
4. The monitoring program and a contingency plan must be designed based on the determined mechanisms for the attenuation process and site characteristics.

A second volume in the series looks at specific MNA information for various non-nuclides including arsenic, cadmium, chromium, copper, lead, nickel, nitrate, perchlorate, and selenium (USEPA, 2007b). The third volume addresses radionuclides (USEPA, 2010) including tritium, radon, strontium, technetium, uranium, iodine, radium, thorium, cesium, and plutonium–americium. In addition to the previously mentioned mechanisms, radioactive decay processes are emphasized for these contaminants.

Precipitation of HMs as hydroxides, sulfides, and carbonates generally classify as part of the assimilative mechanism of soils because the precipitates form distinct solid material species, and are considered as part of the attenuation process. Either as attached to soil particles or as void pluggers, precipitates of HMs can contribute significantly to attenuation of HMs in contaminant plumes. Ion exchange can also play a role. Determination of the chemistry including pH and *Eh* for assessment of lines of evidence should not neglect examination of possibilities of precipitation and solubilization of metals as part of the evidence phase. Hydroxide precipitation is favored in alkaline conditions, for example, when $\text{Ca}(\text{OH})_2$ is in the groundwater in abundance. With available sulfur and in reducing conditions, sulfide precipitates can be obtained. Sulfide precipitates can also be obtained as a result of microbial activity—except that this will not be a direct route. Sulfate reduction by anaerobic bacteria will produce H_2S and HCO_3^- , thus producing the conditions for formation of metal sulfides.

Significant knowledge has been gained over the last decade, particularly with regard to site characterization (USEPA, 2008a,b). For example, at the U.S. Department of Energy Hanford Site, liquid waste with uranium entered an unconfined aquifer. It was estimated that natural attenuation could reduce the uranium levels to less than $20\text{ }\mu\text{g/L}$ in the next 3 to 10 years. Characterization was revised to reduce the uncertainty in the natural attenuation processes. The newer components include laboratory tests for sorption–desorption testing measuring mass fluxes in the smear zone and evaluating reversibility of sorption, uranium speciation measurement with X-ray spectroscopy/diffraction, and electron microscopy with chemical extraction tests, identification of clay minerals in the aquifer, and determining uranium distribution according to particle size. By controlling the flux of uranium into the aquifer and by better characterizing the mass, and speciation of uranium, it is estimated that MNA can play an important role in the remediation.

10.9 Evidence of Success

Evidence of success (EOS) is a requirement specified by Yong and Mulligan (2004) as testimony to the success of utilization of NA as a tool for remediation of contaminated sites. Although monitoring is a necessity in application of MNA, there is a need for one to have knowledge of whether the “signs and signals” (i.e., indicators) registered in the monitoring program testify to a successful MNA treatment program. In essence, EOS takes the role of *indicators* of success or steps toward success by MNA in remediation of contaminated sites.

With the same rationale, EOS can be used in impact mitigation and management programs. Figure 10.18 takes the MNA protocol shown in Figure 10.13 as the basis for determination whether NA can be successfully used as an impact mitigation and management tool. The first two levels of protocol are similar to the MNA steps. At the third step or level, a clear knowledge of the kinds of impact, and mitigation and management requirements needs to be articulated. These are combined with information from laboratory tests that are designed to provide the kinds of information necessary to determine material parameters and interaction processes. Supporting predictions on fate and transport are necessary pieces of information. All of these combine to provide one with the tools to determine whether NA can be successfully used to meet the requirements for impact mitigation and management. Negative responses will require that NA be rejected as a tool or used in conjunction with other technological tools to provide the necessary impact mitigation and management solution.

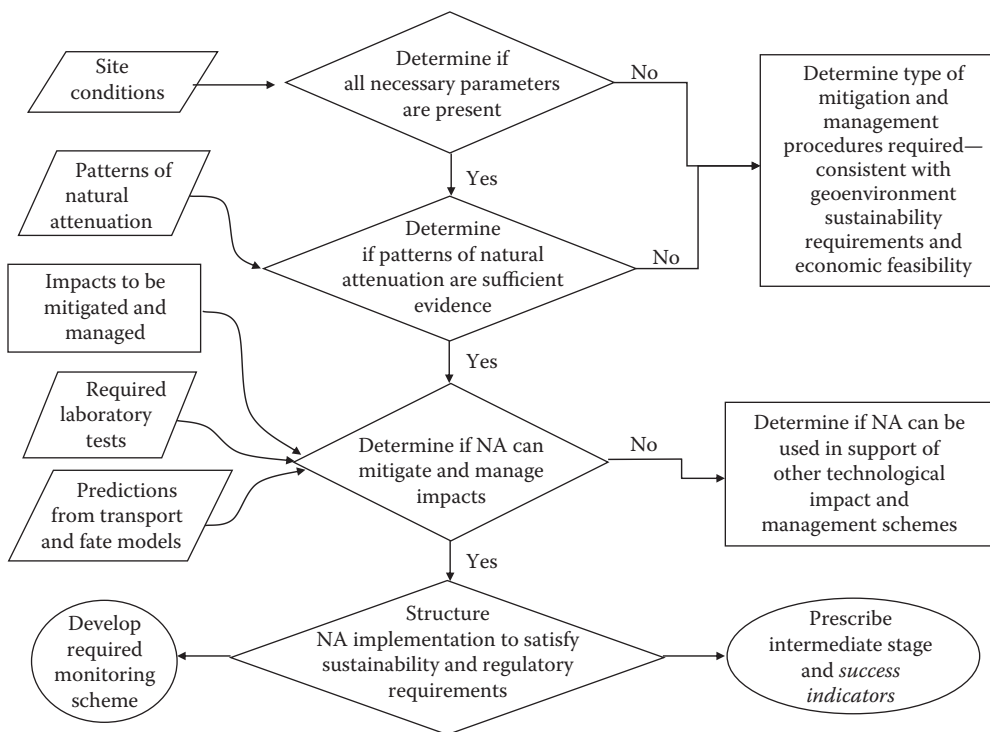


FIGURE 10.18

General protocol to determine feasibility and application of NA as a tool for impact mitigation and management.

A positive response will require structuring implementation procedures and strategies in combination with a competent monitoring scheme to track progress. A very necessary part of the implementation scheme is the specification or prescription of *success indicators* shown in the ellipse at the bottom right-hand corner of Figure 10.18. These indicators also serve as markers for performance assessment of the impact mitigation scheme. We have shown the requirements in terms of intermediate stage indicators and final success indicators. Since the time required for processes contributing to the natural attenuation to fully complete their functions, it is necessary to prescribe intermediate indicators as tracking indicators and as performance assessment markers. Note that we have used *italicized* notation for *indicators* when we mean them as markers and have left them without italicization when we discuss them as general items.

Monitoring and sampling of porewater and soils are needed in the contaminant attenuation zone. The choice of type of monitoring wells and sampling devices and their spatial distribution and/or location will depend on the purpose for the wells and devices. At least three separate and distinct monitoring–sampling schemes need to be considered:

1. *Initial site characterization studies.* Site characterization monitoring and sampling provide information on site subsoil properties and hydrogeology. Subsurface flow delineation provides one with the information necessary to anticipate transport direction and extent of contaminant plume propagation. With a proper knowledge of the requirements of the verification and long-term monitoring–sampling schemes, a judicious distribution of monitoring wells and sampling devices up- and down-gradient can be made such that the information obtained can be used to service the requirements for all the three monitoring–sampling schemes.
2. *Verification monitoring.* This requires placement of monitoring wells and soil sampling devices within the heart of the contaminant plume and also at positions beyond the plume. Figure 10.14 gives an example of the distribution of the wells and devices. Obviously, assuming that the wells and devices are properly located, the more monitoring and sampling devices there are, the better one is able to properly characterize the nature of the contaminant plume. Monitoring wells and sampling devices placed outside the anticipated contaminant plume will also serve as monitoring wells and sampling devices for long-term conformance assessment.
3. *Long-term conformance monitoring.* This is essential to verify success of mitigation scheme and for long-term management of the potential impact.

Analyses of samples retrieved from monitoring wells will inform one about the concentration, composition, and toxicity of the target contaminant. A knowledge of the partition coefficients and solubilities of the various contaminants, together with the monitoring well information will provide one with the opportunity to check the accuracy of predictions from transport–fate models. For organic chemicals detected in the monitoring–sampling program, laboratory research may be required to determine the long-term fate of the transformed or intermediate products. This is not a necessary requirement if modeling predictions and especially if the *indicators* for the intermediate show good accord with the sampling values of contaminant concentrations. Tests on recovered soil samples from the sampling program should determine the environmental mobility of the contaminants and also the nature and concentration of contaminants sorbed onto the soil particles (soil

solids). Detailed discussion of many of the bonding mechanisms and their reactions to changes in the immediate environment has been developed in Chapters 2 and 9.

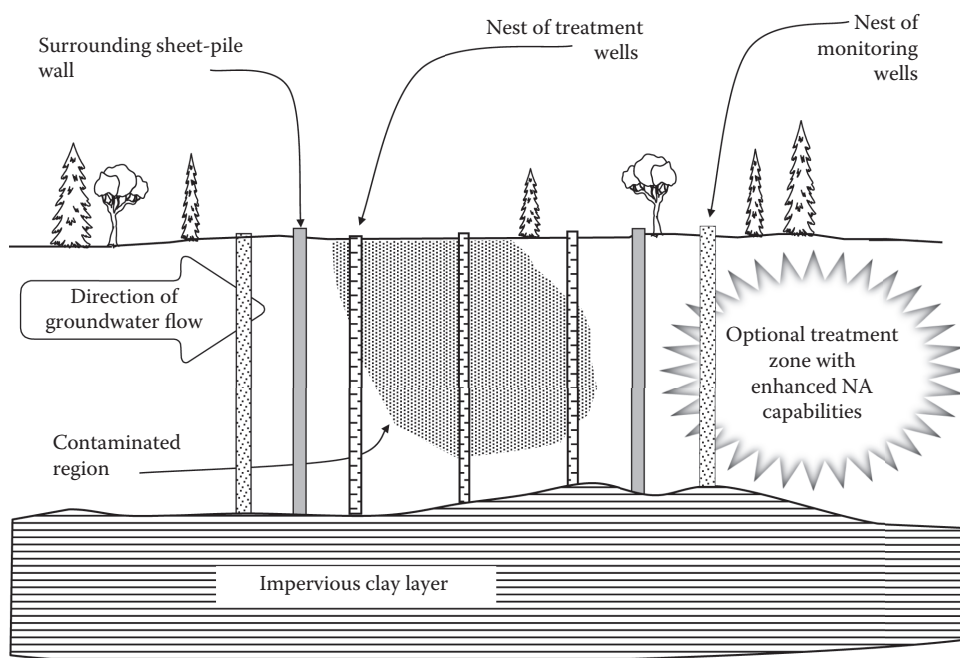
10.10 Engineered Mitigation–Control Systems

As we have indicated at the outset, the use of technological schemes for mitigation and management of contaminants in the ground is probably best utilized for limited and well-defined source locations of contaminants. Good examples of these are waste landfills, leaking underground storage tanks, spills and discharges, and containment ponds. Many of these are shown in the diagram in Figure 2.6 in Chapter 2. Technological solutions for management and control range from construction of impervious barriers that would intercept the plume to removal of the contamination source and the entire affected region. To a very large extent, the methods chosen or designed to manage and control contaminant advance in the subsoil are necessarily site- and situation-specific. Also, to a large extent, the nature of the threats posed by the contaminants and the pathways to the various receptors are considerations that will dictate the type and kind of technological solution sought. Finally, the control–management technological solution sought will always be analyzed within the framework of risks–reward and cost-effectiveness.

The record shows that there are some very difficult-to-treat contaminated sites. By and large, these are sites contaminated with organic chemical compounds that are severe threats to human health. For these kinds of contaminated sites, containment with confining structures has been constructed. These allow these sites to be isolated while awaiting effective and economic remediation solutions. In the case of impervious barriers, these are generally constructed from sheet piles lined in the interior with membranes to deny lateral advance of the contaminant plume. Difficulties arise in controlling the downward advance of the contaminant plume when the plume arrives at the lateral impervious barrier. Suggestions range from driving the sheet piles down into an impervious layer as shown, for example, in Figure 10.19, to injection grouting to develop an impervious base at some depth in the ground, to inclined-to-horizontal placement of sheet piles using techniques similar to the oil industry for inclined drilling.

If an impervious clay layer can be found directly below the contaminated region, the methodology shown in Figure 10.19 is probably the most expeditious means for controlling the escape of fugitive contaminants. By and large, for situations such as the one depicted in Figure 10.19, the contaminants resident in the contaminated site would likely be various kinds of organic chemicals. Heavy metals associated with these chemicals will likely be sorbed by the soil solids and will not be very mobile. Hence, the nest of treatment wells sunk into the contaminated region will be geared toward bioremediation of the organic chemical contaminants. Monitoring wells placed outside the confining sheet-pile wall, particularly downstream, will provide continuous information on the efficiency of the containment system. Note that the schematic representation of the nest of wells (treatment and monitoring) is relatively crude. Wells should be placed with varying vertical and horizontal sampling points and locations. If extra precaution is sought, a treatment zone using enhanced NA capability as described in Section 10.6.1 outside the confining sheet-pile wall can be introduced.

For control of contaminant plumes during treatment as part of impact management, several options are available. If the contaminant source is well delineated and defined,

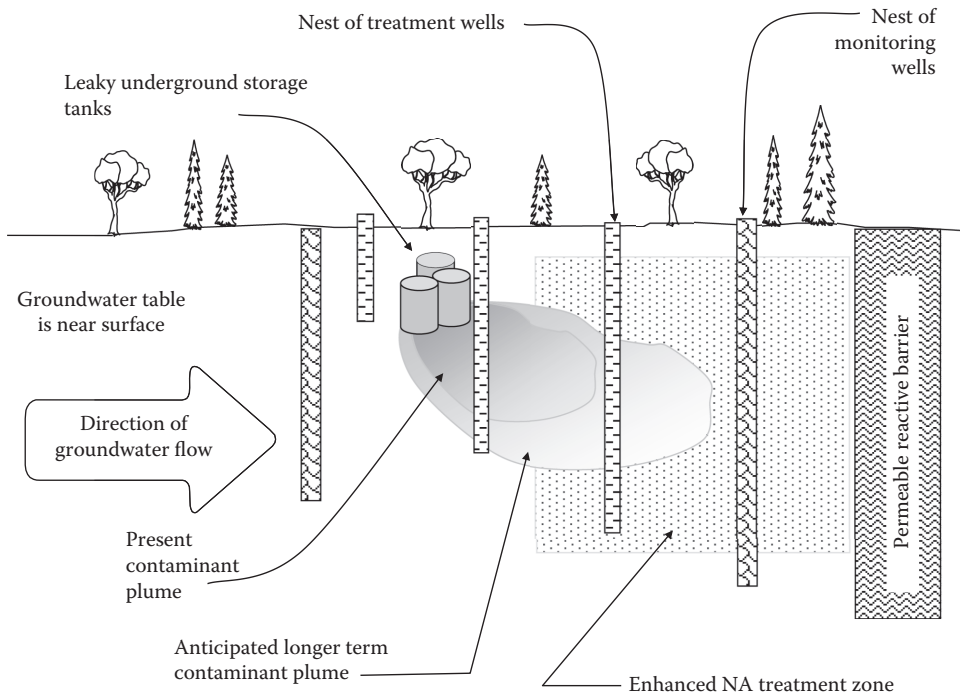

FIGURE 10.19

Containment of contaminants in a contaminated site using a confining sheet-pile wall that surrounds the contaminated region. The sheet-pile wall is sunk into the impervious clay layer to prevent bottom escape of contaminants. Treatment wells are sunk into the contaminated regions, and monitoring wells are placed downstream with some upstream also. Optional treatment zones using enhanced NA capabilities can be used, if needed.

and if site hydrogeology is well understood, the solution shown in Figure 10.20 is one that utilizes the capabilities of enhanced NA in combination of the permeable reactive barrier (PRB) previously described. This procedure is both a mitigation and management tactic for management of contaminant impact. Note again that the monitoring and treatment wells are somewhat simplistic in illustrative portrayal.

The engineered barrier systems for a municipal and a hazardous waste landfill shown in Figure 1.11 are good demonstrations of the extent to which composite barrier systems can be designed and engineered to meet the requirements for management and control of contaminants. The details of the filter, membrane, and leachate collection system are specified by regulatory *command and control* requirements or by performance requirements. In the case of the MSW landfill liner system shown in the bottom right-hand corner of Figure 1.11, the soil material comprising the engineered clay barrier underlying the synthetic membrane must possess hydraulic conductivity values that are below the maximum permissible values. The basic idea in the design details of the engineered barrier for the MSW landfill is that if leachates inadvertently leak through the high density polyethylene membrane (HDPE) and are not captured by the leachate collection system, the contaminants in the leachate plumes will be attenuated by the engineered clay barrier. The engineered clay barrier serves as the second line of defense or containment.

For the hazardous waste (HW) bottom liner system shown in the bottom left-hand corner of Figure 1.11, there are two lines of defense before the soil sub-base. The high-density polyethylene (HDPE) acts as the first barrier. Before this, the leachate collection system is

**FIGURE 10.20**

Use of treatment wells and ENA treatment zone in combination with permeable reactive barrier to mitigate and manage impact from leaky underground storage tanks. Treatments for enhancement can be any or all of the following: geochemical intervention, biostimulation, and bioaugmentation. Treatment occurs in the pollutant plume and down-gradient from the plume.

designed to collect leachates draining down from the waste pile. If the system functions well—i.e., as designed—there should be very little leachate reaching the HDPE barrier. If, however, leachate does collect at the HDPE barrier, and if this barrier is somehow breached, the underlying synthetic membrane (most likely another HDPE) is designed to prevent the leachate from escaping. Above this synthetic membrane there is a leak detection system that will alert the managers of the landfill that the first HDPE has been breached and that the leachate collection system is most likely malfunctioning. If the second membrane fails, the underlying soil subbase can be designed as an attenuation barrier using NA principles.

10.10.1 Remediation as Control–Management

Technically speaking, remediation of sites and regions contaminated with noxious substances and contaminants belongs to a category separate from contaminant impact mitigation. We have included this here because the *treatment wells* shown in Figures 10.19 and 10.20 are in fact wells or devices that introduce remediation aids. In addition, it can be legitimately argued that remediation of a contaminated site in effect removes the contaminant source—assuming of course that the remediation–treatment process is successful.

The priority requirement in remediation–treatment of a contaminated site is to eliminate the health and environmental threats posed by the presence of contaminants in the affected site. Traditionally, this objective is met with the *dig and dump* technique. Replacement with clean fill material will now ensure that all the contaminants have been removed from the

affected site or region. If total removal of all contaminants is not an option, minimization of the risk posed by the presence of the contaminants is the next priority. This latter course can take several forms. The basic factors to be considered include

- *Contaminants*: Type, concentration, and distribution in the ground
- *Site*: Site-specificities, i.e., location, site constraints, substrate soil material, lithography, stratigraphy, geology, hydrogeology, fluid transmission properties, etc.
- *Economics and risks*: Cost-effectiveness, timing, and risk management

The techniques that can be considered fall into five groups: (1) physicochemical, (2) biological, (3) thermal, (4) electrical–acoustic–magnetic, and (5) combination. Physicochemical techniques rely on physical and/or chemical procedures for removal of the contaminants. These include precipitation, desorption, soil washing, ion exchange, flotation, air stripping, vapor and vacuum extraction, demulsification, solidification, stabilization, reverse osmosis, etc.

Biological techniques are generally used to treat organic chemicals, but as we have pointed out previously, these can also be used for remediation of heavy metal contaminated sites. The techniques used include bacterial degradation and/or transformation, biological detoxification, aeration, fermentation, and biorestauration. Thermal procedures include vitrification, closed-loop detoxification, thermal fixation, pyrolysis, super critical oxidation, etc. Electrical–acoustic–magnetic methods include electrochemical oxidation, electrokinetics, electrocoagulation, ultrasonic, and electroacoustics. Finally, the last group that specifies *combination* implies that any of the four previous groups may be combined in a series-type technical solution to provide the necessary remediation–treatment. This is sometimes called a *treatment train*.

Remediation of contaminated sites is a very large challenge that offers innumerable opportunities for technological innovation. The basic means for treatment given in the preceding paragraph have been used in many different technologically clever ways to effect remediation of contaminated sites. The reader is advised to consult specialized manuals and textbooks devoted exclusively to remediation and treatment of contaminated sites. Bioremediation occupies perhaps the greatest attention of most researchers and practitioners attending to remediation. Much research is being conducted and reported in the various specialized journals.

10.11 Concluding Remarks

Geoenvironment impact mitigation requires one to have information not only on the kinds of stressors responsible for the impacts, but also on the nature of their effects on the land compartment of the geoenvironment (which is the subject of interest of this book). Although mitigation of stressor impacts is a necessary requirement and goal in protection of the health of biotic receptors and the geoenvironment, impacted site restoration is also another pressing issue that needs to be addressed. To do so, it is first necessary to determine the goals of site restoration, i.e., the type of site functionality that restoration should achieve. Determination of site functionality requires attention to the kinds of attributes and indicators required.

We have shown, from the discussions in the first part of this chapter and in previous chapters that our knowledge of the nature of impacts from mechanical- and most hydraulic-type stressors has resulted in the development of standard practice guidelines and codes in civil and geotechnical engineering. We have also learned that perhaps the biggest source of threats to the geoenvironment and its land compartment is the presence of chemical contaminants in the ground. The previous chapters have shown that the various discards, spills, and loss of materials (chemicals, etc.) and discharge of wastes, either in liquid form or as solids, are common to all types of human activities that are associated with (a) households, (b) cities, (c) industries, (d) farms, and (e) mineral and hydrocarbon exploitation. These pose significant threats to the land environment and the receiving waters that are well perceived. Not as well perceived are the threats presented by atmospheric-based non-point sources such as those shown in illustrative form in Figure 10.21. Under rainfall conditions, pesticides, herbicides, and other pest control chemical aids have the potential not only to combine with the rainfall runoff to contaminate the receiving waters, they also have the potential to infiltrate into the ground and threaten groundwater supplies. In addition to the non-point sources of contaminants that originate on the land surface (land-based), there are the non-point sources that originate from precipitation through the atmosphere containing noxious gas emissions and airborne contaminants (as particulates) from offending smokestacks and other types of smoke discharges. These can be called atmospheric-based non-point source contaminants. Included in this list are NO_x

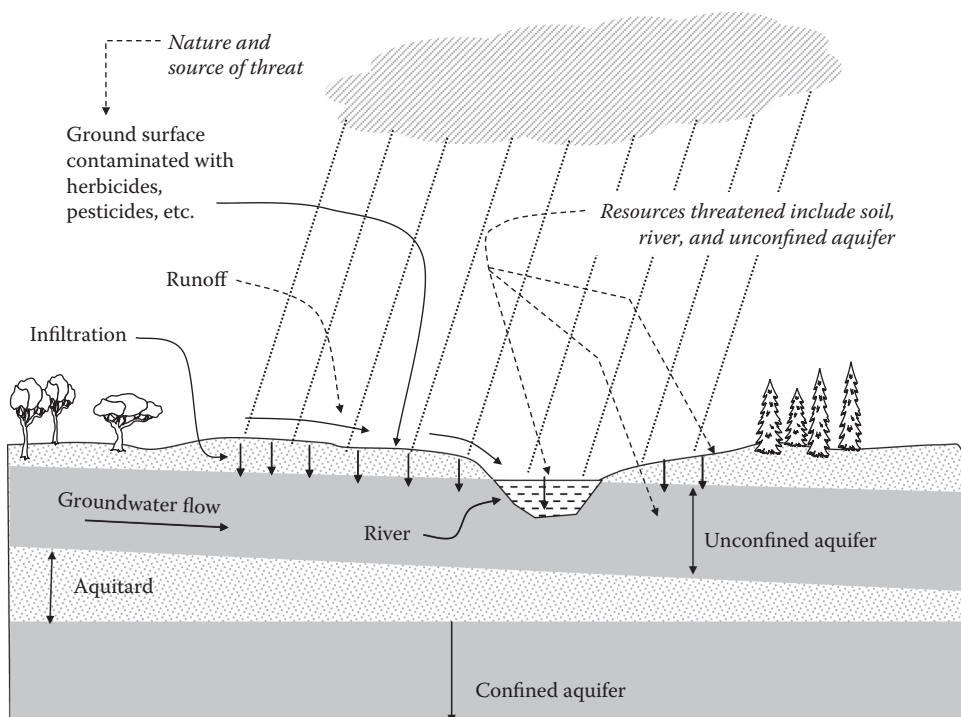


FIGURE 10.21

Demonstration of threats and impacts from atmospheric- and land-based non-point sources. Resources threatened include the river, soil, and unconfined aquifer. We presume that the aquitard is sufficient to protect contamination of the confined aquifer. If this is incorrect, the confined aquifer will eventually be contaminated by the water in the unconfined aquifer.

(nitrogen oxides), SO₂ (sulfur dioxide), CO (carbon monoxide), Pb and other metals such as Al, As, Cu, Fe, La, Mg, Mn, Na, Sb, V, and Zn (Lin et al., 1997) as airborne particulates, and VOCs (volatile organic chemicals) and PAHs (polycyclic aromatic hydrocarbons) such as benzene, toluene, and xylene, and particulate matter PM₁₀ and PM_{2.5}. Particulate matter PM_{2.5}—i.e., particulate matter less than 2.5 µm in size—will in all likelihood remain suspended in the ambient air; PM₁₀ (particulate matter less than 10 µm but greater than 2.5 µm) will be deposited eventually or with the aid of precipitation. Although acid rain is one of the outcomes of precipitation through this type of atmosphere, deposition of the airborne contaminants has not received the attention that is deserved. Airborne particulate matter is a great concern to public health in the ambient air because of their effect of these particulates on the hearts and lungs of those who are exposed to these.

The impacts to the health and quality of biotic receptors and the land environment presented by atmospheric- and land-based non-point sources of contamination cannot be readily mitigated by limited point-directed technological solutions. We recognize that the broad-based nature of the affected regions—i.e., land surfaces and water bodies—make containment and management of the spread of contaminants prohibitively difficult and costly. In consequence, the use of the natural in-place soil as a tool for mitigation of the impact of such contaminant sources is a solution that needs to be exploited. To do so, we need to develop a better appreciation of the assimilative properties of soils and also of the various geochemical and biological aids that will increase or enhance the assimilative capability of the soils. This has been the focus of this chapter. Contaminated land detracts considerably not only from one's ability to provide the necessary food supply, but also compromises the receiving waters and sources of water supply for humans. In summary form, the main issues addressed include

- Impacts from contaminants in the ground need to be mitigated and managed as a beginning step toward protection of the resources in the environment and also as a first step toward achievement of a sustainable geoenvironment.
- Using the properties of the natural soil–water system as the primary agent for such purposes allows one to address contamination sources that encompass the range from point source to both land- and atmospheric-based non-point sources.
- Enhancing the natural attenuation properties of the subsoil to make it more effective as a control tool allows the subsoil to remain in place as a mitigation–management tool. This is the essence of a semipassive remediation–treatment of contaminated sites.
- The physical, mechanical, chemical, and biological properties of soil made it a good resource material for management of contaminants and waste products. These properties are responsible for the assimilative capacity of soils and the natural attenuation capability of the soil.
- Mitigation and management of contaminants in the subsoil should seek to reduce and eliminate the presence of contaminants in the soil. Engineering the natural attenuation capability of soils, through enhancements of the attenuation capability with geochemical, biological and nutrient aids will provide greater management options.
- Reduction in the concentration and toxicity of contaminants is the ultimate goal. Achievement of this goal can be obtained using various strategies involving technology and the properties of the soil. The various options discussed are by no means the complete spectrum of capabilities. More innovative schemes are being developed to address the problems of contamination of the land environment.

Until the threats and problems of land environment contamination are successfully managed and essentially rendered harmless, the road to sustainability will not be clear. Although the treatment in this book does not address the monumental problem of depletion of nonrenewable resources, it nevertheless argues that the impacts from contamination of the land environment need to be mitigated and managed—as a very necessary step toward the road to sustainability of the geoenvironment.

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Remediation and Management of Contaminated Soil

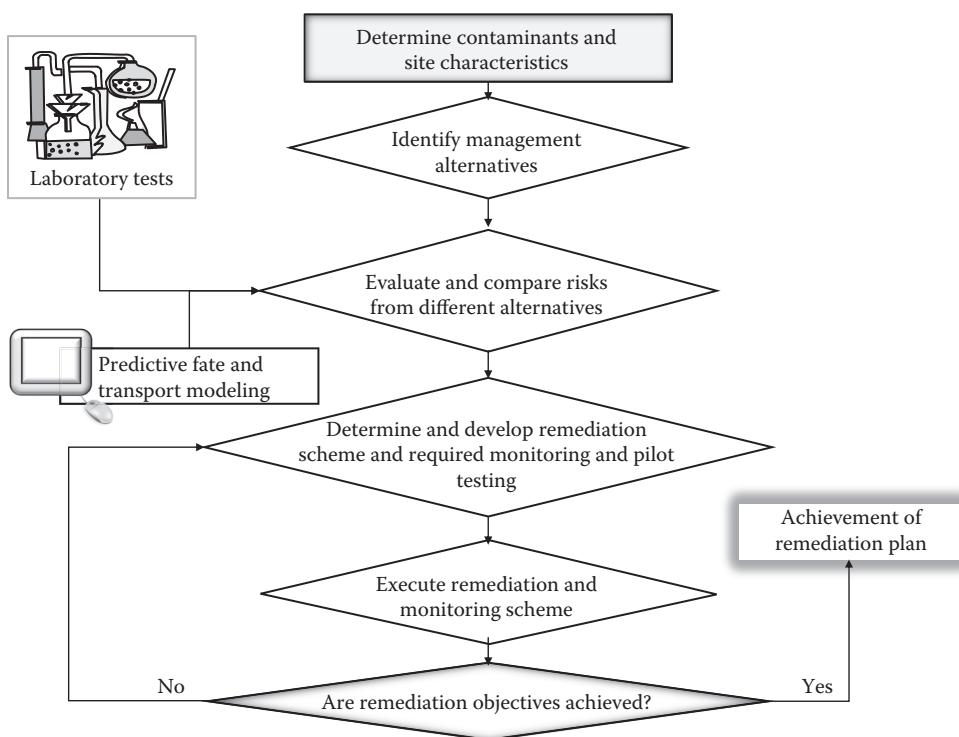
11.1 Introduction

The dumping of materials, bankrupt and abandoned manufacturing plants, insufficient methods for waste storage, treatment, and disposal facilities have contributed to the contamination of many sites as indicated in previous chapters. Chemical waste categories include organic liquids such as solvents from dry cleaning, oils including lubricating oils, automotive oils, hydraulic oils, fuel oils, and organic sludges/solids and organic aqueous wastes and wastewaters. Most soil contamination is the result of accidental spills and leaks, generation of chemical waste leachates and sludges from cleaning of equipment, residues left in used containers and outdated materials and indiscriminant dumping. Smaller generators of chemical contaminants include improperly managed landfills, automobile service establishments, maintenance shops, and photographic film processors. Household wastes including pesticides, paints, cleaning, and automotive products may also contribute significantly as sources of organic chemicals (LaGrega et al., 2010). The more common heavy metals include lead (Pb), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), iron (Fe), mercury (Hg), and zinc (Zn).

A variety of in situ and ex situ remediation techniques exists to manage the contaminated sites. For evaluation of the most appropriate technique, the procedure in Figure 11.1 should be followed. Ex situ techniques include excavation, contaminant fixation or isolation, incineration or vitrification, washing, and biological treatment processes. In situ processes include (a) bioremediation, air or steam stripping, or thermal treatment for volatile compounds, (b) extraction methods for soluble components, (c) chemical treatments for oxidation or detoxification, and (d) stabilization/solidification with cements, limes, and resins for heavy metal contaminants. Phytoremediation, although less developed, has also been used. The most suitable types of plants must be selected based on pollutant type and recovery techniques for disposal of the contaminated plants. Other technologies related to nanotechnologies are also being developed.

Most in situ remediation techniques are potentially less expensive and disruptive than ex situ ones, particularly for large contaminated areas. Natural or synthetic additives can be utilized to enhance precipitation, ion exchange, sorption, and redox reactions (Mench et al., 2000). The sustainability of reducing and maintaining reduced solubility conditions is key to the long-term success of the treatment. Ex situ techniques are expensive and can disrupt the ecosystem and the landscape. For shallow-ground contamination, remediation costs, worker exposure, and environmental disruption can be reduced using in situ remediation techniques.

In this chapter, various soil remediation technologies will be described. Groundwater remediation techniques and monitored natural attenuation techniques have been described

**FIGURE 11.1**

Flowchart demonstrating development of a program to ensure achievement of remediation objectives.

in Chapters 3 and 10, respectively, and will not be repeated here. The discussion in this chapter will focus on in situ and ex situ techniques in soil and sediment remediation.

11.2 Physical Remediation Technologies

Two options are available for disposal of contaminated soil: (1) disposal in a secure landfill or disposal facility and (2) treatment of the contaminated soil and reuse of the treated soil. Option (1) is not a preferred option as it is not sustainable. Treatment of contaminated soil can be an expensive procedure, especially when the quantities are large.

11.2.1 Isolation

Contaminated soil can be isolated to prevent further movement of the contaminants. This management scheme is usually of low to medium cost. Steel, slurry, cement, or bentonite barriers and grout walls and synthetic membranes can be used singly or in combination to reduce the permeability of the soil to less than 10^{-7} cm/s. They are considered as passive containment systems and can be temporary to complement remediation systems or be permanent. Vertical or horizontal barriers or capping are modes of reducing the movement. Vertical barriers should extend (or be keyed in) to an impermeable clay or bedrock layer

so that the contaminants will not bypass the barrier. The materials of the barrier must be compatible with the contaminants (USEPA, 1989). Slurry materials can include Portland cement, soil–bentonite, and cement–bentonite mixtures that are pumped into an excavated trench by a backhoe. Grout curtains are made of materials such as Portland cement, sodium silicate, or consist of polymers or bitumen. The materials are injected through a series of drilled holes. The spacing of the holes is dependent on the soil permeability and type of grout used. Sheet piling involves driving steel or concrete sheets. The sheets are connected through sealing or interlocking. This method is often used during removal of underground storage tanks (UST) or for prevention of erosion.

Capping can be used to reduce the infiltration of surface water to provide stability over the contaminated site, prevent mobilization of contaminants or to improve the appearance of the site. Capping can be simple or consist of multiple layers and can be temporary or permanent. Ditches and berms can be used to manage surface water runoff. Synthetic membranes can be used by installing sheets that are overlapped and seamed together. They can be made of polymers, fabrics, rubber, and other materials. The installation must be done properly without puncturing or tearing. Weathering and root penetration over time can be problematic. Other materials for capping include low permeability (10^{-6} to 10^{-7} cm/s) soils and clays in the compacted state. A clean soil can then be added over the cap as a topsoil to allow vegetative growth on the site. Liming, fertilization, and seeding of plants such as grasses without the potential for deep roots will prevent erosion and not penetrate the cap. For landfills, multilayer caps as previously discussed can be employed. A groundwater extraction system may be used to reduce the level of the water table. The barriers can also be placed either upstream or downstream or totally around the contaminated area. Horizontal barriers through horizontal drilling and grout injection can be used to restrict downward movement.

11.2.2 Confined Disposal

In the case of contaminated soil or sediment, in situ/ex situ remediation can be performed. If remediation is not possible, the excavated or dredged material can be disposed of in a confined land-disposal facility designed and constructed to contain the contaminants. In the case of sediments, they must be previously dewatered such as in a contained disposal facility since landfill facilities cannot handle slurries. Large volumes cannot usually be accommodated since landfills do not have the capacity. Potential mechanisms for contaminant release are due to leachates, runoff, effluents, volatilization, uptake by plants, and ingestion by animals. Therefore, pretreatment by stabilization/solidification may be necessary. Secure containment facilities (not landfills) can be used for storage, dewatering, and pretreatment for other processes. These costs are usually less than those for landfill. Contained aquatic disposal, such as the placement of material in a confined aquatic area is called a *confined disposal facility* (CDF). These areas can be strategically placed in depressions and confined by dikes. This technique can be used for disposal of contaminated soils or sediments. Clean material can be placed above and at the edges. A good accounting of the use of CDFs for dredging project in the Great Lakes can be found in the review published by the U.S. Army Corps of Engineers (USACE) and U.S. Environmental Protection Agency (USEPA, 2003).

Confined aquatic disposal (CAD) is used for placement of contaminated materials in a natural or excavated depression. It has been used mainly for navigational purposes such as in Boston Harbor, but not for disposal of contaminated material. It may be appropriate if landfill disposal or in situ capping is not possible. Maintenance costs are low and there can

be an increased resistance to erosion. Depths can be a few to more than 10 m and widths are in the range of 500 to 1500 m. As they are filled, capping is used.

Another approach is to place the material in woven or nonwoven permeable synthetic fabric bags, geo-tubes, or containers (NRC, 1997). Costs at the demonstration trial in California were approximately \$65/m³ (Clausner, 1996). The contaminants must not seep through the fabric into the water, and these uncertainties must be further investigated.

11.3 Extraction Processes

11.3.1 Physical Separation

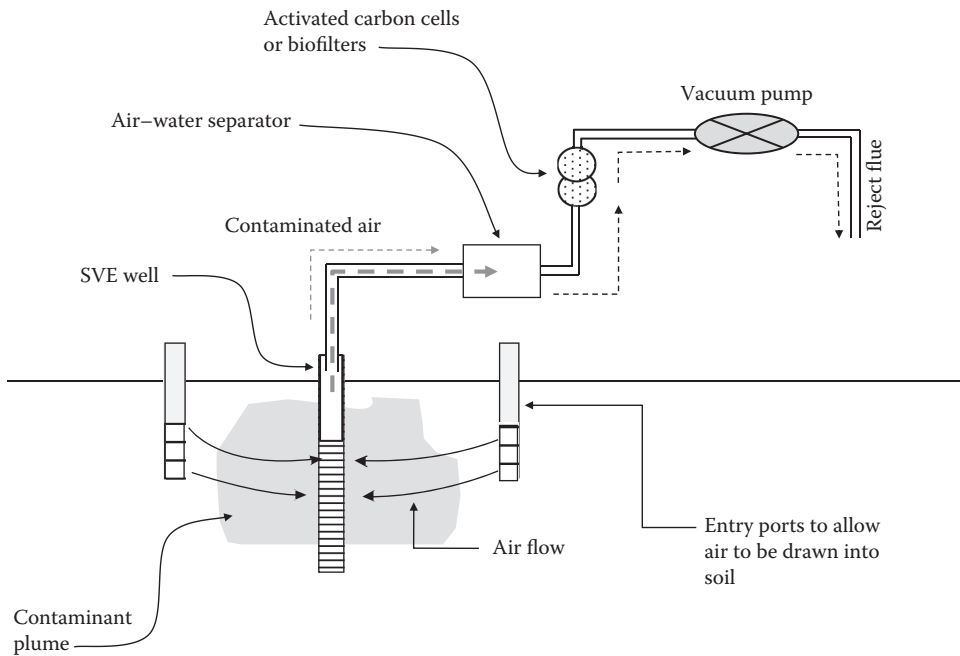
Physical separation processes are generally technically simple methods for separation of solids on the basis of size and density and are often used as pretreatments. These processes have been applied in the separation of contaminated fractions from the clean coarser particles. As coarser particles, such as sand and gravel fractions, have less contamination on their surfaces, washing is often enough to clean for beneficial use. This is important to reduce the amount of material to be disposed of. The most contaminated fractions may require further treatment or restricted disposal. The volume of the fine residuals may be minimized using mechanical dewatering techniques (Olin-Estes and Palermo, 2001).

Physical separation processes include centrifugation, flocculation, hydrocyclones, screening, and sedimentation. Hydrocyclones separate the larger particles greater than 10 to 20 μm by centrifugal force from the smaller particles. Fluidized bed separation removes smaller particles at the top (less than 50 μm) in countercurrent overflow in a vertical column by gravimetric settling and flotation, which is based on the different surface characteristics of contaminated particles. Addition of special chemicals (flotation agents) and aeration causes these contaminated particles to float. Screening is most applicable for particles larger than 1 mm. Magnetic extraction also may be used. If the solids content is high, mechanical screening can be used. Gravity separation or sedimentation is applicable if the contaminated fraction has a higher specific gravity than the rest of the soil fraction. According to the U.S. Army Engineer Detroit District (U.S. Army Engineer Detroit District, 1994), costs are in the range of \$30–70/m³ for quantities in the range of 7600 to 76,400 m³ and for soils/sediments with 75% sand and 25% contaminated silt or clay. The expense is only justified if the soil contains more than 25% sand, which is rare (NRC, 1997). Physical techniques only concentrate the contaminants in smaller volumes and are thus useful before thermal, chemical, or other processes.

In Japan, similar techniques and processes are used to obtain aggregates from soils for concrete. The soils taken from mountainous areas are washed. The fine and light fractions are separated from coarse particles (concrete aggregates) in a centrifugal tank, and dewatered using the filter presser or belt presser. The water content is usually controlled as about 40% from the energy cost and treatability of the materials. The technology can also be used for dredged materials.

11.3.2 Soil Vapor Extraction

Soil vapor extraction (SVE) (Figure 11.2) involves the removal of VOCs and some fuels with a Henry's law constant greater than 0.01 or a vapor pressure greater than 0.5 mm Hg through either air injection or vacuum vapor extraction. SVE is an in situ unsaturated

**FIGURE 11.2**

Schematic of a SVE process. (Adapted from Yong, R.N., *Compatible Technology for Treatment and Rehabilitation of Contaminated Sites*, Nikken Sekkei Geotechnical Institute, Japan, NNGI Report No. 5, pp. 1–33, 1998.)

(vadose) zone soil remediation technology in which a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semivolatile contaminants from the soil (USEPA, 1997). The extracted vapor may then be treated to recover or destroy the contaminants, depending on applicable regulations. The area of the extraction is called the zone of influence. Vertical extraction vents are typically implemented to depths of greater than 1.5 meters up to as much as 91 meters. Horizontal extraction vents (trenches or horizontal borings) can be used as warranted by contaminant zone geometry, drill rig access, or other site-specific factors.

The treatment is usually in situ for highly permeable soils. Groundwater levels may require lowering to decrease the moisture content. The contaminants pass through the void space in the soil by vaporization and are captured for further treatment on the soil surface by condensation, combustion, oxidation, incineration, activated carbon absorption, or bio-filtration. Field and pilot studies are usually necessary to determine the feasibility and subsequently the design of the method as well as to obtain information necessary to design and configure the system. The process may be used in combination with other methods such as bioremediation. A surface seal consisting of a geomembrane, concrete, or asphalt caps, or natural materials such as clay or bentonite can be employed to control vapor flow. Typically, in situ SVE processes can require 1 to 3 years. Costs vary significantly between sites.

11.3.3 Fracturing

Fracturing differs from the method for extraction of oil or gas and is used to enhance the efficiency of other in situ technologies in difficult conditions such as silts, clays, shale, and

bedrock (USEPA, 2012a). Most fracturing for remediation purposes does not exceed depths of 30 m. Existing fissures are enlarged or new fractures are introduced—particularly horizontally. After fracturing, vapor extraction, or forced air injection is performed. Technologies commonly used in soil fracturing include pneumatic fracturing (PF), blast-enhanced fracturing, and Lasagna™ process (USEPA, 1996). Blast-enhanced fracturing is used at sites with fractured bedrock formations. In the Lasagna™ process, in situ electro-osmosis is combined with hydraulic fracturing to enhance sorption/degradation zones horizontally in the subsurface soil. For the PF process, fracture wells in the contaminated vadose zone are drilled and short bursts (~20 seconds) of compressed air are injected to form fractures and repeated at various intervals. Overall, the cost range for pneumatic fracturing has been estimated at \$9 to \$13 per metric ton (FRTR, 2007).

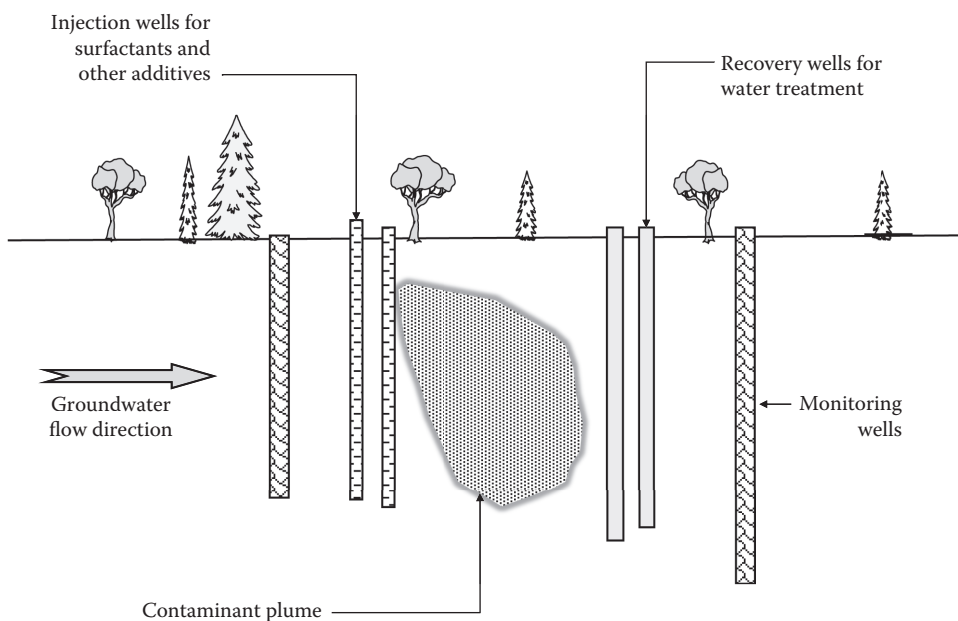
11.3.4 Soil Flushing

Soil remediation can be performed with or without excavating the contaminated soil by soil washing or in situ flushing (Mulligan et al., 2001). Solubilization of the contaminants can be performed with water alone or with additives. The solubility of the contaminant is thus a key factor. Contaminants such as trichloroethylene (TCE), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) are of very low solubility.

To remove nonaqueous phase liquids (NAPLs) from the groundwater, extraction of the groundwater can be performed by pumping to remove the contaminants in the dissolved and/or free phase NAPL zone in a pump and treat system. However, substantial periods can be required and effectiveness can be limited. Drinking water standards of the extracted water can be achieved after treatment with water treatment systems such as activated carbon, ion exchange, membranes, and other methods. To treat the contaminated soil, extraction solutions can be introduced into the soil using surface flooding, sprinklers, leach fields, and horizontal or vertical drains to enhance the removal rates of the contaminants. Water alone can be utilized for water soluble salts, and anions such as arsenate, arsenite, cyanide, nitrate, and selenate. Surfactant or solvent solutions are utilized to solubilize and extract the less water soluble contaminants as shown in Figure 11.3 in soil flushing. Additives can include organic or inorganic acids or bases, water soluble solvents, complexing or chelating agents such as ethylenedinitrotetraacetic acid (EDTA), or nitrilotriacetic acid (NTA) and surfactants.

To reduce further environmental problems due to the sorption of residuals during flushing, the additives must be of low toxicity and biodegradable. Various factors including soil pH, type, porosity, and moisture content, cation exchange capacity, particle size distribution, organic matter content, permeability, and the type of contaminants can influence the effectiveness of the treatment.

Highly permeable soils (k values greater than 1×10^{-3} cm/s) are more amenable for treatment as the washing solution must be pumped through the soil by injection wells or surface sprinklers or other means of infiltration. Depth to groundwater can increase costs. The washing solution should be treated to remove and/or recover the contaminants and reuse the water through recovery wells or drains. However, resultant spreading of contaminants and the fluids must be contained and recaptured. Control of these infiltrating agents may be difficult, particularly if the site hydraulic characteristics are not well understood. Emissions of volatile organic compounds (VOCs) should be monitored and treated if required. Recycling of additives is desirable to improve process economics and reduce material use. Metals, VOCs, polychlorinated biphenyls (PCBs), fuels, and pesticides can be removed through soil flushing.

**FIGURE 11.3**

Schematic diagram of a soil flushing process for removal of contaminants.

In choosing the most appropriate remediation technology, factors to be considered must include exposure routes, future land use, acceptable risks, regulatory guidelines, level and type of contaminants, site characteristics, and resultant emissions. Laboratory and field treatability tests should be performed to obtain site-specific information. Soil flushing has been demonstrated at numerous Superfund sites with costs in the range of \$18–50/m³ for large easy to small difficult sites (FRTR, 2007). A schematic illustration of the criteria and tools for evaluating technologies and protocols for environmental management of contaminated soils and sediments is shown in Figure 11.1.

A variation of soil flushing is foam injection (Wang and Mulligan, 2004). Foam consists of tiny bubbles, making an emulsion-like two-phase system where the mass of gas or air cells is dispersed in a liquid. Surfactants assist in creating and stabilizing the foams. A number of interesting applications have been investigated regarding its ability to remove various soil contaminants and its compatibility with pump-and-treat systems and bioremediation. As an innovative technology, there are various requirements for future development including the effect of soil matrix characteristics, contaminant speciation, pulsed operation, and surfactant partitioning on the effectiveness of in situ foam flushing to the subsurface conditions. Site geological conditions must be investigated and proper selection of the foaming surfactant and its concentration must be determined. The mechanism of the surfactant actions on the remediation of contaminated soils is still not clear. Development of predictive mathematical models will be helpful for optimal surfactant selection for the subsurface.

11.3.5 Soil Washing

Soil washing is applicable for soils contaminated with metals and/or organic contaminants (El-Shafey and Canepa, 2003). Soil washing is an ex situ process that uses water to

remove contaminants from soil and sediments by physical and/or chemical techniques. Soil washing involves the addition of a solution with the contaminated soil to transfer the contaminants to the wash solution. It is most appropriate for weaker bound metals in the form of hydroxides, oxides, and carbonates. Mercury, lead, cadmium, copper, nickel, zinc, and chromium can be recovered by electrochemical processes if the levels of organic compounds are not significant. Metals can also be removed from precipitation or ion exchange. Precipitation is not applicable for metal sulfides. Pretreatment to remove uncontaminated coarser fractions can be used. Various additives can be employed such as bases, surfactants, acids, or chelating agents. Nitric, hydrochloric, and sulfuric acids can be used. However, if sulfuric acid is used, 50% of the amount is required compared with hydrochloric acid (Papadopoulos et al., 1997).

Figure 11.4 illustrates a typical soil washing process where the separation consists of size separation, washing, rinsing, and other technologies similar to those used in the mineral processing industry. Larger particles are separated from the smaller ones as they have lower contamination levels. The smaller volumes of soil can be treated less expensively. Surfactants may be added in the washing water. The more contaminated size range is 0.24 to 2 mm due to the surface charges of the soil clay particles that attract anionic metal contaminant and the organic fraction that binds organic contaminants. Wash water and additives should be recycled, or treated prior to disposal. The mechanical dewatering of particles is performed via a filter press, conveyer filtration, centrifugal separation, or froth flotation by the introduction of air bubbles in to the slurry (Vennghuis and Werther, 1998).

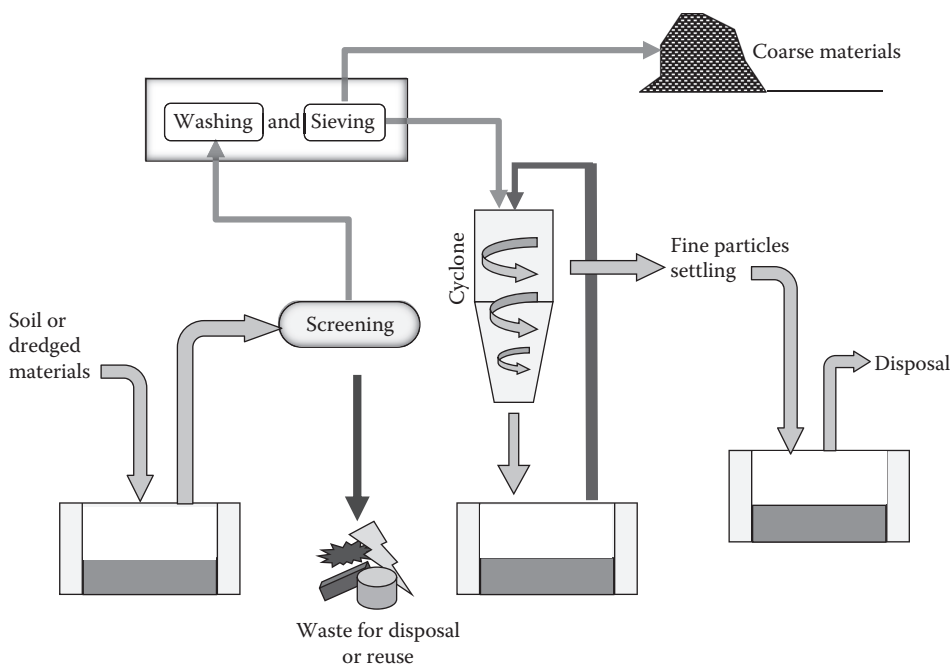


FIGURE 11.4

Size separation and washing of excavated and dredged materials.

The disposal of the treated fine particles varies depending on the type and levels of the contaminants.

Mixtures of metals and organic contaminants may require sequential washing with different additives to target the various contaminants. Soil washing processes generally use hot water to reduce the viscosity of hydrocarbons. The increased temperature also increases the solubilities of metal salts. The treated soil can then be washed to remove any residual wash solution prior to disposal. Ideally, the wash solution should be recycled. Costs of soil washing are usually in the order of \$70 to \$190/m³ depending on site size and complexity (Racer Software, Remedial Action Plan, 2006). Although extensively used in Europe, fullscale processes are less common in the United States. Laboratory feasibility tests should be conducted to determine optimal conditions (chemical type and dosage, contact time, agitation, temperature, and extraction steps to meet regulatory requirements). As spent washwater can be a mixture of soluble contaminants and fine particles, treatment is thus required to meet reuse or disposal requirements. Full-scale demonstrations may be required to demonstrate the feasibility of newly developed treatment processes. Presently, wastewater management systems act as a foundation for modern public health and environment protection. The idea of most suitable wastewater management systems is to use less energy, allow for elimination or beneficial reuse of biosolids, restore natural nutrient cycles, have much smaller footprints, be more energy efficient, and design to eliminate exposed wastewater surfaces, odors, and hazardous by-products (Daigger and Crawford, 2005). In addition to the technical aspects of a wastewater treatment technology, selection of a particular technology should be based on all aspects that determine its sustainability.

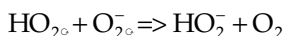
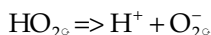
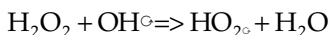
11.4 Chemical/Thermal Remediation

Chemical remediation includes the use of amendments, oxidation as well known by Fenton's reactions, and electrochemical remediation.

11.4.1 Oxidation

Oxidation (USEPA, 2006) has been used in situ or ex situ for complete chemical destruction of many toxic organic chemicals and partial oxidation prior to bioremediation. The compounds become less hazardous or toxic. The oxidants can include ozone, permanganate, hydrogen peroxide, sodium persulfate, and Fenton's reagent. High treatment efficiencies of greater than 90% can be achieved for unsaturated aliphatics such as TCE and aromatic compounds such as benzene. Efficient degradation depend on the concentration of oxidant, the contaminant properties and concentration and site characteristics such as pH, temperature, and the concentration of other oxidant-consuming substances including natural organic matter, minerals, carbonate, and other scavengers of free radicals.

The oxidant, known as Fenton's reagent, destroys a variety of wastes and generates no harmful by-products. Fenton's reagent was invented by Fenton in 1894. Today there are several methods known as "modified" Fenton's reaction where different additives increase the oxidizing efficiency by increasing the pH tolerance, increasing the reaction time, and producing more and more stable radicals.



The coexisting oxidation–reduction reactions associated with a modified Fenton’s process promote enhanced desorption and degradation of recalcitrant compounds (Fenton, 1893, 1895; Fenton and Jackson, 1899). These include compounds such as carbon tetrachloride and chloroform, which were previously considered untreatable by Fenton’s chemistry. There is a complete mineralization of organic matter. The breakdown is fast, within days, typically minutes to hours, depending on the concentration of H_2O_2 . The process has some effects on the residual free phase.

Modified Fenton’s reagent, hydrogen peroxide, and potassium permanganate were applied to aromatic hydrocarbons (PAHs) contaminated sediments (Ferrarese et al., 2008). They concluded that the optimal oxidant dosages determined were quite high, as sorbed PAH mineralization requires very vigorous oxidation conditions, especially for soils and sediments with high organic matter content. Their results indicated that the optimal oxidant dose must be carefully determined under site-specific conditions. Kellar et al. (2009) have used a sodium-based Fenton reagent in the United States in in situ and ex situ applications. The method has been proposed for the remediation of sediments near a chlorinated solvent site in Pennsylvania. Wet air oxidation requires high temperatures and pressures but is capable of destroying PCBs and PAHs. Large quantities of water are not detrimental to the process. Costs are high at large scale, however.

Oxidation/reduction of heavy metals is another method for remediating in situ and ex situ soils, sediments sludges, and ash. A detoxification technology called TR-DETOX involves the percolation of inorganic and organic reagents to reduce heavy metals to their lowest valence state. The stabilized solids achieve the TCLP requirements and are considered as no longer leachable. The TR-DETOX technology can also be applied along with biological treatment (bioremediation) to ensure degradation of organic contaminants. One of the main chemicals is sodium polythiocarbonate that forms a precipitate that becomes less soluble over time. Lime, silicates, and Portland cement are not added, and costs are usually about one quarter of stabilization/solidification processes. A unique characteristic is electronic addition of reagent. Pilot tests are required to determine the most appropriate formulation (Mulligan et al., 2001).

11.4.2 Nanoremediation

Nanoremediation involves the application of nanomaterials to transform or reduce the toxicity of the contaminants. The advantage of the addition of the nanoparticles to soil is that they can be transported further due to their small size. Zero-valent iron (nZVI) is the most common with particles ranging from 10 to 100 nm in size. Information from 45 sites was reviewed as a representative of the total projects under way using nanomaterials for site remediation (Karn et al., 2009). They concluded that nanoremediation could reduce costs and the time of cleaning up large-scale contaminated sites but eliminating the need disposal of contaminated soil, and reducing some contaminant concentrations to

negligible levels. However, potential adverse environmental impacts must be avoided due to the unknowns regarding nanoparticle transport.

An example of a nanotreatment remediation site (USEPA OSWER Selected Sites Using or Testing Nanoparticles for Remediation) is at the BP Prudhoe Bay Unit, North Slope, AK, abandoned oil field RCRA Pilot Site. The soil is organic-rich over an alluvial gravel and was contaminated with TCA and diesel fuel. The maximum initial TCA concentration was 58,444 $\mu\text{g}/\text{kg}$, TCA reduction was 96% for a shallow test (up to 1.2 m depth) after 1 year of application (mean concentration) whereas for the deep test (up to 2.3 m depth), TCA reduction was 40%. Treatment and control plots for each delivery method were subjected to identical treatment processes to validate the results. Two different mixing methods were used: (1) For the shallow test, physical mixing with lake water and (2) for the deep test, pressurized injection via 20 injection points. The work was performed by PARS Environmental and Lehigh University.

11.4.3 Electrokinetic Remediation

The electrokinetic remediation process can remove metals and organic contaminants from low permeability soil, sludge, and dredged sediment. The technique uses electrochemical and electrokinetic processes to desorb and then remove the contaminants. Electrochemical remediation uses a low DC current or a low potential gradient to electrodes that are inserted into the contaminated soil or sediment (Virikutyte et al., 2002). When DC electric fields are applied to the contaminated soil, ions migrate toward the corresponding electrodes (Figure 11.5). Cations are attracted to the cathode, and anions to the anode. An electric gradient initiates movement by electromigration (charged chemicals movement), electroosmosis (movement of fluid), electrophoresis (charged particle movement), and electrolysis (chemical reactions due to electric field) (Rodsand and Acar, 1995). For example, under an induced electric potential, the anionic form of Cr(VI) migrates toward the anode, whereas the cationic forms of Cr(III), Ni(II), and Cd(II) migrate toward the cathode. Contaminants that accumulate at the electrodes are extracted by methods such as pumping water near

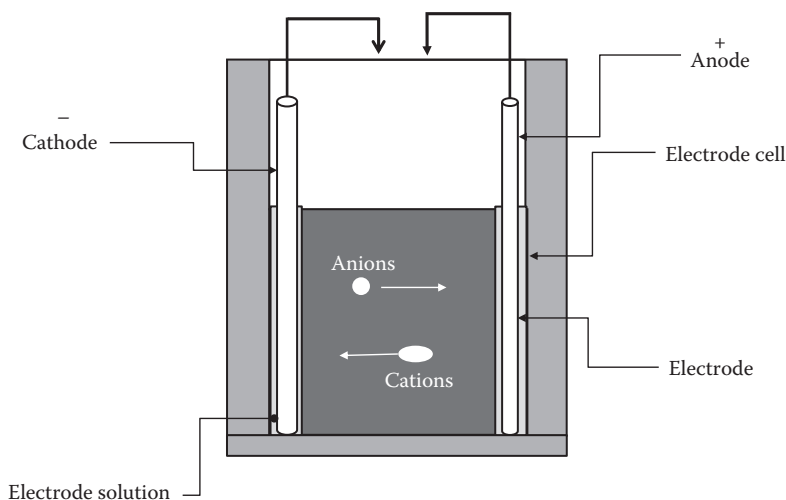


FIGURE 11.5

Electrokinetic treatment of contaminated soil.

the electrodes, precipitation/co-precipitation, electroplating, or complexation with ion-exchange resins (Reddy et al., 2001). This method is well suited for fine-grained soil and dredged sediment.

Control of pH and electrolyte conditions within the electrode casings is essential in the optimization of process efficiency. The process can be used to recover ions from soils, muds, dredging, and other materials (Acar et al., 1993). Metals as soluble ions and bound to soils as oxides, hydroxides, and carbonates are removed by this method. Other nonionic components can also be transported with the flow. Unlike soil washing, this process is effective with clay soils.

Demonstrations of this technology have been performed but are limited in North America (Mulligan et al., 2001). At pilot and full scale, the electrokinetic technology has been tested for demonstration purposes at the following sites: (1) Louisiana State University, (2) Electrokinetics, (3) Geokinetics International, and (4) Battelle Memorial Institute. Geokinetics International has successfully demonstrated the in situ electrokinetic remediation process in five field sites in Europe for copper, zinc, lead, arsenic, cadmium, chromium, and nickel. In the United Kingdom, it was evaluated for treatment of highly contaminated mercury in canal sediments. Other ions such as cyanide, nitrate, and radionuclides such as uranium and strontium can also be treated by electrokinetics. Interferences include large metal objects, moisture content, temperature, and some other contaminants. Metal recovery from highly contaminated soils could improve the process economics.

Since soil and sediment particles have buffering capacity, release adsorbed substances from the surfaces occurs when the value of pH decreases. Therefore, acidification may be a very effective method to solubilize the metal hydroxides and carbonates, other species adsorbed onto sediment particles, as well as protonate organic functional groups (Yong et al., 2006). Generally, in electrochemical remediation process, the development of an acidic front is often coupled with a successful remediation (Nystroem et al., 2006). However, because of the higher buffering capacity of sediments, acidification of dredged materials may not be an acceptable method. Surfactants can increase the solubility and mobility of heavy metals during electrochemical remediation, depending on its function on decreasing the ζ potential of sediment and then reducing the Van der Waals interactions (Nystroem et al., 2006). Therefore, using surfactants improves metal removal (Abidin and Yeliz, 2005). Direct costs have been estimated at \$15/m³ with energy expenditure of \$0.03/kW h. Addition of the cost of enhancement could result in direct costs of \$50/m³ or more. Another study has estimated full scale costs at \$117/m³. For remediation of metal-contaminated fine-grained and heterogeneous soils, this technique could potentially be competitive (FRTR, 2007).

11.4.4 Solidification/Stabilization

The purpose of solidification/stabilization (S/S) processes is to reduce the mobility of the contaminants by addition of an agent that solidifies and then immobilizes the metals or hydrocarbons. Binders include cement, fly ash, sodium silicates, lime, sulfur- and organic-based binders, and pozzolans are added in situ or ex situ (USEPA, 2000). Other processes or groups include bituminization, emulsified asphalt, polyethylene extrusion, pozzolan/Portland cement, and soluble phosphates. Ex situ S/S requires disposal of the stabilized residue. Solidification/stabilization is often utilized for metal contamination as there are few destructive techniques available for metals. Some metals such as As, Cr(VI), Pb, Cu, Ni, Zn, and Hg are suitable for this type of treatment. The metals are hydrolyzed to form hydroxides, oxides, carbonates, sulfates, etc. that are of limited solubility. Liquid monomers

that polymerize and cement are injected to encapsulate the soils. Leaching of the contaminants must, however, be carefully monitored as is the case for vitrification, the formation of a glassy solid. Cement- or silicate-based (5% to 10% by weight additives) processes are useful for soils and sediments and are economical as the mixing equipment and materials are readily available. Other materials containing iron (red mud, sludge from a water treatment plants, bog iron ore, unused steel shot, and steel shot waste) have been evaluated (Mulligan and kamali, 2003) for immobilizing cadmium and arsenic contaminants in sediments. All were effective in reducing the bioavailability of the metals to plants, but the safest was sludge from a drinking water plant with low levels of As. However, if there are different types of metals present, the treatment may not be as effective.

Water contents greater than 20% or chlorinated hydrocarbons contents greater than 5% increase the amount of agents required. Variability in the water content, grain size, and the presence of debris can make handling of the materials difficult and decrease the efficiency of the solidification process. In addition, since immobilization leads to an increase in volume, larger areas of land are required for disposal. Thus, smaller volumes for treatment are more appropriate. Costs range from \$30 to 250 per tonne (Hazardous Waste Consultant, 1996).

For organic contaminants such as oil or gasoline, thermoplastic binder and organic polymerization have been utilized. The most commonly used thermoplastic material is polyethylene or asphalt. Organic polymerization for immobilization has also been used for radioactive wastes, organic chlorides, phenols, paint sludge, and cyanides (ASTM, 1985). The organic materials can include polyethylene, polypropylene, urea formaldehyde, or paraffin. The contaminated soil is dried and mixed into the polymer that is cooled to form a solid. The mix can be extruded into a metal drum for easy transport and disposal. Full-scale projects have been performed in the United States, Canada, Japan, and Belgium. If the process is performed *ex situ*, the soil is usually screened to remove large materials, mixed with the binder and water (e.g., in a rotary drum), and then transferred to a disposal area. Off-gases would need to be treated for dust or volatile organic contaminants. The process can be performed in a mobile unit or at a fixed site.

For *in situ* applications, the reagents must be prepared, an auger can be used to mix the binder directly into the soil and off gases should be treated, particularly for organic contaminants. Dust generation is minimal, and costs related to excavation and transport are eliminated. Boulders, bedrock, and clay can cause mixing problems. Contamination of the groundwater must be avoided. Therefore, mobile contaminants such as Cr(VI) should be converted first to the less mobile Cr(III) form. After solidification, reuse of the land for buildings may be possible. Backfill may be required as a cover for revegetation. Durability testing will be required. In all cases, compatibility testing should be performed to determine the most appropriate binding material and TCLP tests after the binding will indicate the leachability of the contaminants.

Halogenated semivolatiles, nonhalogenated semivolatiles, and nonvolatiles, volatile, and nonvolatile metals, low-level radioactive materials, corrosives, and cyanides have been treated effectively. In the Netherlands, a rotating drum was used in a full scale experiment (Rienks, 1998). Six hundred eighty tonnes of dewatered sediment were treated at 600°C for 38.5 h for mineral oil, PAHs, and mercury. Mercury levels decreased by 80% from 1.5 to 0.3 mg/kg while mineral oil and PAHs decreased by greater than 99.8%. Leaching of arsenic, molybdenum, and fluoride increased after thermal treatment, which can have implications in the reuse of the treated sediments as road or construction materials. At a former wood-preserving plant in Fresno, California, contaminated groundwater with As, Cr, Cu, and PCP was found (USEPA, 2005). Various hydrocarbons, PAHs were found in the first 2 m

of the soil. The Silicate Technology Corporation (STC) immobilization with proprietary organophilic materials was used. The soil was removed from the unlined disposal pond and transported to the processing area for mixing, addition of reagents, and discharge into concrete forms. Neutral conditions were required for As stabilization as mobility increased at lower pH values. Arsenite could not be converted to arsenate by the process. PCP and other organic contaminants were below TCLP threshold levels before and after treatment. Mixing had to be thorough and dust was a problem that had to be minimized.

11.4.5 Vitrification

Another immobilization technique is vitrification, which involves the insertion of electrodes into the soil, which must be able to carry a current to heat the soil up to 1400°C to 2000°C and then to solidify as it cools. Toxic gases from the organic contaminants can also be produced during vitrification and must be collected and treated. Volume reduction of 20% to 50% occurs leading to subsidence above the melt and thus backfill is required to fill the volume (Weston, 1988). The heavy metal and radionuclide contaminants remain in the glass-like substance (USEPA, 2006). Costs can be high since fuel values are low and moisture contents are high (above 20%). Vitrification operation costs are directly related to water and electricity consumption and treatment depth and area. Estimates of vitrification costs are in the order of \$375–425 per tonne of soil treated.

A technology developed for the remediation of organic contaminants and immobilization of metals in a glassy matrix has been evaluated for treatment of dredged sediments from New York/New Jersey harbor (Institute of Gas Technology [IGT], 1996). The technique uses a plasma torch to heat the sediments. Feeding of the wet sediments into the plasma reactor and adjustment of residence times can be difficult, however. Cadmium, mercury, and lead levels were reduced efficiently (97%, 95%, and 82%). Glass tiles and fiber glass materials were produced and could be used as valuable end products.

Temperatures higher than 1200°C could possibly degrade organic compounds and volatilize heavy metals. Solids, such as minerals, will melt at this temperature. The technique that utilizes this temperature range is called *vitrification technique* or *GeoMelt process*. The materials can be burned, electrically melted or other means. According to Kurion, in the United States, Japan, and Australia, the GeoMelt process has been in commercial use since the 1990s and has treated more than 26,000 metric tons of waste, including remediating sites contaminated with heavy metals, radioisotopes, pesticides, herbicides, solvents, PCBs, dioxins, and furans.

The GeoMelt processes are designed to be an in situ or mobile container thermal treatment process that involves the electric melting of contaminated soils, sludges, or other earthen materials and debris either in situ or ex situ for the purpose of permanently destroying, removing, and/or immobilizing hazardous and radioactive contaminants. Ex situ technology for vitrification is illustrated as shown in Figure 11.6.

Excavated materials are first dried and transported into a forge. The materials are melted at a temperature higher than 1200°C. The produced gas is cooled down and treated with activated carbon. After contaminants are removed by the activated carbon, the gas is released into the air. Since hazardous materials, such as organic compounds and heavy metals, in the materials are vaporized, the solids after vitrification are usually clean. This technique is recommended as one of treatment techniques for sediments contaminated with dioxin, in the Japanese technical guideline of sediments contaminated with dioxin. The process flow is shown in Figure 11.7.

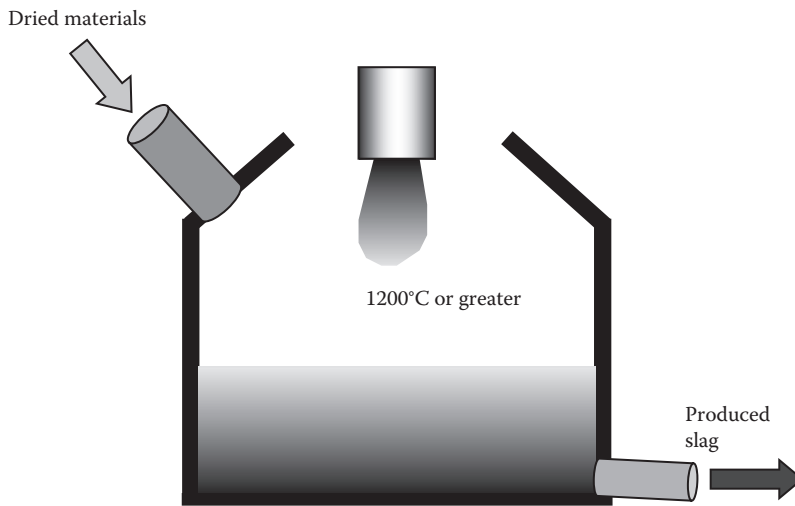


FIGURE 11.6
Vitrification of contaminated soil or sediment.

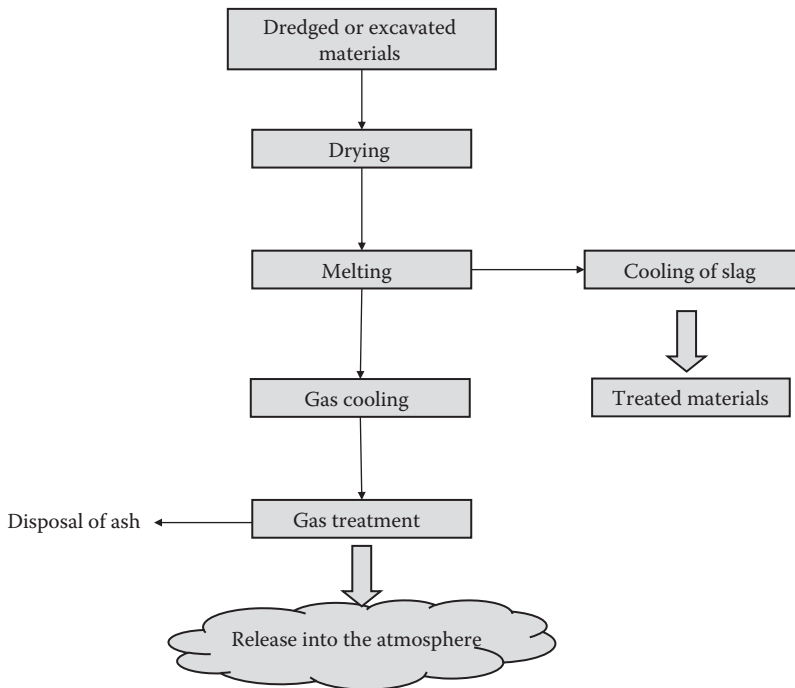


FIGURE 11.7
Japanese process for dioxin-contaminated sediments. (Adapted from Mulligan, C.N., Fukue, M. and Sato, Y. *Sediments Contamination and Sustainable Remediation*, 320 pp., CRC Press, 2010.)

11.4.6 Incineration

Incineration by rotary kiln has been used to treat hazardous materials including waste, contaminated soils, and sediments. Other types of incineration include fluidized bed, circulating bed combustor, and infrared combustion. In the rotary kiln technique, heat is supplied with a burner in a kiln, as shown in Figure 11.8, and the materials can be carbonized when the contaminants are released by vaporization. Flue gas treatment is required in this case. Temperatures for organic contaminants are in the range of 800°C to 1200°C (USEPA, 1998). On-site mobile units or off-site treatment facilities are employed. In Japan, this rotary kiln technique is also recommended as one of the treatment techniques for sediments contaminated with dioxin. PCBs can also be treated. Costs can be high in the range of \$1000 to 1500/m³ (FRTR, 2007).

There are soils contaminated with hydrocarbons in many industrial sites and oil refineries. Thermal treatments are the most popular and versatile because they can be effectively applied to a wide range of organic contaminants (Merino and Bucalá, 2007). At different temperatures (150°C–800°C), results from Merino and Bucalá (2007) showed that at about 300°C the hexadecane can be removed almost completely from the soil matrix (99.9% destruction removal efficiency, DRE) and that temperatures above this value do not improve the removal efficiency noticeably. In Japan, treatment of excavated and dredged materials is required for materials with dioxin levels higher than 3000 pg-TEQ/g. The recommended techniques are as follows:

- Melting (geo-melting technique) (>1200°C)
- Incineration (rotary kiln incinerator) (1100°C)
- Low-temperature thermal degradation (400°C–600°C)
- Chemical decomposition (350°C)

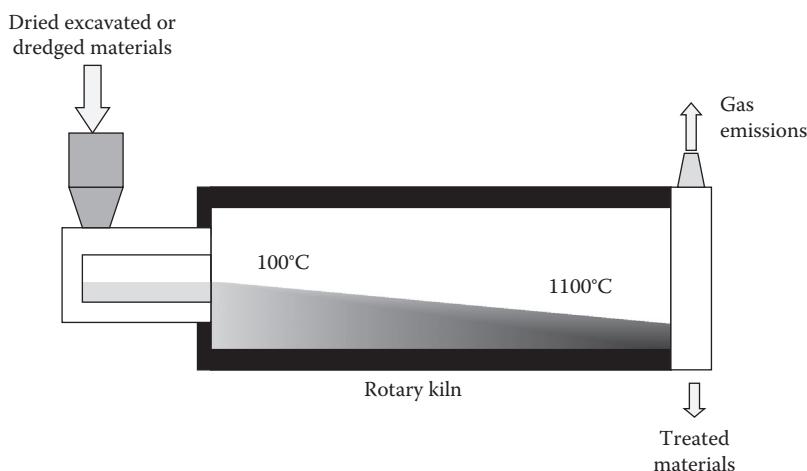


FIGURE 11.8
Rotary kiln treatment of contaminated soil or sediments.

11.4.7 Thermal Extraction

In situ thermal treatment or thermal enhancement of SVE is used to enhance volatilization or decompose contaminants and can be performed using a variety of techniques including electrical resistance, conductive heating, electromagnetic/fiber optic/radio frequency heating, or hot-air, water, or steam injection to increase the volatilization rate of semivolatiles, DNAPLs, LNAPL, and facilitate extraction. These methods can be completed in the short to medium term such as less than 40 days. Recent examples are three- and six-phase soil heating (USEPA, 2013b). Large-scale in situ projects employ three-phase soil heating, whereas six-phase soil heating is for the demonstration phase. Electrical resistance heating uses electrodes to produce a current that heats the soil above 100°C for steam generation and causes soil drying and fracturing. Vacuum extraction then removes the contaminants.

The radiofrequency technique can heat soils to over 300°C and enhance SVE by (1) increasing the contaminant vapor pressure and diffusivity, (2) drying the soil, which increases permeability, (3) increasing the volatility of the contaminant by stripping with the water vapor, and (4) increasing the mobility by decreasing the viscosity. The current stops once the soil is dried. Incineration or granular activated carbon is used to treat the extracted vapor.

Steam injection or steam-enhanced extraction (SEE) heats the soil and groundwater and can destroy contaminants. The steam drives the contaminants that can be removed by groundwater and vapor extraction. Thermal conduction heating destroys contaminants by electrical conductance or evaporates them for subsequent removal by a carrier gas or a vacuum system. Costs are in the range of \$40–80/m³ (FRTR, 2007).

Another ex situ technique is a process that involves thermal desorption by heating the soil to 90°C to 320°C for VOCs or 320°C to 540°C for SVOCs removal. The low temperature process works well for oil contaminated soils. A major advantage is that the decontaminated soil retains its physical properties and organic matter in the soil is not damaged. Therefore there is the potential for reinstating the past ability of the soil to support future biological activity. The vapors subsequently obtained must be treated by thermal oxidation for complete destruction (USEPA, 2012b).

With regard to heavy metals such as mercury, arsenic, and cadmium and their compounds, these can be evaporated at 800°C with the appropriate air pollution control system. Some of the metals remain in the solid residues and will have to be properly disposed. Thermal extraction is applicable mainly for mercury since this metal is highly volatile. Costs are in the order of \$35 to 1000/tonne (Environment Canada, 1995).

There are several commercially available thermal chemical treatment processes for soil, sediment and other hazardous wastes. The temperatures used differ according to the process. Cement Lock (<http://www.cement-lock.com>), developed by the IGT, has been used for dredged sediment in the New York/New Jersey harbor (Stern et al., 1997). The sediment contained metal contamination (33 mg/kg As, 37 mg/kg Cd, 377 mg/kg Cr, 617 mg/kg Pb, 1.3 mg/kg Hg, 3.2 mg/kg Se, and 1.8 mg/kg Ag) and was fed with lime into the rotary kiln reactor smelter at 1200°C–1600°C. The mixture was then melted and quenched, forming micrometer-sized fibers. The mixture was then mixed with cement to produce a suitable type I Portland cement construction material. The sediment passed the Toxicity Characteristic Leaching Procedure (TCLP) for all metals. Volatilized heavy metals and acid gases and other combustion products were treated in the offgas by filtration to remove particulates, and activate carbon to remove heavy metals gas removal. A demonstration plant was completed in Bayonne, New Jersey, in July 2003 (Mensinger and Roberts, 2009). Two decontamination tests were performed between 2003 and 2007. Destruction and

removal efficiencies (DRE) for the contaminants were in the order of 99.9%. The produced Ecomelt passed leachability tests and could be added for beneficial use in concrete, thus replacing up to 40% Portland cement. Increased tipping fees could enhance the economics of the process and could lead to break-even scenarios.

Mercury Recovery Services (MRS; <http://www.hgremoval.com>) developed and commercialized a process that mixes a proprietary material and a mercury-contaminated material at temperatures of 150°C–650°C (Weyand et al., 1994). The process can be mobile or fixed, batch, continuous, or semicontinuous. Unit capacities ranged from 0.5 to 10 t/h. The mercury can be as an oxide, chloride, and sulfide. No liquid or solid secondary products were generated. The treated material contained less than 1 ppm of mercury. The process consisted of two stages, feed drying and mercury desorption, which was then condensed as a 99% pure metallic form from the vapor phase. Air emissions did not contain mercury. Costs were high, in the range of \$650–1000/t. Soils from approximately 6000 metering sites along the natural gas pipeline system in the western United States were treated using the MRS process. Over 18 months, a 12-tonne/day mobile unit processed a total of 6000 tonnes of soil with 100–2000 mg/kg of mercury. The treated soil contained less than 2 mg/kg of Hg. The results from the TCLP tests indicated that leaching was minimal at less than 0.0025 mg/kg, which is substantially below the 0.2-mg/kg EPA limit. In addition, more than 1590 kg of metallic mercury were recovered for sale and recycling.

11.5 Biological Remediation

For heavily contaminated soils, various approaches can be used to enhance the rate of bioremediation. Substances must be biodegradable and not toxic for treatment. Experience to date shows that ex situ bioremediation has been more successful than in situ processes due to easier control of environmental parameters such as mixing that allows uniform nutrient and oxygen contents. Proprietary biological mixtures for bioaugmentation are also available. Ex situ biotreatment systems include the use of slurry bioreactors, biopiles, landfarming, and composting. In general, the more sophisticated the process, the more expensive the treatment. Treatability studies are usually performed to determine the efficiency of the bioremediation for the type of contaminants and sediments at the site. Microbial population, nutrient levels, pH, moisture content, contaminant type and concentration, and sediment characteristics must be determined and followed. Bench, pilot, and demonstration scale tests are needed to properly design the remediation technology.

Microorganisms have been effective in treating organic contaminated sediments such as PAHs. Zhao et al. (2004) have demonstrated that anaerobic degradation of RDX was possible in a Halifax sediment. Degradation rates of TNT>RDX>HMX were found. *Shewanella* and *Halomonas* bacterial isolates were found (Zhao and Hawari, 2008). Khodadoust et al. (2009) showed that PCBs could be degraded anaerobically with the periodic addition of iron (0.01 to 0.1 g/g).

11.5.1 Slurry Reactors

Slurry bioreactors use 5% to 30% solid content in a highly agitated treatment process. Mass transfer, aeration, and environmental conditions such as pH can be optimized more easily

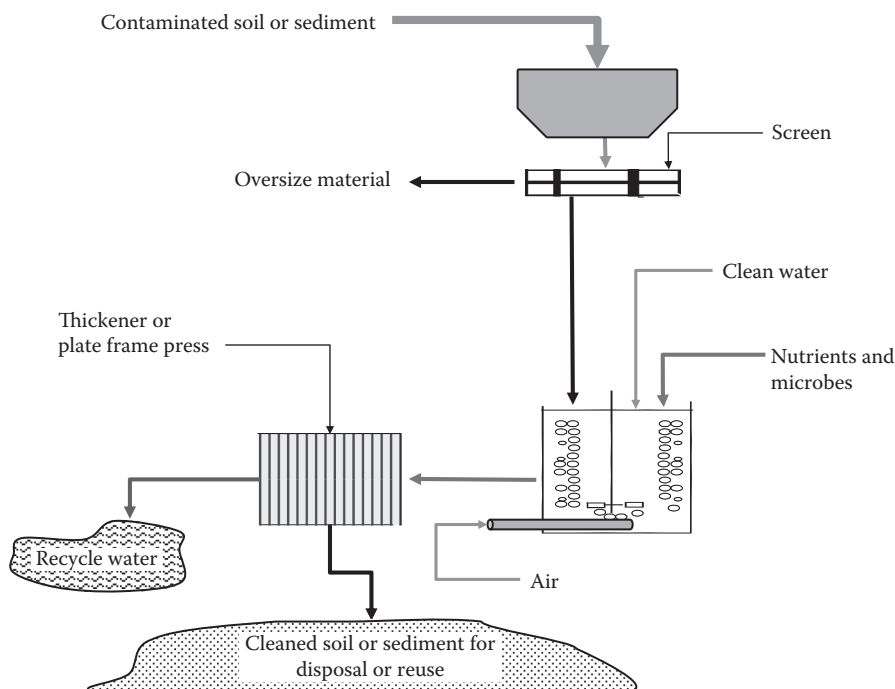


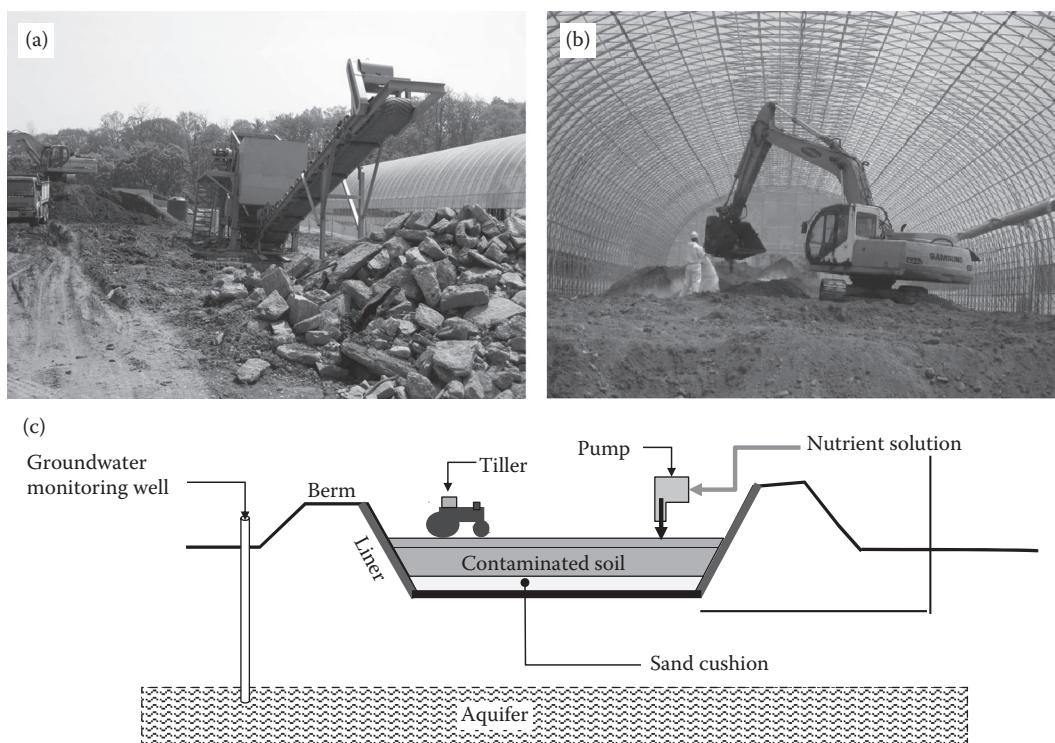
FIGURE 11.9
Schematic of a bioslurry process.

than for in situ remediation. This type of treatment is particularly applicable for compounds of low biodegradability such as SVOCs, VOCs, ordnance, pesticides, PCBs, and PAHs of soils and sediments. Slurry methods can be used since dewatering is not required (Figure 11.9). Bioremediation is a low-cost technology and therefore has the potential for wide use. However, metal remediation technologies are not as developed as organic treatments. Costs are in the range of \$130 to 200/m³ (FRTR, 2007). After treatment, water must be separated from the solids and may require subsequent treatment.

Surfactants can be added to enhance contaminant solubility or the natural bacteria could be stimulated to produce natural biosurfactants. The latter approach, which was investigated for an oil- and heavy metal-contaminated harbor soil (Jalali and Mulligan, 2008) has shown potential. Results showed that over the 50-day experiment, nutrient amendments enhanced biosurfactant production to up to three times their critical micelle concentration (CMC). Limiting the inorganic source of nitrogen showed an enhancement of biosurfactant production by 40%. The biosurfactants produced by the indigenous soil microorganisms were also able to solubilize 10% of TPH and 6% of the metal content of the soil and enhance biodegradation of petroleum hydrocarbons.

11.5.2 Landfarming

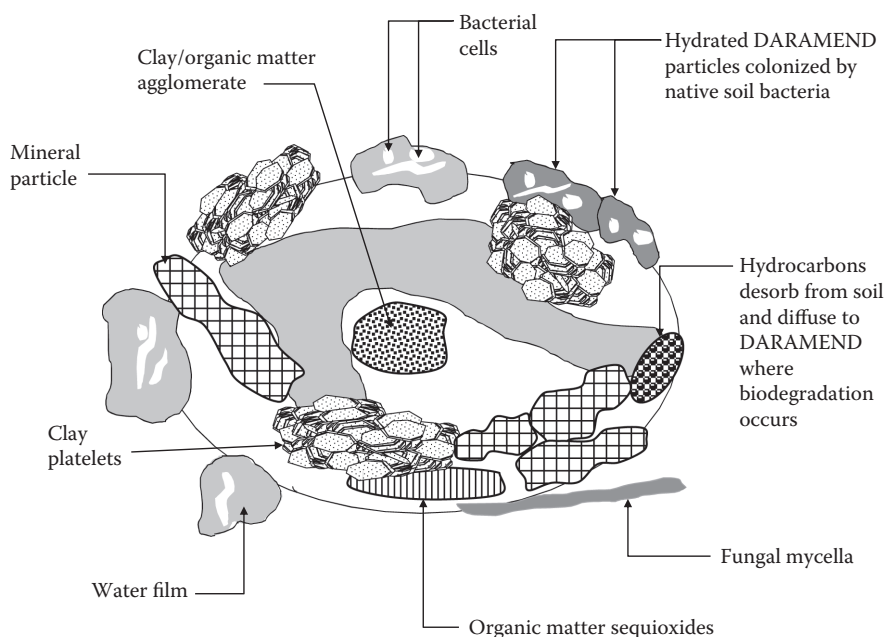
Land farming includes mixing the surface layer of soil with the contaminated sediment (Rittmann and McCarty, 2001) (Figure 11.10). Soil microorganisms are utilized for biodegradation of the contaminants including oil sludge, wood preserving wastes, coke wastes, JP-5, fuel oils, diesel fuel, and some pesticides (FRTR, 2007). The resulting product is compost.

**FIGURE 11.10**

Schematic of a land-farming process. (a) Removal of large debris, (b) equipment for soil mixing with cover, and (c) land farming process itself.

Moisture must be monitored and nutrients can be added to enhance biodegradation. Occasional turning of the soil increases the oxygen content and permeability of the sediment/surface soil mixture. Bulking materials and nutrients may also be added. The process is simple but could lead to contaminant volatilization and leaching. Therefore, monitoring is required. Land requirements can be extensive. In the United States and Belgium, bioremediated dredged materials have been mixed with compost and/or municipal sewage sludge to produce soil for landscaping projects and in Germany, it has been used in orchards.

An additive that has been used with land farming is DARAMEND™ (A+Environmental Solutions, 2014). It is a solid phase amendment (Figure 11.11) to promote anoxic conditions to enhance the bioremediation of pesticides such as toxaphene, DDT, dieldrin, TNT, RDX, PCE, TCE, DDD, and DDE. The reduction in the redox potential enhances the dechlorination of organochlorine compounds. With tilling equipment, the material can be mixed in to a depth of 0.6 m. Hydrated lime is used to maintain the pH between 6.6 and 8.5. Redox potential and moisture were monitored at an evaluated at a Superfund Site (Montgomery, Alabama) of a soil/sediment contaminated with pesticides (USEPA, 2004). Approximately 4500 tonnes were treated, and all contaminated reached specified levels. Santiago et al. (2003) evaluated DARAMEND for PAH contaminated sediment. However, PAH concentrations were higher than expected (average of 900 ppm) and thus could be reduced by bioremediation to CCME criteria (260 ppm) in bench-scale experiments. Thermal treatment was successful, however.

**FIGURE 11.11**

Schematic of the DARAMEND technology. (Adapted from Mulligan, C.N., *Environmental Biotreatment*, Government Institutes, Rockville, MD, 2002.)

In Asia, a land-farming process was performed on hydrocarbon-contaminated soil (Figure 11.10). The TPH content of 3700 mg/kg was reduced to less than 450 mg/kg. The BTEX was reduced from greater than 80 mg/kg to undetectable levels in 90 days. Commercial microbes and nutrients were added, and the soil was tilled three times a week. The soil moisture was maintained at 40% to 60% soil capacity. Weekly monitoring for TPH, BTEX, nitrates, phosphorus, ammonia, aerobic respiration, pH, microbial counts, and moisture contents were conducted. Volumes of greater than 4000 m³ were treated in each batch.

11.5.3 Composting

Composting involves the biodegradation of organic materials to produce carbon dioxide and water for soils and sediments. Typical temperatures are in the range of 55°C to 65°C due to the heat from the biodegradation process. Animal or vegetable wastes such as sewage sludge are often used as organic amendments. Bulking agents to increase the porosity of the material such as woods chips are added. Moisture content and temperature must be monitored. Composting processes include windrows and biopiles, and in vessel composting. Gaseous emissions and leachates may be produced and thus will need to be managed. Thermophilic composting can be applied to the treatment of explosive or PAH contaminated soils. Composting costs can range from \$320 to \$460/m³.

The contaminated sediment composting study evaluated by Khan and Anjaneyulu (2006) consisted of a mixture of 10 kg of sediment with 0.5% fertilizer and 50% compost. The sediment contaminants included phenols (16–24 mg/kg) and benzene (3.4 mg/kg).

TABLE 11.1

Comparison of Bioremediation Technologies

Parameter	Windrow Composting	Landfarming	Biopile Composting
Applicability	PAHs, explosives	Fuel oil, diesel fuel, PCBs, pesticides	Fuels, solvents
Site requirements	Excavation, and special mixing equipment	Excavation, and earthmoving equipment, liners	Excavation, and earthmoving equipment, aeration, liners
Limitations	Bulking agents that increase volume, and may need to be removed	Permanent structures required	Static process without mixing
Cost	\$180–270/m ³	Less than < \$100/m ³	\$130 to 260/m ³

Sources: Adapted from Myers, T.E. and Williford, C.W., *Concepts and Technologies for Bioremediation in Confined Disposal Facilities*, DOER Technical Notes Collection (ERDS TN-DOER-C11), U.S. Army Engineer Research and Development Center, Vicksburg, MS. Available at <http://el.erdc.usace.army.mil/elpubs/pdf/doerc5.pdf>, 2000; Federal Remediation Technologies Roundtable (FRTR), *Remediation Technologies Screening Matrix and Reference Guide*, 4th ed., 2007.

Fertilizer was added as a nutrient and compost was used to inoculate with microorganisms. Wood chips were added for support and aeration in the pile for composting. The parameters, pH, total volatile solids, microbial count, temperature and contaminant concentration, were monitored over the period of five weeks. Whereas benzene was almost completely biodegraded, lower levels of phenol degradation were obtained (80% to 85%). It was concluded that composting was technically feasible at lab scale.

Myers and Williford (2000) examined the bioremediation of contaminated sediments in a CDF. Composting (windrows and biopiles), landfarming, and land treatment were examined for PAHs, PCBs, and PCDDs/F (Table 11.1). Land treatment is similar to land farming except that the contaminated soil or sediments interact with the surrounding soil. Monitoring for potential leaching and volatilization of contaminants is essential. Composting and land treatment have the potential to be cost-effective but require pilot and demonstration studies. According to Myers et al. (2003) composting tests were not successful for remediating PAHs but PCB degradation may be more promising.

11.5.4 Bioleaching

Bioleaching involves *Thiobacillus* sp. bacteria, which can reduce sulfur compounds under aerobic and acidic conditions (pH 4) at temperatures between 15°C and 55°C, depending on the strain. Leaching can be performed by indirect means, acidification of sulfur compounds to produce sulfuric acid, which can then desorb the metals on the soil by substitution of protons. Direct leaching solubilizes metal sulfides by oxidation to metal sulfates. In laboratory tests, *Thiobacilli* were able to remove 70% to 75% of heavy metals (with the exception of lead and arsenic) from contaminated sediments (Karavaiko et al., 1988).

Options are available for bioleaching including heap leaching and bioslurry reactors. For both heap leaching and reactors, bacteria and sulfur compounds are added. In the reactor, mixing is used and pH can be controlled more easily; leachate is recycled during heap leaching. Copper, zinc, uranium, and gold have been removed by *Thiobacillus* sp. in biohydrometallurgical processes (Karavaiko et al., 1988).

As pyrometallurgical, and hydrometallurgical techniques are either very expensive, energy-intensive, or detrimental to the environment, various studies have been performed to develop a process to treat and microbially recover metals in low-grade oxide

ores (Mulligan, 2002). Biohydrometallurgical techniques such as those utilizing the fungus *Aspergillus niger* are thus potentially more sustainable. *A. niger* has shown potential for producing citric acid and other organic acids effective for metal solubilization (Mulligan and Kamali, 2003). Effectiveness for leaching was enhanced when sulfuric acid was added with organic acids to the medium. Different agricultural wastes such as potato peels were tested as growth substrates for the fungus. Maximum solubilization levels of 68%, 46%, and 34% were achieved for copper, zinc, and nickel, respectively. Also minimal iron dissolution was obtained (7%), which allows for further metal purification.

In the research study to evaluate the potential for mobilization of arsenic (As) from mine tailings in the presence of natural organic matter (NOM), humic acid (HA) was used as a model for NOM (Wang and Mulligan, 2009). By introducing HA at a low mass ratio (below 2 mg HA/g mine tailings) under acidic conditions As mobilization was inhibited. However, As mobilization increased with increasing mass ratios and under alkaline conditions, As mobilization was significantly HA enhanced.

11.5.5 Bioconversion Processes

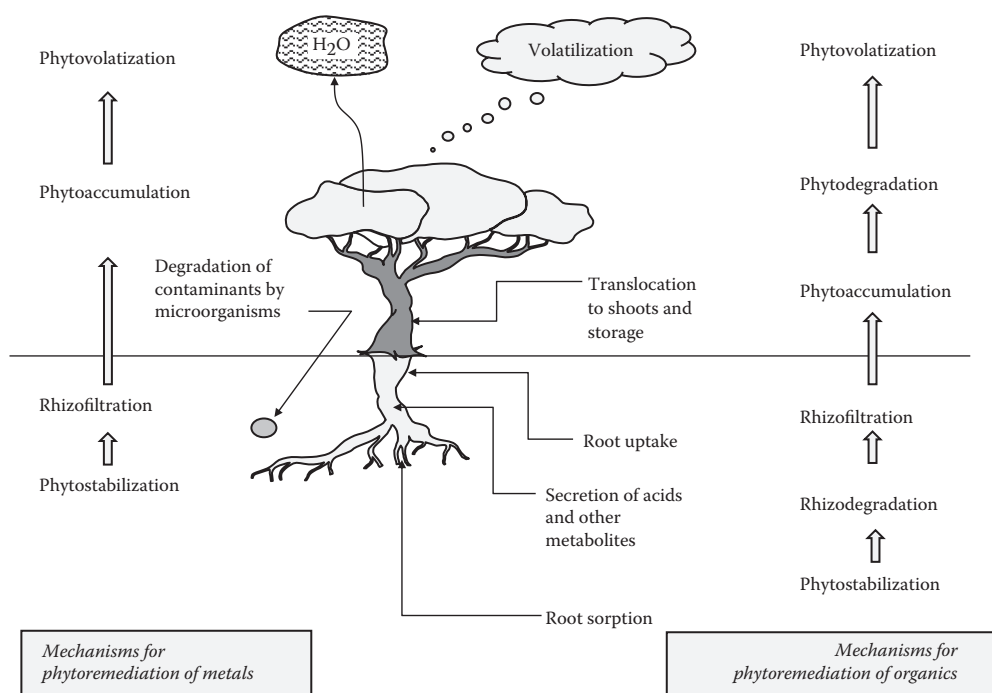
Microorganisms are also known to oxidize and reduce metal contaminants. Mercury and cadmium can be oxidized, whereas arsenic and iron can be reduced by microorganisms. This process (called mercores) has been developed and tested in Germany for removal of concentrations greater than 100 ppm. Since the mobility of the metal contaminants is influenced by their oxidation state, these reactions can affect their mobility. It needs to be noted that organic contaminants such as benzene can also be degraded.

Chromium conversion is also affected by the presence of biosurfactants. In the study by Massara et al. (2007) on the removal of Cr(III) from kaolinitic soil, the effect of addition of negatively charged biosurfactants (rhamnolipids) on chromium contaminated soil was evaluated. The sequential extraction results showed that rhamnolipids removed Cr(III) mainly from the carbonate, and oxide/hydroxide portions of the soil, stable forms from the soil. The rhamnolipids were also capable of reducing close to 100% of the extracted Cr(VI) to Cr(III) over a period of 24 days.

11.5.6 Phytoremediation

Some plants have been shown to retain contaminants in their roots, stems, and leaves via phytoextraction, phytodegradation, phytostabilization, and biodegradation in the rhizosphere (Hazardous Waste Consultant, 1996) (Figure 11.12). Phytoaccumulation is the transport of contaminants from the roots to the shoots and leaves. Contaminants are metabolized in the plant via enzymes for phytodegradation. Phytostabilization immobilizes contaminants by excretion of various chemicals from the roots. Around the plants root, microorganism growth is stimulated by the nutrients in the soil. These microorganisms can then biodegrade the contaminants in the soil. Various examples are shown in Table 11.2.

Vegetative caps consisting of grasses, trees, and shrubs can be established in shallow freshwater. The resulting vegetative mat can hold sediments in place. The construction of wetlands is growing for wastewater treatment, and thus, the knowledge on wetland configurations is growing. However, vegetative caps have not yet been applied to the remediation of sediments (Mulligan et al., 1999). Phytoremediation can be implemented where dredged sediments have been placed in contained areas and a wetland is then constructed to remediate and contain the sediments. Lee and Price (2003) indicated that although phytoextraction of Pb with chelates may be troublesome due to potential leaching into groundwater,

**FIGURE 11.12**

Mechanisms of phytoremediation. (Adapted from Mulligan, C.N., *Environmental Biotreatment*, Government Institutes, Rockville, MD, 2002.)

TABLE 11.2

Phytotechnology Mechanisms

Mechanism	Description
Phytodegradation	Uptake and degradation of contaminants within plant tissues by enzymatic activity for remediation
Phytoextraction	Uptake of contaminants by plants and sequestration into the plant tissue
Phytohydraulics	Ability of plants to take up and transpire water to control hydrology
Phytosequestration	Ability of plants to sequester certain contaminants into the rhizosphere through release of phytochemicals, and sequester contaminants on/into the plant roots and stems through transport proteins and cellular processes
Phytovolatilization	Ability of plants to take up, translocate, and subsequently volatilize contaminants in the transpiration stream for remediation
Rhizodegradation	Ability of released phytochemicals to enhance microbial biodegradation of contaminants in the rhizosphere for remediation

Source: Adapted from Interstate Technical Regulatory Council (ITRC), *Phytotechnology Technical and Regulatory Guidance and Decision Trees*, revised, 2009.

immobilization, and phytostabilization can be appropriate in CDFs. The site could potentially be restored for beneficial use as a wildlife habitat.

11.5.7 In Situ Bioremediation

Bioremediation involves the use of microorganisms to degrade organic contaminants completely or to less toxic components (USEPA, 2013a). Usually, an electron donor or energy

sources, an electron acceptor, and nutrients are required for a successful process. Naturally occurring microorganisms are often used as these are adaptable to changing conditions. Biostimulation is the seeding of known organisms if the site is deficient in required organisms. Nutrients can be pumped in or percolated.

For aerobic processes, dissolved oxygen is added either by aerating water used for saturating and adding hydrogen peroxide. For shallow soils, nutrients and oxygenated water can be added via infiltration galleries or spray irrigation. For deeper soils, injection wells are required. High temperatures enhance bioremediation rates. However, at lower temperatures bioremediation still occurs but more slowly. Heat blankets to cover the soil surface can increase the soil temperature and subsequently the biodegradation rate. Bioremediation can take several years to clean the site.

Under anaerobic conditions, methane, carbon dioxide, and trace amounts of hydrogen gas will be produced. Various electron acceptors are necessary in place of oxygen. These include sulfate, Fe(III), or nitrate. Under sulfate-reduction conditions, sulfide or elemental sulfur is produced, and under nitrate-reduction conditions, nitrogen gas is the final product. A disadvantage of anaerobic procedures is that contaminants can be degraded to products that are as or more hazardous than the original contaminant. A good example of this is the biodegradation of TCE to the more toxic vinyl chloride. To avoid this problem, aerobic conditions can be created to biodegrade the vinyl chloride.

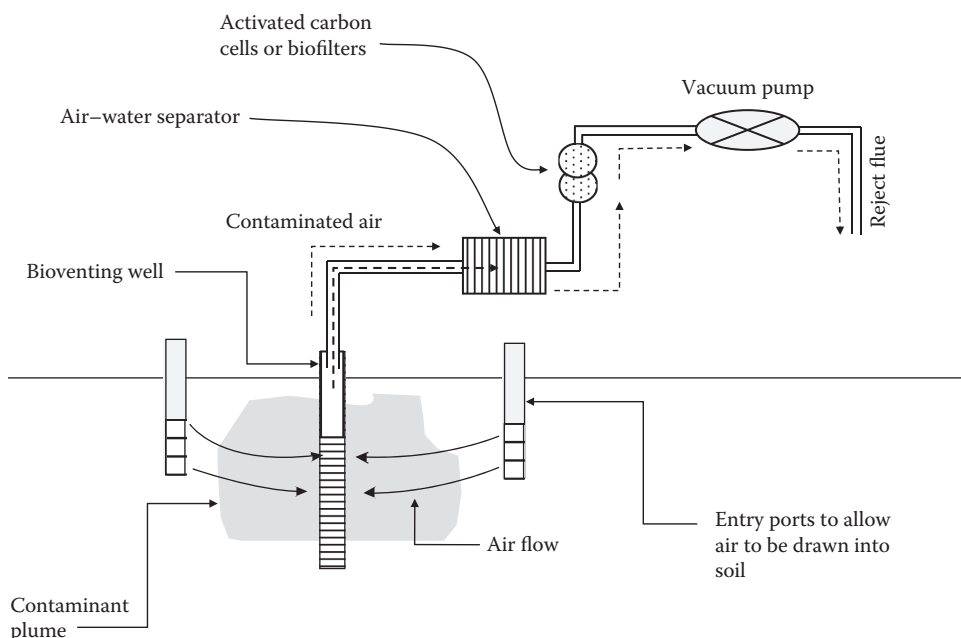
Bioremediation techniques have been successfully used to remediate soils, sludges, and groundwater contaminated with petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals. Bench- and pilot-scale studies have demonstrated the effectiveness of anaerobic microbial degradation of nitrotoluene in soils contaminated with munitions wastes. Bioremediation is especially effective for remediating low-level residual contamination in conjunction with source removal.

The most common contaminants treated by bioremediation include PAHs, nonhalogenated SVOCs, and BTEX. Superfund sites are commonly bioremediated if they contain wastes associated with wood preserving (creosote), and petroleum refining and reuse (BTEX). Excavation of contaminated soil is not required. Bioremediation is often less costly compared with other technologies including thermally enhanced recovery with heating, chemical treatment with expensive chemical reagents, and in situ flushing (which may require further treatment of the flushing water) and thermal desorption and incineration, which require excavation and heating. Typical costs for enhanced bioremediation range from \$30–100/m³.

Although bioremediation cannot degrade inorganic contaminants, bioremediation can be used to change the valence state of inorganics and cause adsorption, immobilization onto soil particulates, precipitation, uptake, accumulation, and concentration of inorganics. These techniques are promising for immobilizing or removing inorganics from soil and other wastes. Bacteria (Bader et al., 1996) and biosurfactants (Massara et al., 2007) can reduce Cr(VI) to Cr(III), which is less toxic and mobile. Sulfate-reducing bacteria can form insoluble metal sulfides. Heap leaching and in situ leaching have been used by the metal industry for copper recovery (Rawlings, 1997). *Thiobacillus* bacteria produces sulfuric acid that can be used to solubilize metal sulfides to metal sulfates. Fungus such as *Aspergillus niger* can produce citric and gluconic acids (Mulligan et al., 1999).

11.5.8 Bioventing

Bioventing (Figure 11.13) is an in situ process that involves forced aeration in the vadose zone to enhance the biological degradation of SVOCs and nonvolatile contaminants with

**FIGURE 11.13**

Schematic of a bioventing process. Note that although the bioventing process is similar to SVE, the air flow is lower so as to allow bioremediation.

Henry's law coefficients less than 0.1. These contaminants can include petroleum hydrocarbons, nonchlorinated solvents, some pesticides, wood preservatives, and other organic chemicals. A high soil permeability (k value greater than 10^{-6} cm/s) is needed, and sufficient nutrients must be supplied. Feasibility testing should evaluate air permeability of soil and in situ respiration rates. Aeration levels are substantially lower than in SVE processes to avoid emissions and enhance biodegradation. However, as some volatilization will occur, emissions must be monitored and captured and treated if required. Air treatment can include biofiltration, activated carbon or catalytic oxidation, or thermal treatment. High soil moisture contents can decrease process efficiency. Cleanup times can range from a few months to several years. Bioventing is becoming more common, and most of the hardware components are readily available due to experience with soil vapor extraction (SVE). The U.S. Air Force is demonstrating bioventing at 135 sites (FRTR, 2007). Costs can be as low as \$80 to \$100 per m^3 at large sites.

11.6 Comparison between Treatment Technologies

11.6.1 Treatment Technologies Overview

The overall trend in remediation technologies has been overviewed by USEPA (2004) in the U.S. between 1982 and 2002, 863 treatment technologies were applied at 638 Superfund sites. In situ technologies were used at 42% of the sites. The majority of

the sites were treated using SVE, bioremediation, and solidification/stabilization in descending order. The majority of ex situ remediation technologies were by S/S, incineration, thermal desorption, and bioremediation in descending order. Over the years, in situ remediation has been increased from 31% (in 1985 to 1989) to 49% (1998 to 2002). The reasons included cost-effectiveness, decreased exposure to contaminants, as no excavation is required, and willingness by professionals to use this approach. In fiscal year (FY) 2009–2011, 300 decisions were made for Superfund source materials. About half were in situ treatment, SVE, chemical treatment, bioremediation, S/S, multiphase extraction, bioremediation, and in situ thermal treatment were common. Off-site methods included physical separation, S/S, off-site treatment, and recycling. Physical separation includes sieving, sifting, removal of solid media, dewatering (for sediments), and decontamination. A variety of technologies are utilized as summarized in Table 11.3.

TABLE 11.3

Soil Treatment Technologies Utilized for Superfund Sites

Technology	% decision documents (FY 2005–2008)	% decision documents (FY 2009–2011)
<i>In situ</i>		
Chemical treatment	21	21
SVE	7	14
S/S	9	9
Thermal treatment	9	6
Multiple phase extraction	7	3
	4	3
Constructed wetland	0	2
Reactive cap	0	2
Flushing	1	1
Fracturing	1	1
Phytoremediation	1	0
Total	48	80
<i>Ex situ</i>		
Physical separation	21	28
S/S	19	13
Pump and treat	12	11
Off-site treatment	7	9
Recycling	10	8
On-site treatment	1	5
Phytoremediation	0	4
Chemical treatment	3	3
Bioremediation	3	3
NAPL recovery	1	1
Thermal desorption	2	1
Other	9	0
Total	65	67

11.6.2 Design of a Remediation Process

In choosing the most appropriate remediation technology or process, the approach shown in Figure 11.14 should be used. The first step of any remediation program is to develop a conceptual site model (CSM) to evaluate the potential for applying bioremediation at a site. The nature and extent of contamination and site characteristics; site hydrogeology, geochemistry, and oxidation–reduction conditions; biodegradation potential; contaminant fate and transport; and receptor and exposure pathways must be determined. Once the CSM is established and refined, activities undertaken prior to the implementation of a remediation program often involve treatability studies, examination of soil to ensure that undesirable reactions with the contaminants or their degradation products are prevented. The success of a remediation application highly depends on characterization and monitoring and an effective model for lowering natural resource consumption and waste generation, completed before and during its implementation. Monitoring and operation should also be designed to reduce emissions and energy requirements. For example, low-temperature processes require less energy. The advantages of the various options must be weighed. In addition to past practices to obtain a more sustainable remediation approach, other aspects must also be evaluated to

- Enhance land management practices and maintain biodiversity and the ecosystem population
- Reduce water consumption and pollution
- Reduce total energy use and increase the use of renewable energies
- Reduce air and GHG emissions

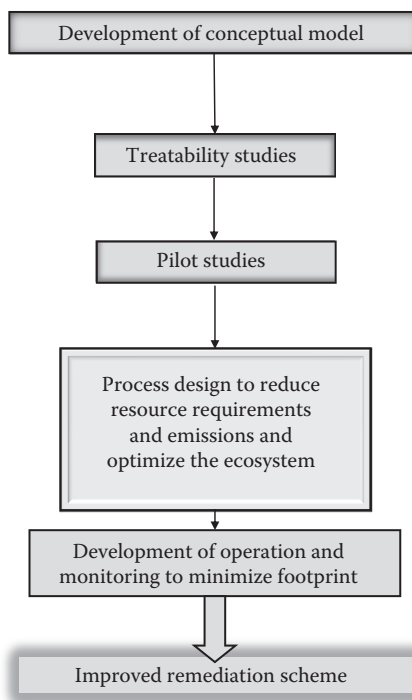


FIGURE 11.14

Flowsheet for design of an enhanced sustainable remediation technology or process.

Demonstration of the designed process will enable larger-scale evaluation of various factors before final design. Bioremediation has been suggested as a green remediation scheme (USEPA, 2010). In the example shown for bioaugmentation at the MAG-1 Site, Fort Dix, New Jersey, laboratory tests were used to evaluate the potential of a bacterial culture for treating chlorinated VOCs. A new well system was devised to disperse the inocula in the groundwater recirculation systems. The system was optimized to reduce material consumption and maintenance of the equipment. The contaminants were reduced by 99% with negative impacts.

Pilot scale field tests of composting (Former Joliet Army Ammunition Plant, Will County, Illinois) were performed to optimize amendments for composting and the turning frequency (USEPA, 2010). Additives included manure, wood chips, spent digester waste, and stable bedding. An 8.1-ha windrow composting facility was constructed to treat 280,000 tonnes of explosives-contaminated soil. Soil cleanup was 3 years ahead of schedule. The land will be used for a business parks and an engineer training center. Another site in Upper Arkansas River used municipal biosolids and limes for composting mine waste for composting, which led to complete vegetative cover.

A case study by Aecom involved a sediment cleanup alternative analysis at Lower Duwamish Waterway, Seattle, Washington (Fitzpatrick and Woodward, 2013). The site was an 8.3-km waterway contaminated by industrial inputs situated in an economic corridor. Issues involved tribal fishing rights and proximity to residential neighborhoods. Recontamination was occurring due to urban sources. EPA preferred dredging, but agreed to a green sustainable remediation (GSR) evaluation. Alternatives cost between \$200 million and 1.2 billion dollars. Carbon dioxide emissions were compared for the various alternatives. Dredging/landfilling/backfilling exhibited the highest level (5500 tonnes) compared with minimal amounts from monitored natural recovery (MNR).

According to the New York State Department of Environmental Conservation (DEC) (2011) DER-31 green remediation is defined as "the practice of considering all environmental effects of remedy implementation and incorporating options to minimize the environmental footprint of cleanup actions." Some practices are easily implantable. Renewable energy can be used as much as possible. Idling of vehicles must be limited. Materials should be reused as base or fill to reduce waste as much as possible. Ideally, the alternatives the most sustainable will have the following characteristics:

- Little impact on the environment in the short and long term
- Low GHG emissions
- Smaller environmental footprint
- Complete and permanent cleanup
- Optimal reuse
- Reduction of toxicity, mobility, and volume of contamination
- Achievement of remedial objectives

According to the EPA Green Remediation Best Management Practices Mining Sites (USEPA, 2008), potential practices include a better understanding of the contamination behavior, and implementation of passive treatment systems for acid mine drainage (slippery rock watershed), agricultural waste (mushroom compost and limestone) was used for neutralizing 82 kg of acidity per day. About 2 tonnes of MnO_2 were recovered over 8 years. Other waste materials such as industrial by-products such as chitin, and food

waste as biosorbents could also be used. Other approaches can also be implemented. These include:

- Employment of renewable energy for cleanup and land reuse
- Soil amendments such as compost soil covers consisting of noninvasive grasses or shrubs
- Drought-resistant plants to reduce exposure to contaminated soil and waste
- Metal (copper, zinc, gold, nickel) recovery from waste materials
- Phytoremediation to treat soil and water

There is a growing need to incorporate sustainability into projects due to pressure from all stakeholders. To integrate this into projects, decision support tools are needed. According to the EPA (2008), minimization of energy use, air emissions, water impacts, material and waste use, land, and ecosystems is required. The focus should be more on sustainable remediation such as phytoremediation and biobarriers, and use of renewable energies. In Canada, some sustainable remediation initiatives are led by the Interstate Technology and Regulatory Council (<http://www.itrcweb.org/gd.asp>), the Government of Canada (Public Works, Health Canada), and more recently by Surf Canada (<http://www.surfcanda.org>).

The Surf UK framework was used in the tender phase to evaluate alternatives for a site 7 km northwest of Bicester, Oxfordshire (Bardos et al., 2013). As it was a former airbase, it was designated as a heritage site. The 505-ha site was targeted for redevelopment for 1000 homes and related infrastructure while maintaining the heritage interest and included a petroleum, oil, and lubrication (POL) system with 13 km of pipework and 71 tanks. After fuel removal, the system was filled with water and alkaline solution to inhibit corrosion. Some oily water, however, existed in the system. The risk analysis conducted indicated that there was potential groundwater contamination from oily water and sludge, and thus, remediation was required. For the site remediation selection, preservation of the ecological and heritage characteristics, minimization of site disruption, and consideration of potential unexploded ordinance (UXOs) on site were required. The sustainability assessment at the tender stage was employed to show that the selection retained was the most sustainable.

Initially, remediation options were selected to achieve the remediation goals. These included breaking contaminant pathways, effectiveness, practicality, and ease of operation. The scoring system was distributed equally. After an initial screening process, a more detailed assessment was performed. Qualitative indicators were identified and quantitative indicators such as embodied carbon data from the ICE database, environmental agency carbon calculator, and data for suppliers were calculated. The selected option included filling of the pipelines with foam (not the most cost efficient), and the tanks with a PFA grout, water treatment was on site with discharge to the land. The approach allowed the involvement of stakeholders and allowed the choice of the most balanced approach, not necessarily the most economic.

Reddy and Adams (2010) have indicated that efforts are being made toward standardization of sustainability frameworks. Specific indicators could include energy and water consumption, greenhouse gas emissions, waste generation, cost of remediation. Various assessment tools have been developed. Some include screening matrices and others are life cycle assessments. Various public agencies including the Minnesota Pollution Control Agency, Illinois EPA, and the California DTSC have developed preliminary assessment tools. For the Air Force Center for Engineering and the Environment (AFCEE), GSI Environment developed the Sustainable Remediation Tool (SRT). The EPA has a GHG calculator tool. Life cycle assessment is another approach. However, it can be complicated and

expensive to determine and obtain the appropriate data. Comparison of various remediation options at a baseline is a simplified and logical approach.

Some of the requirements for successful implementation of sustainability assessment tools are:

- Involvement and training of stakeholders
- Clear guidance documents regarding definitions
- Standardized metrics and validation
- Well-defined frameworks
- Documentation of sustainable remediation practices
- Regulatory and/or financial incentives

Implementation of sustainability assessment tools will allow evaluation and selection of the remediation technologies that will minimize environmental impact and reduce resource requirements. In addition, it will enable and promote implementation of more sustainable practices.

11.6.3 Case Study Using a Sustainability Approach

GoldSET® (Golder Sustainability Evaluation Tool), a sustainability decision support tool for project planning and design, was created by Golder Associates (<http://www.goldset.com>) (Mulligan et al., 2013). It is a robust and transparent framework to embed sustainable development practices into design, construction, and operational decision-making phases of any project. The sustainability tool has been applied for various applications such as site remediation and mining tailings around the world. The tool operates through the assessment of different project options against a number of quantitative and qualitative indicators for each of the three dimensions of sustainability: environment, society, and economy. Indicators provide a way of describing the situation surrounding the project with a weighting scheme allowing the relative importance of each indicator to be reflected.

The first step in an evaluation involves the description of the site, the definition of the project objectives, and the identification of key issues of concern to all stakeholders. The second step is to identify and elaborate on various remediation options and/or alternatives that are thought to be suitable for the site specificities and project restrictions. Those options will then be assessed from an economic, social, and environmental viewpoint, and in some cases, from a technical viewpoint. The scoring scheme attached to each indicator provides a mechanism to assess the performance of each option with respect to the indicator. Together, the entire set of indicators should be representative of a project's performance, impacts, and cost.

All qualitative indicators have scoring schemes minimally consisting of three levels. Quantitative indicators have both relative and absolute scoring schemes. For the specific quantitative indicators such as greenhouse gas emissions and net present value (NPV), the framework is adopted to a level of detailed calculators. Relative scoring schemes assign a score of 0 to the lowest performing option while assigning 100 to the best performing option. Absolute scoring schemes have a fixed scoring scale independent of the options, and score the options relative to this fixed scale. These fixed values were adopted from accredited organizations (UNEP, WHO, etc.) as benchmarking values for consumption of natural resources or concentration of pollutants in the media.

11.6.3.1 Case Study For a Benzene-Contaminated Site

A benzene spill occurred along the highway near a small town of 1600 residents following a train derailment, resulting in the leaching of a certain amount of benzene into the groundwater aquifer used by the residents for their domestic well water. The area of the affected site was 6 ha. Since the concentration of benzene in the groundwater was 55 µg/L, this needed to be reduced to the maximum allowable contaminant level (MCL) of 5 µg/L for drinking water. The software was used for comparison of remediation options for benzene contaminated groundwater at the given site. Identified options included:

- Pump and treat followed by activated carbon treatment of the groundwater
- Pump and treat and followed by air stripping of the groundwater
- Biosparging and soil vapor extraction (SVE)
- Monitored natural attenuation

Table 11.4 provides a list of the indicators used for the analysis. Weights (1–3) were assigned to each indicator listed in Table 11.4. Although a life cycle assessment is not performed by the software, the indicators should be designed to consider the changing technological and environmental conditions and at different stages in the process. Results showed that, with respect to the environment, natural attenuation and biosparging and SVE appear to be more appropriate for this site. They appear to have minimum impact on soil quality and on fauna and flora resulting from the project, soil vapor intrusion, greenhouse gas emissions, energy consumption, and quantity of wastes. Meanwhile, activated carbon and air stripping seem to be less appropriate because of the disturbance to the natural condition of the site due to excavation and groundwater extraction, higher energy consumption due to pumping of groundwater, and higher production of greenhouse gases due to the heavy trucks usage.

Activated carbon and air stripping have the highest initial costs, whereas natural attenuation and biosparging have higher monitoring costs. However, the selection of natural attenuation may require additional institutional controls to adhere to local regulations and

TABLE 11.4

List of Selected Sustainability Indicators Considered for the Analysis

Type of Indicator		
Environmental Aspects	Economic Aspects	Social Aspects
Soil quality	NPV of option costs	Community health and safety
Sediment quality	Potential litigation	Worker's health and safety
Contaminated soil erosion	Financial recoveries	Drinking water supply
Groundwater quality	Environmental reserve	Direct local employment
Free product	Standards, laws, and regulations	Opportunities for local business generation
Surface water quality	Service reliability and performance	Public disruption
Waterborne contaminant migration	Reuse of the property	Quality of life
Water usage	Corporate image	Public use
Impact on fauna during project	Reliability	Cultural heritage
Impact on fauna after project	Technological uncertainty	Impact on the landscape
Soil vapor intrusion	Logistics	Management practices
Greenhouse gas emissions		
Energy consumption		
Quantity of wastes		
Hazardous wastes		
Residual impact of technology		

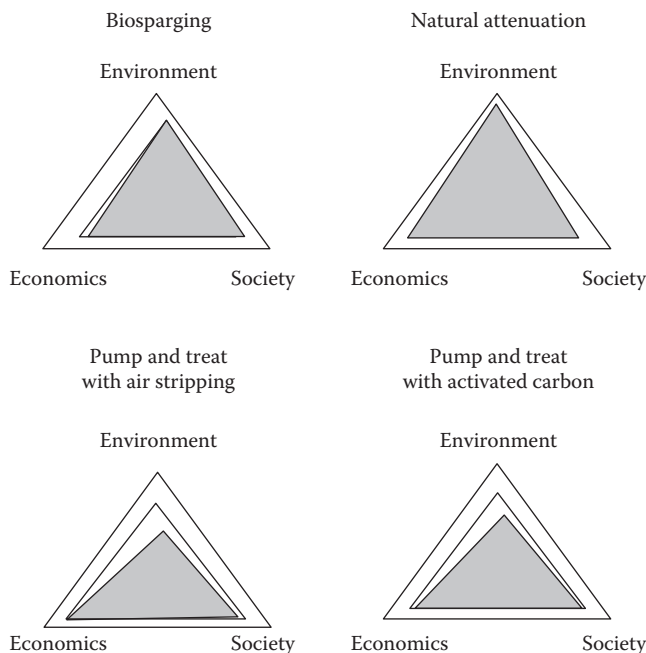
continuous monitoring. Natural attenuation and biosparging would have less impact on the local community, whereas activated carbon and air stripping have more impact on the community due to potential accidents, truck traffic, and excavation of wells. Furthermore, there is no limitation in terms of remediation time. Natural attenuation and biosparging appear to be best options among the selected options for remediation of the contaminated aquifer.

Meanwhile, if the contaminated aquifer is the only drinking water supply for the society, other remediation options such as activated carbon or air stripping should be considered. The required costs for site remediation are higher than bioremediation options due to the urgency for an acceptable source of drinking water. The overall comparison can be shown in Table 11.5 and Figure 11.15. It is not surprising that natural attenuation is the most sustainable and balanced approach in terms of percentage (%) for environment, society, and economics due to the low impact on the site and costs. However, the duration of the remediation, which is approximately 20 years, would be a major issue if the site is needed in the

TABLE 11.5

Comparison of the Sustainability of Remediation Technologies for a Benzene-Contaminated Site

Alternative	Environment (%)	Society (%)	Economics (%)	Lifetime (years)	Cost (\$ millions)
Biosparging/SVE	74	67	63	2	4.5
MNA	87	67	76	20	3.2
Pump and treat with air stripping	48	64	74	5	3.5
Pump and treat with activated carbon	53	74	68	2	4.5

**FIGURE 11.15**

Comparison of various options using the GoldSET sustainability tool. (Adapted from Mulligan, C.N. et al., Sustainable remediation of contaminated sites, *Coupled Phenomena in Environmental Geotechnics CPEG*, Torino, Italy, July 1–3, 2013.)

TABLE 11.6
Summary of Selected Technologies for Site Remediation

Factor	Technology				
	Vitrification	Electrokinetics	Soil Washing/ Flushing	Stabilization/ Solidification	Bioremediation
Effect on contaminants	Thermal oxidation and metal immobilization	Decomposition of organics, metal immobilization on electrodes	Metal and chemical removal and possible organic oxidation	Immobilization within matrix	Biodegradation of organic contaminants or conversion of metals
Commercial viability	Commercially available	Commercial scale	Some custom design needed	Commercially available	Commercially available
Beneficial use	Glass aggregate	Manufactured soil by addition of bulking agents	Manufactured soil by addition of bulking agents	Compacted fill, capping material	Soil can potentially be reused
Waste streams generated	Debris from screening and wastewater	Limited residues, some fluids, electrodes may require disposal	Debris from screening, wastewater, sludge from wastewater treatment	Debris from screening,	Wastewater, air emissions, debris from screening
Requirements	Plasma arc facility/ dewatering/ Desalination, water, fuel, power	In or ex situ, power requirements	Water, power	Land area, mixing equipment, additives, power	Water, additives power for mixing equipment if slurries or aeration systems, land if landfarming
Costs	\$350–425/tonne	\$50 to 100/m ³	Flushing: \$18 to 50/m ³	\$30 to 250 per tonne	Slurries: \$130 to 200/m ³ In situ: \$30 to 100/m ³ Composting: \$300 to 500/m ³ Landfarming: <100/m ³
					Vaporization of contaminants
					Potential recovery of solvents
					Gaseous emissions that require treatment
					Power for generating air flow, wells, gaseous treatment
					\$10 to 150/m ³

near future. In this case, biosparging would be the next most sustainable option that could be accomplished in a reasonable time frame.

11.7 Concluding Remarks

The oldest method in dealing with contaminated soils is referred to as excavation and disposal or dig and dump, an unsustainable method of managing contaminated soils. Remediation is essential for land reuse. The remediation techniques include the processes of washing, solidification/stabilization, decomposition or/and biodegradation. The techniques for soils and sediments are similar. When dredged materials are obtained from the sea, the existence of salt may prevent use of some of the techniques established for soils.

The cost performance of the remediation processes is complex in terms of availability of disposal site, price of construction materials, remediation operation cost, and the international and domestic constraints in the environmental situation and time required for remediation and site characteristics. A summary is shown in Table 11.6. Ex situ bioremediation allows superior control of environmental parameters such as pH, oxygen, and mixing than in situ bioremediation. However, there are still many challenges related to bioavailability of the contaminants. This issue can be remedied through the use of biological surfactants. In situ techniques offer decreased costs and increased worker safety. Site characterization and conceptual model development are essential for consideration of alternate remediation approaches in addition to laboratory and pilot testing. To reduce the impacts of the remediation technologies and enhance sustainability, new efforts are required and thus frameworks are being developed to ensure reduction in resource requirements and reduction in emissions and waste generation to protect the public and environment. The evaluation for sustainable remediation should be transparent and should allow for consultation with the various stakeholders to enable incorporation of the environmental, social, and economic aspects. Innovative techniques need to be developed and demonstrated to optimize land reuse.

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12

Sustainable Ground Improvement Technique for Geo-Disaster Mitigation

12.1 Introduction

One of the major set of challenges in the constructed environment is the problem of ground incompetence such as inability of the natural ground to provide proper supporting capability for overlying structures, and vulnerability of slopes and ground to catastrophic ground movement due to metastability of the soil mantle. Failure to recognize the challenges or failure to properly account for potential hazardous and catastrophic natural or anthropogenic events can lead to geo-disasters. Chapter 10 has defined *geo-disasters* as disasters that occur in the land compartment of the geoenvironment as a result of natural and human-associated catastrophic events such as earthquakes, floods, hurricanes, landslides, embankment and dam failures, etc.

To overcome deficiencies in ground support capability, or to strengthen the capability of the soil mantle to withstand the physical forces resulting from hazardous and catastrophic events, ground improvement techniques have been devised—the intent of which are to strengthen the ground (soil mantle) so as to provide the proper resistance to undesirable and unplanned ground and soil movement. The discussion in this chapter is the use of a new innovative and sustainable technique for ground improvement to withstand the stressors resulting from the geo-disasters, and hence to prevent or mitigate geo-disasters. The basis for the new innovative technique discussed in this chapter requires a brief review of the natural processes involved in producing the type of ground conditions that are resistant or vulnerable to geo-disaster stressors.

12.2 Soil Origin and Stability

The underlying basis for the new innovative technique for sustainable ground improvement is the phenomenon of *diagenesis*. Diagenesis is a critical factor in a geological cycle that one could call rock–soil–rock cycle. To understand what natural processes are involved in soil formation from rocks and how these processes can be exploited to improve ground stability, it is useful to take note of the three processes that are involved in the formation of soil from rocks and the formation of rocks from soils, i.e., weathering, diagenesis, and metamorphism. The relationship between the three processes—weathering, diagenesis, and metamorphism—for rock and soil are shown in schematic illustration in Figure 12.1.

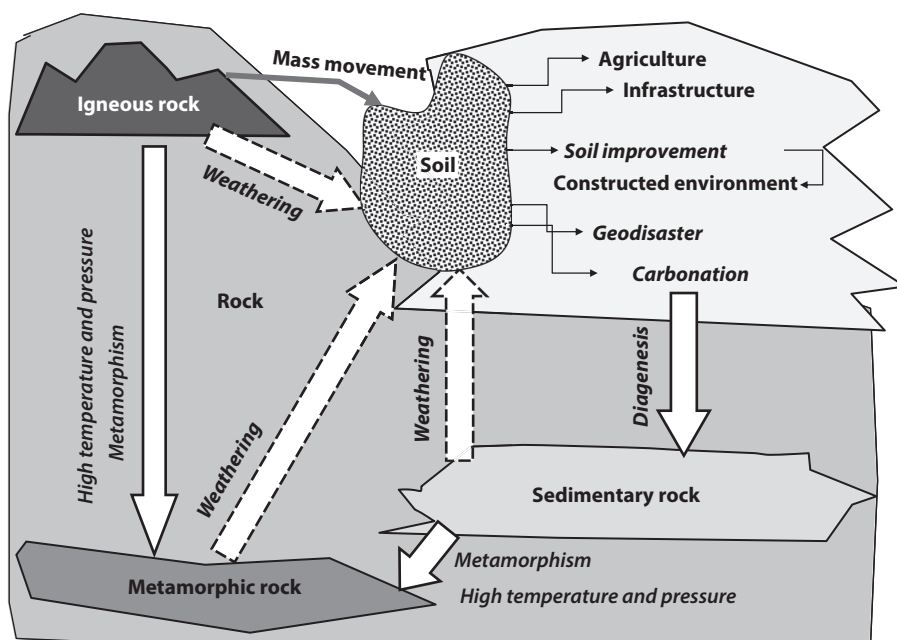


FIGURE 12.1

Weathering of rock, formation of soil, diagenesis, and metamorphism.

The “lesson” to be learned from Figure 12.1 is that the most stable state of the material in the rock–soil–rock cycle is a solid rock mass. Weathering of rock creates soil, and as we have discussed in the previous chapters, soil is both a resource material, a significant part of the natural capital of the geoenvironment, and is also the primary constituent of the surface layer (soil mantle) overlying subsurface rock.

Physical and chemical weathering of rock are the two main natural processes involved in the disintegration of rock into various sizes of soil particles. Physical weathering processes include cyclical heat–cold that shatter rocks because rock components have different coefficients of expansion. Other physical weathering processes include expansion of water in rock fissures as a result of freezing, and abrasion due to movement of ice and suspended particles in water. It is useful to note that the weathering processes continue to act on the disintegrated products (soil particles), altering their sizes and chemical composition.

Chemical weathering processes include hydrolysis, hydration, carbonation, oxidation, reduction and solution. The processes involve loss of some constituents, addition of protons, and rearrangement of constituents into new materials—with rates dependent on temperature, moisture, composition, potential for leaching, and composition of the leaching solution. Protons in the leaching solution can be supplied from CO_2 in the air or from decaying vegetation or other acids added to the system.

Although the common definition of diagenesis states that the process sometimes requires conditions of “high temperature and high pressure,” Worden and Burley (2003) claim that diagenesis can form sedimentary rocks under conditions of low temperature and pressure. With this claim, one can readily separate the process of diagenesis from that of metamorphism. Properties of rock that will be changed when subjected to high temperatures and high pressures can be deemed to have undergone the process of *metamorphism*.

Although metamorphism is sometimes considered to be a part of diagenesis, these two processes should be separated because the mechanisms involved between diagenesis and metamorphism are basically different. Metamorphism is the recrystallization of rocks under changes in physical and chemical conditions, primarily heat and pressure.

Natural catastrophic events such as hurricanes, typhoons, earthquakes, tornadoes, tsunamis, volcanic eruptions, rainstorms, and blizzards can trigger or cause soil movements such as landslides, rock falls due to dislodgement of rocks at higher elevations, debris flow, liquefaction, etc. Such events of soil movements can be classified as geo-disasters—the level of impact of such disasters being magnified when damage to the built environment and loss of human lives and other life forms are involved.

12.2.1 Soft Soils and Stability

Unconsolidated compressible soils of medium to low densities—often called *soft soils*—are susceptible to excessive distortion and deformation when subjected to overpowering external forces, i.e., external forces larger than internal resisting forces. The problem becomes acute when such soils are located on slopes or constitute part of a load support system. The behavior of soft soil under loads is well-recognized and understood in geotechnical engineering practice, and normal procedures for avoiding distortion–deformation and excessive soil movement have been (and still are) to increase the density of the soil by applying soil stabilization procedures such as mechanical compaction, consolidation procedures, binder additives (lime, cement, fly ash, pozzolans, etc.). Soil density is a direct reflection of soil particle packing—meaning that the higher the density of a soil, the tighter is the packing of particles. The combination of particle packing and physicochemical forces acting between particles results in interparticle action or particle interaction. The closer the soil particles are to each other, the greater is the bonding established as a result of interparticle action—with the obvious end-point of a tight-packing soil mass being that of a rock. The lesson that one learns is that the physical stability of a soil is increased in proportion to its compactness, and that the bonding achieved through interparticle action, especially when tight particle packing exists, provides for the optimum scenario for a stable soil mass. As long as soil particles are held tightly together, the soil mass should be stable, and the likelihood of occurrence of geo-disaster such as landslides, ground settlement under load will be minimized.

12.2.2 Soft Soil Engineering and Ground Improvement

Conventional techniques in soft soil engineering for stabilizing soft soil—i.e., increasing the bearing strength or capability of the ground to support heavier loads and to withstand greater displacement forces—include such procedures as cement mixing, use of lime, fly ash, and other types of binding agents, pile foundations, drainage work, etc. These techniques are designed to improve ground functionality—otherwise called *ground improvement*. Evaluation and adoption of a suitable ground improvement procedure should be based on at least four key considerations: (a) capability of improved ground or site to meet site functionality requirements, (b) ability to meet objectives or requirements for sustainable management of the geoenvironment, (c) total life cycle cost, and (d) durability of improved ground. The selection of materials and procedure to be used should take into account the durability of the materials involved to avoid failure of the improved site because of failure of the material used in the ground improvement procedure.

The lesson learned from the example of rocks is that if the role of diagenesis could be successfully used as a ground improvement technique, this should provide one with a robust and durable treatment for soft ground. There is, however, a problem. The natural rate of process of diagenesis is too slow for practical application. Accordingly, if one wishes to use diagenesis as a tool, one needs to overcome this problem. The innovative technique discussed in this chapter demonstrates the efficacy of artificially induced diagenesis techniques that are both robust and sustainable solutions for ground improvement.

12.3 Carbonate Diagenesis: Carbonate as a Cementing Agent

12.3.1 Definition of Carbonate Diagenesis

It is commonly understood that the strength of sediments is a function of its density—with density increases due to consolidation and/or compaction—and that the greater the density, the greater the strength. For example, the values for strength parameters, c (cohesion), and ϕ (friction angle), for fine-grained soils will increase during consolidation, with the increases attributed to the decrease in the separation between particles and bonding due to interparticle action, which has often been confused with the strength increase by binders between particles, such as carbonates, organic matter, clay, etc.

In geology and lithology, diagenesis is usually defined as *carbonate diagenesis* since carbonate acts as a binder for sedimentary rocks (Morse, 2005). In many cases, sandstone and shale have been formed with carbonates (Worden and Burley, 2003). Recently, diagenesis has been defined as *compaction and carbonation processes at low temperature and low pressure for the formation of sedimentary rock*. This is a more advanced definition because some obscure factors have been removed. As will be described later, carbonates can be dissolved and recrystallized under certain conditions—low temperatures and low pressures, which strongly suggest that these processes can be included in explaining the process of diagenesis.

12.3.2 Origin and Fate of Carbonates

12.3.2.1 Sea Bottoms and Ocean Floors

There are several origins in the formation of carbonates. The largest proportion of carbonate formation is attributed to the bodies of coccolith (phytoplankton) and foraminifers (Fukue et al., 1996). The dead bodies deposited on the seafloor are transformed into limestone or carbonate binders between soil particles, depending on the carbonate content. The carbonate content of marine sediments varies from less than 1% to more than 80%. In general, the carbonate content is low near the coast and increases with the distance from the coast due to the burial effects of materials discharged from the land environment. Fukue et al. (1996) estimated that from the sedimentation rate of deposits and carbonate content, the sedimentation rate of the carbonate was approximately 0.95 g/1000 years/cm². Considering the discharged amount from land, the relationship between total deposits m_{tv} (g/1000 years/cm²) and carbonate content C (%) is

$$m_{tv} = \frac{95}{C} \quad (12.1)$$

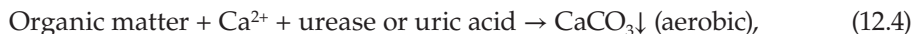
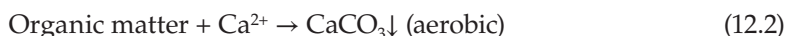
The sea floor moves at a rate of several centimeters per year. The past upheaval formed the mountains consisting of marine sediments containing carbonates. The formation of high mountains by limestone is a typical example of the fate of carbonates formed by coccolith and foraminifers. Sedimentary rock and soil contain varying amounts of carbonate, and over long time periods, the carbonate fractions in rock and soil may be subjected to metamorphism.

12.3.2.2 Coral Reef and Shells in Coastal Areas

Coral reefs are well-known sources of carbonates. At the beach, shells constitute sources of carbonates. The carbonates of coral reefs and shells are widely distributed as a result of past mass movements, and may have undergone metamorphism—usually in the form of dissolution and recrystallization.

12.3.2.3 Microbially Induced Carbonates

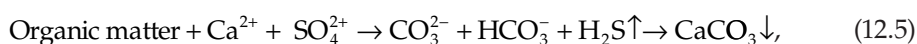
There are microbial processes that can produce carbonates. In chemical reactions with nitrogen (organic matter), carbonate can be produced as follows (Castanier et al., 1999):



where the organic matter can be degraded by the proper (aerobic or anaerobic) microbes.

In a sulfur cycle, carbonate will be produced as follows:

In the case of reduction of SO_4^{2-}



where the organic matter can be degraded by anaerobic microbes. If hydrogen sulfide (H_2S) exists under aerobic conditions, the following reaction occurs.



Thus, sulfuric acid (H_2SO_4) is obtained. In this case, the pH decreases and no carbonate will be produced.

A good example of a form of artificial diagenesis is beachrocks, which are cemented by carbonates. According to Vieira and De Ros (2006), beachrocks are sediments cemented with carbonate in tropical coastal areas. There are, however, other views on the mechanisms involved in the formation of beachrocks. Neumeier (1999), for example, indicates that the binder for beachrock is Mg-calcite or aragonite. Regardless of the type or types of mechanism involved in the formation of beachrocks, there are certain necessary conditions for the formation of beachrocks. Neumeier (1999) and Khadkikar and Rajshekhar (2003) have pointed out that microbes play an important role in the formation of beachrocks—a fact that was experimentally confirmed by Neumeier (1999).

12.3.3 Formation of Sedimentary Rock due to Carbonate Diagenesis

Examples of diagenesis resulting from precipitation of carbonate are sandstones cemented with carbonate (Morad, 1998; Moore, 2001). Fukue et al. (1999) found that the strength of marine sediments was strongly related to their carbonate content—with the dead bodies of marine animals such as foraminifer and phytoplankton (coccolith) as the source of the carbonates. The relationship between strength and carbonate content of marine sediments in Sagami Bay (Fukue et al., 1999) is shown in Figure 12.2. Although the proportions of clay silt and sand below a depth of 0.5 m remain relatively constant, the vane shear strength shows a decrease in strength with depth after a depth of approximately 1.2 m—indicating the fallacy of assuming a strength relationship between sediment strength and depth of sediment. The results clearly show, however, that the vane shear strength of sediments is strongly influenced by carbonate content.

Figure 12.3 shows that the trend lines for the profiles of unconfined compressive strength and carbonate content for the sediments obtained from Tokyo Bay (the off-shore Haneda Airport at a soil depth ranging from 42 to 44.5 m) are remarkably similar—indicating that a quantitative relationship can be established between strength and carbonate content. Using the slopes of the trend lines (“fitting” lines), a correlation between unconfined compressive strength and carbonate content can be obtained as shown in Figure 12.4. The vertical axis in Figure 12.4 represents the slope of unconfined compressive strength, i.e., $\Delta q_u/\Delta D$, and the horizontal axis represents the slope of carbonate content $\Delta C/\Delta D$, where q_u is the unconfined compressive strength, C is the carbonate content and D is the sediment depth. Using data from the sediments from off-shore Urayasu (Chiba Prefecture, at a soil depth ranging from 42 to 43 m) and those from Figure 12.3, the results show that $\Delta q_u/\Delta C$, i.e., increasing rate of strength, is approximately 64 kPa/%.

Surface sediments obtained from Tokyo and Osaka Bays were also examined to obtain relationships between strength and carbonate content, with the results showing a similar

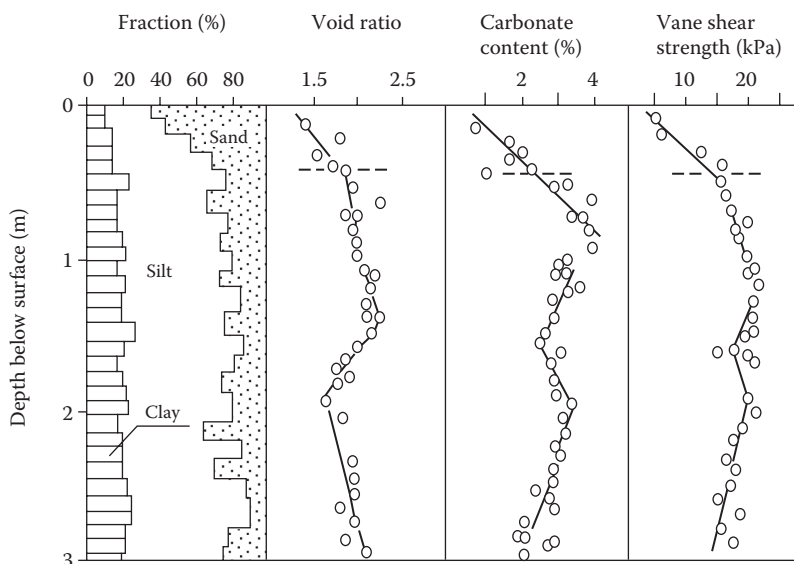


FIGURE 12.2
Profiles of sediments from the Sagami Bay at water depth of 1020 m.

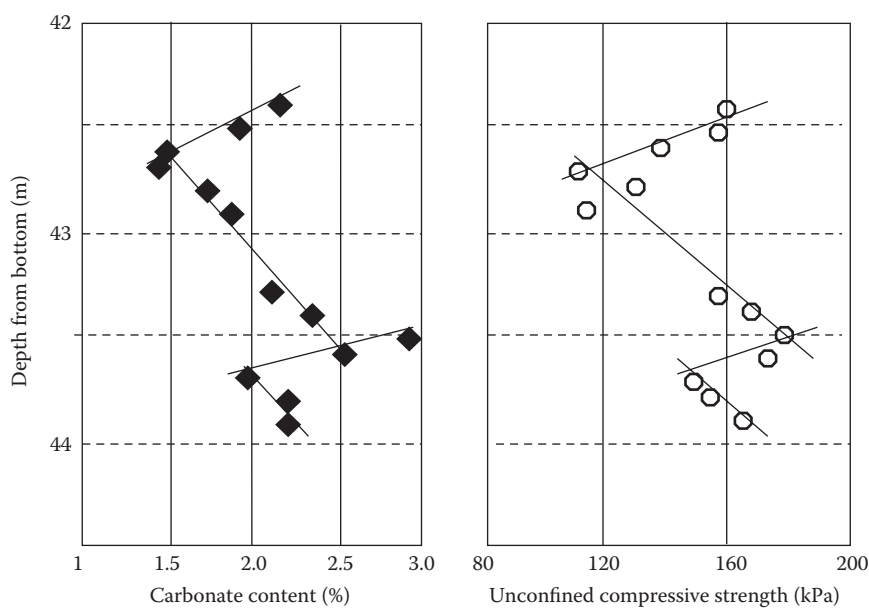


FIGURE 12.3 Profiles of carbonate content and unconfined compressive strength for sediments from the off-shore Haneda.

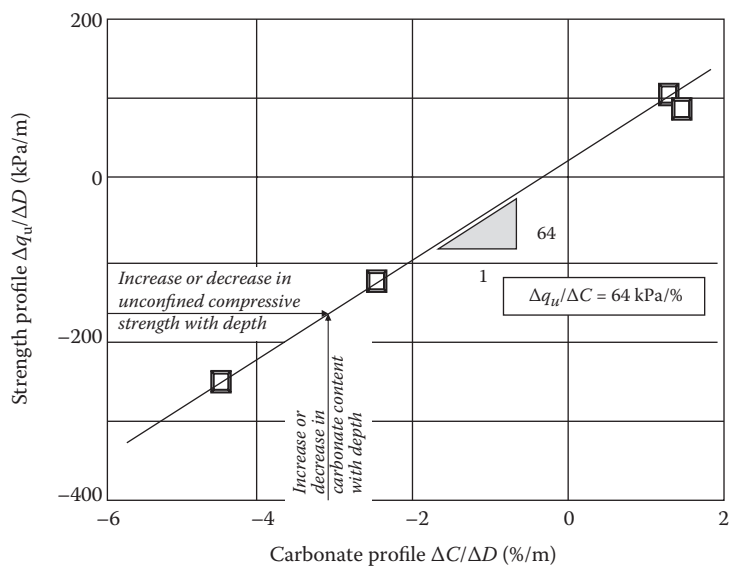


FIGURE 12.4 Effects of carbonate content on unconfined compressive strength for silty sediments with a depth of approximately 40 m.

trend to those shown in Figures 12.3 and 12.4 (Fukue et al., 1999)—but with lower values because the surface sediments were looser and much younger in age in comparison to the deeper sediments shown in Figures 12.3 and 12.4.

12.3.4 Formations of Carbonate Nodules and Sandstones

Carbonate nodules can be found in the mines of bentonite clay, as shown in Figure 12.5a. The nodules consist of calcite (calcium carbonate) and soil particles. They are very hard but are easily dissolved with strong acid. Carbonate nodules can also be found in old and newly formed sediments as shown, for example, in the carbonate nodules found in the alluvial sediments shown in Figure 12.5b. Although the mechanisms responsible for formation of the nodules are not fully understood, it is likely that the natural processes of nodule formation involved some element of microbial activity.

Another natural process of carbonate precipitation is the formation of sandstone, with a likely process involving the dissolution of shells and the recrystallization of carbonates binding sand particles (Worden and Burley, 2003; Morad, 1998; Moore, 2001). These natural processes that produce cementation of soil particles with carbonate can be defined as

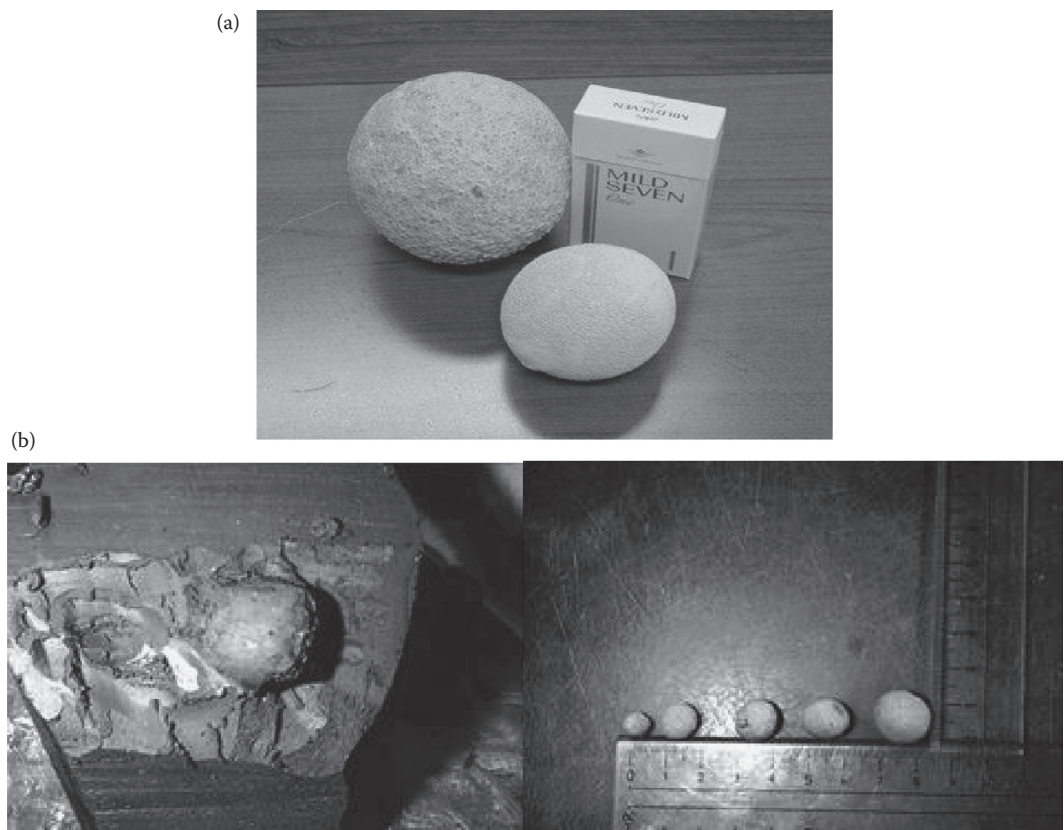


FIGURE 12.5

(a) Carbonate nodules found in bentonite mine. (b) Carbonate nodules found in alluvial sediments near a river mouth.

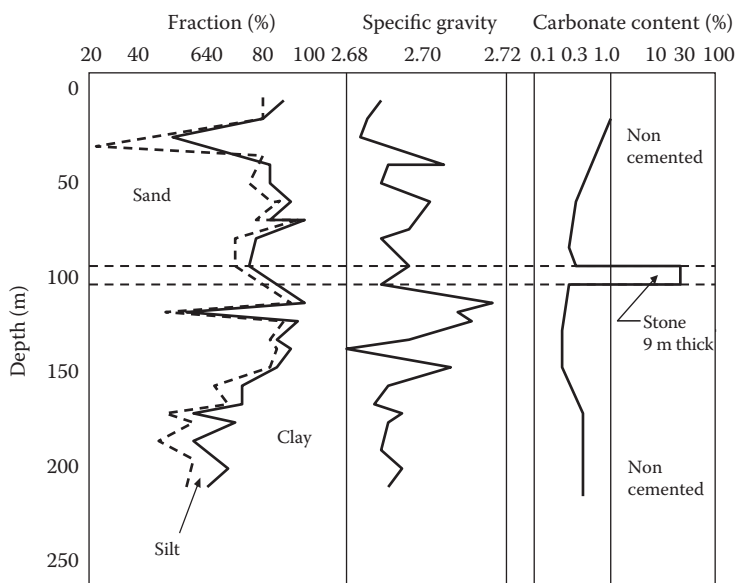
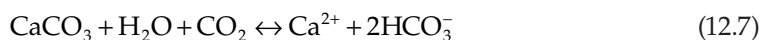


FIGURE 12.6
Floating sandstone in the diluvial formation, Sakura City, Japan.

diagenesis (Worden and Burley, 2003). A typical example of such a sandstone is the *floating sandstone layer* in granular sand layers in Sakura City, Chiba prefecture, Japan. The subsurface profile shown in Figure 12.6 shows the sandstone layer, thickness of about 10 m, at a depth of 90 m embedded in the diluvium sand layers (Narita sand formation). Unconfined compressive strengths of about 19 MPa were obtained from samples retrieved from the site (Fukue et al., 1999). Vertical fracture planes obtained under compression suggested tensile failure of the samples, meaning that the compressive strength of the sandstone would likely be higher than 19 MPa. With a carbonate content of 24% in comparison to the less than 1% carbonate content in the granular sand layers above and below the sandstone, one can conclude that carbonate contribution to strength is approximately 800 kPa/% (Fukue et al., 1999).

12.3.5 Calcirudite

Dissolution of limestone (calcite) occurs as follows:



The reaction shown in the relationship is reversible. Limestone dissolves and recrystallizes as stalactite. Ca^{2+} and HCO_3^- are transported by groundwater and precipitated in the soil horizon resulting in the formation of calcirudite—a conglomerate bound with calcite. This reversible reaction (dissolution–precipitation process) is not limited to limestone. It also occurs with carbonate-composed materials such as shells, coral reefs, carbonates contained in soils, etc. This dissolution–precipitation process results in a complicated circulation of calcium and carbon dioxide when it occurs in soils. As an interesting piece of



FIGURE 12.7

(See color insert.) Calcirudite cemented with calcite as a result of the precipitation of carbonate.

historical note, the reference to calcirudite in the Japanese national anthem is based on one of the 31-syllable Japanese poems on *Kokin-Wakasyu*, published in the early tenth century. In the poem, carbonate diagenesis was, for a very long time, hopefully compared with national prosperity. Accordingly, calcirudite is called *sazare stone* (stiff megalith) and is worshipped in Japan (Figure 12.7).

12.3.6 Carbonate Diagenesis Summary

Diagenesis occurs in the form of metamorphic reactions of carbonate, such as dissolution–precipitation (dissolution–recrystallization) of carbonate and/or changes in other types of carbonates, such as siderite, dolomite, etc. The strength of a sedimentary soil is strongly influenced by its carbonate content—the higher the carbonate content, the greater its strength. The evidence suggests that carbonate diagenesis may be one of the principal means for the formation of nodules of carbonates, calcirudite, and other minerals, such as siderite, magnesite, pyrite, hematite, etc.

12.3.6.1 The Case for Using Diagenetic Process in Ground Improvement

The success of carbonate cementing of granular soil particles in diagenesis leads one to speculate that if the diagenetic process can be accelerated so as to produce the final product in a short time period, this could work to improve the physical functionality of soft ground. The discussion in the remaining part of this chapter focuses on the development of an artificial diagenetic process that obtains carbonate diagenesis in a time period that permits its practical application as a ground improvement technique. The technique, which is called *artificial diagenesis*, has the following advantages (a) since the process is essentially generated from microbial activity, the technique is deemed to be sustainable, (b) the time frame for application of the technique is sufficiently short—thus allowing its use in ground improvement projects, (c) the technique is economic, durable, and is

applied in situ into the soil subgrade or soil mantle, thus essentially rendering it a soil stabilization procedure.

12.4 Artificial Diagenesis

The term *artificial diagenesis* is defined as the cementation process due to microbially but artificially induced production of carbonates—a process similar to that of natural diagenesis. Artificial diagenesis, as a technique for strengthening soil (ground improvement) has been used successfully by Bachmeier et al. (2002), Ciurli et al. (1996), and Fukue et al. (2011). The most efficient technique utilizes ureolytic microbes that produce the enzyme *urease*. It is useful to note that while there are many species of ureolytic microbes, the ureolytic ability of the microbes varies widely with species.

Artificial diagenesis can be used to mitigate geo-disasters by strengthening soils and weathered rocks. The concept is simple; soils can be rendered as rock by artificial diagenesis. Figure 12.8 illustrates the main elements of the technique. Ureolytic bacteria are cultivated with the appropriate medium. If the medium is not the proper one, cultivation will not be complete. When successful cultivation has been achieved, the culture solution is mixed with the reactive solution consisting of CaCl_2 , MgCl_2 , NaCl , buffer materials, etc., before injection into the soil.

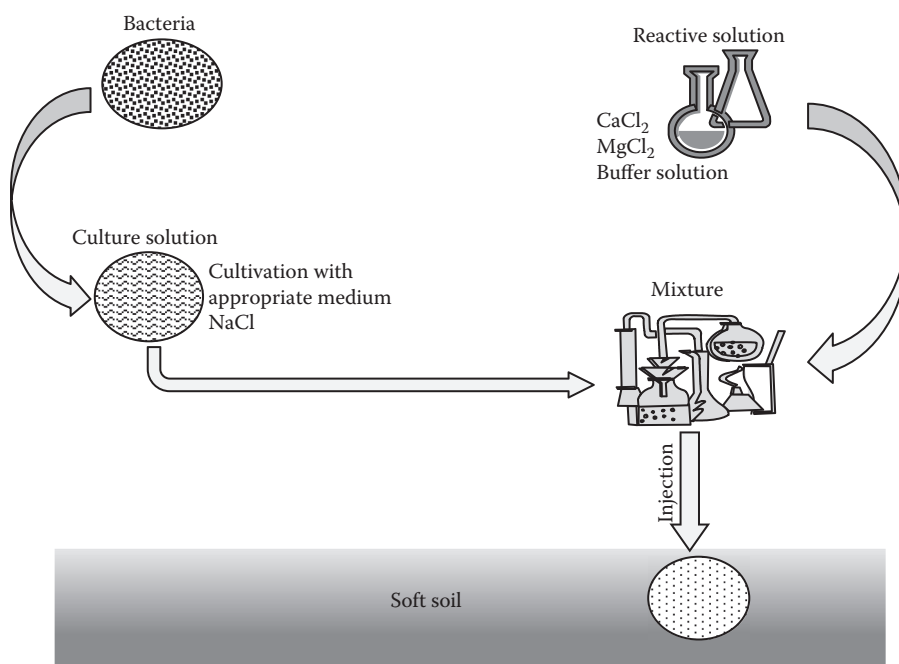


FIGURE 12.8
Procedure for application of artificial diagenesis in soil mantle.

A variation to the technique shown in Figure 12.8 is to cultivate the bacteria in the soil to be treated. This requires that the medium be also introduced into the soil (together with the bacteria) so that cultivation in situ can progress, with the reactive solution subsequently infiltrated into the soil.

12.4.1 Microbes

There are many species of microbes that can induce precipitation of carbonate (De Muryncka et al., 2010). The processes of carbonate precipitation are basically dependent on the degradation of organic matter by microbes and the consequent production of CO_2 , under the existence of Ca^{2+} . However, the necessary and sufficient conditions for production of carbonate depends on many factors, such as species of microbes, type of organic matter, pH, and dissolved oxygen. Some microbial species used in reported studies have generally produced calcium carbonate (De Muryncka et al., 2010; Lian et al., 2006). Adolphe et al. (1990) obtained the proprietary rights for the 'Calcite Bioconcept' process that uses the microbe. Since then, many researchers have used *Sporosarcina pasteurii*, formerly known as *Bacillus pasteurii*, because of its strong urease activity (Whiffin et al., 2007; DeJong et al., 2006; Bang et al., 2001; Ferris et al., 2003).

12.4.2 Ureolytic Bacteria

Fukue et al. (2011) isolated a strong ureolytic microbe (NO-A10) from a Japanese soil and used the microbes to improve the strength of sandy soils through microbially produced calcite (CaCO_3). The alkalophilic microbe, with a diameter of approximately $1\text{ }\mu\text{m}$ and a length of a few μm is smaller than *S. pasteurii*—a beneficial attribute when it comes to application of the microbes into fine-grained soil and rock with small fissures and cracks. NO-A10 has urease activity up to a Ca^{2+} concentration of 1.5 M and the rate of activity is very high, as will be discussed in Section 4.3.1.

12.4.3 Chemical Reactions in Artificial Diagenesis

12.4.3.1 Urease Activity

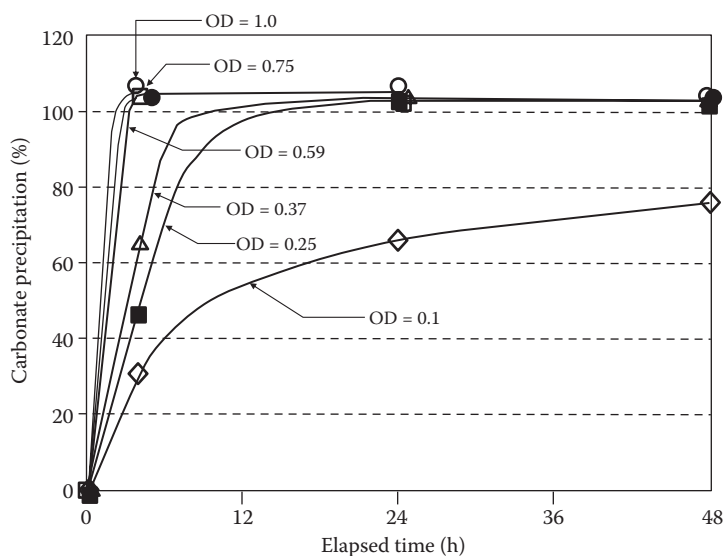
To obtain large amounts of carbonate precipitation, the reaction shown in Equation 12.4 can be utilized. Since calcite (calcium carbonate) may be unstable with pH changes and/or increase in the partial pressure of CO_2 , the following chemical reaction is recommended for application of artificial diagenesis. In the reaction, the urease enzyme produced by ureolytic bacteria can be used to induce hydrolysis of urea ($(\text{NH}_2)_2\text{CO}$), as follows:



The reaction is followed by the production of carbonate.



In the reaction shown in Equation 12.8, the ammonium will increase pH, which explains why urease is used. Since the enzyme is a protein, it will be inactivated by changes in temperature and pH, and given the fact that protein changes with temperature and pH

**FIGURE 12.9**

Carbonate precipitation rates with different concentrations of microbes. OD is the optical density at a wavelength of 600 nm. The 100% point on the vertical axis indicates 1 M CaCO_3 , i.e., 100 g/L.

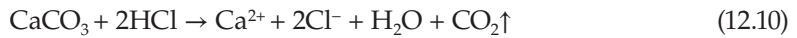
are irreversible, the altered urease will never recover. Meanwhile, the increase in pH due to ammonia production will counter the drop in pH resulting from the death of microbes. If the pH becomes low, then hydrolysis will produce NH_3 and CO_2 . This means that no carbonate will be produced. If the pH remains at a relatively high range, NH_4 and CO_3 ions will be produced.

12.4.3.2 Carbonate Precipitation

The rate of microbial carbonate precipitation varies with species of microbes. The example of precipitation rates with different concentrations of microbes shown in Figure 12.9 shows that most of the data lie in the region of greater than 100% carbonate precipitation, meaning that some crystalline water was produced. For an optical density (OD) value of 1.0, the precipitation rate is approximately 6 mM/min. The greater the OD, the higher is the precipitation rate. The precipitation rate can influence the crystalline characteristics of calcium carbonate. Calcite is the main calcium carbonate produced when the reaction rate is rapid, whereas aragonite and vaterite are most likely produced when the rate is slow. It is useful to note that the chemical compositions of calcite, aragonite, and vaterite are essentially identical, i.e., CaCO_3 .

12.5 Definition and Measurement of Carbonate Content

A closed vessel device is used as a rapid method for measuring CO_2 gaseous pressure by mixing soil and acid (Fukue et al., 2010), utilizing the following reactions.



If the amount of CO_2 is obtained, the mass of calcium carbonate (CaCO_3) can be estimated from Equation 12.10. The amount of CO_2 is estimated using the relationship between CO_2 gaseous pressure produced and pure reagent of CaCO_3 used. The conversion from CaCO_3 to $\text{CaMg}(\text{CO}_3)_2$ can be made by calculation. The content of carbonate C is defined as

$$C = \frac{m_c}{m} \times 100 \quad (12.12)$$

where m_c is the mass of carbonate and m is the mass of dry soil.

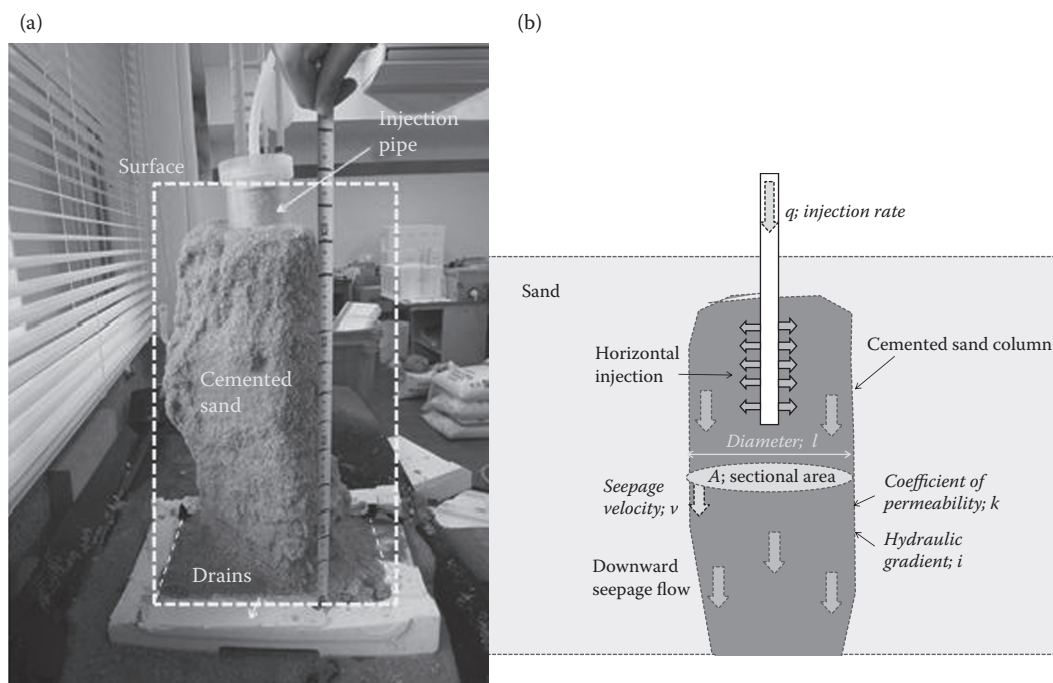
12.6 Artificial Diagenesis for Geo-Disaster Mitigation

The vulnerability of soft soils to geo-disasters is in large measure because of low quality (undesirable) soil properties such as high compressibility, low strength, low bearing capacity, and high liquefaction potential. Utilizing artificial diagenesis as a tool for improvement of low quality soil properties has considerable merit since this technique can be applied in situ and is robust, sustainable, economic, and “environmentally friendly.” As seen in Figure 12.9 with respect to laboratory studies, the time required to obtain carbonation—carbonates that would act as cementation bonds between soil particles—is relatively short.

12.6.1 Injection of Microbes and Reactive Solution

Interactions between microbes and soil particles are dependent on many factors (Scheibe et al., 2007). Since microbes usually have negatively charged surfaces, they tend to disperse when mixed in the cultivated solution. After mixing with the reactive solution, the microbes may adsorb cations (Ca^{2+} , Mg^{2+} , etc.) and since the surfaces of soil particles are predominantly negatively charged, partitioning of microbes with adsorbed cations to the soil particles will result. Transport of bacteria in soils is dependent on the flow velocity of the injecting solution, which in turn is related to the permeability of the soil and the hydraulic gradient. A high flow velocity can hinder partitioning of microbes onto the surfaces of soil particles.

Designating the cultivated solution of ureolytic strains as B-solution and the reactive chemical solution as R-solution, if the concentration of microbes is high, e.g., $B/R > 1.0$, flocculation with the cations in the R-solution will occur—resulting in the formation of precipitates that cannot act as binders. Lower B/R ratios are more effective in producing cementation of soil particles. Examples for injecting the B–R solution into dry and saturated sands reported by Fukue et al. (2012, 2013) showed that the distribution of microbes and the flow pattern in the cemented sands were influenced by the boundary condition and permeability of the sands and were different for coarse and fine sands. Application of a relatively high hydraulic gradient induces a jet flow. Figure 12.10a shows a cemented

**FIGURE 12.10**

(a) Sand column formed in relatively deep sand layer. (b) Horizontal and downward flow of the mixture of bacteria and reactive solution in sand.

sand column obtained by injection of bacteria and reactive solution from a larger injection mouth into a deeper soil layer—with the diameter of the sand column being a few folds greater than that of the injection mouth.

To estimate the size of the cemented zone, one assumes that the injection rate of mixture of bacteria and reactive solution is equal to the downward flow rate at a horizontal section with an area of A under a hydraulic gradient of one, as shown in Figure 12.10b. With these assumptions, the size of the cemented sand column can be estimated using the following relationship,

$$q = vA = kiA = \frac{v_e A}{n / 100} \quad (12.13)$$

where q is the injection rate, v is apparent seepage velocity, A is the sectional flow area, k is the coefficient of permeability, i is the hydraulic gradient, v_e is the advection velocity, and n is the porosity.

12.6.2 Increased Strength due to Artificial Diagenesis

12.6.2.1 Unconfined Compressive Strength

Unconfined compression test results for a soil cemented by carbonate with a carbonate content of 0.84% reported by Fukue et al. (2011) showed that carbonate cementation endowed

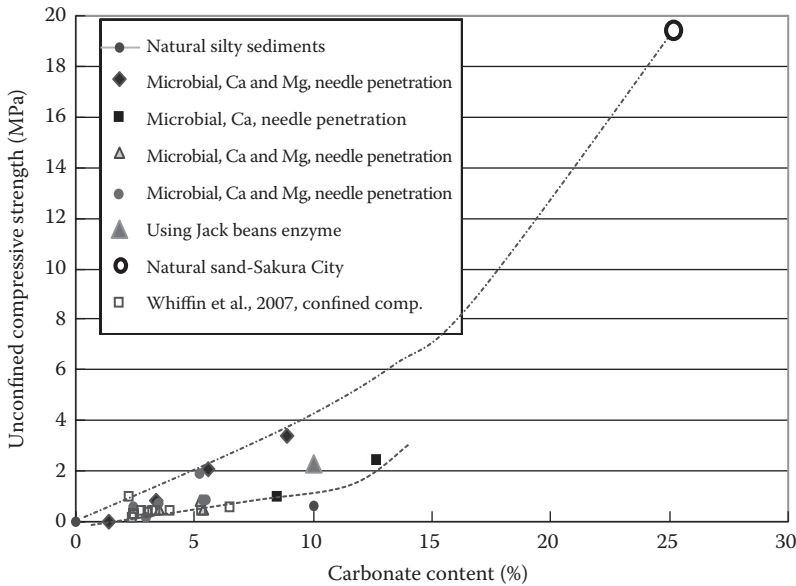


FIGURE 12.11

Correlations between unconfined compressive strength and carbonate content for both the natural and microbially cemented soils.

the material with a brittle behavior—with a failure axial strain of 0.14% and a stiffness, E_{50} of 67 MPa, which is an extremely high value for soils. Figure 12.11 shows the unconfined compressive strength in relation to the carbonate content of the treated soil. The test results reported in Figure 12.11, which include those obtained from other studies (Whiffin et al., 2007; Fukue et al., 2013), indicate that 1% carbonate introduced into ordinary loose sand can increase the unconfined compressive strength of the treated sand.

12.6.2.2 Triaxial Compressive Strength

The shear strength of cohesionless soils (sands) can be expressed by the Mohr-Coulomb failure criterion, as shown in Figure 12.12a, where σ'_1 and σ'_3 are the maximum and minimum principal stresses, respectively, and the shear strength τ_f for sand is

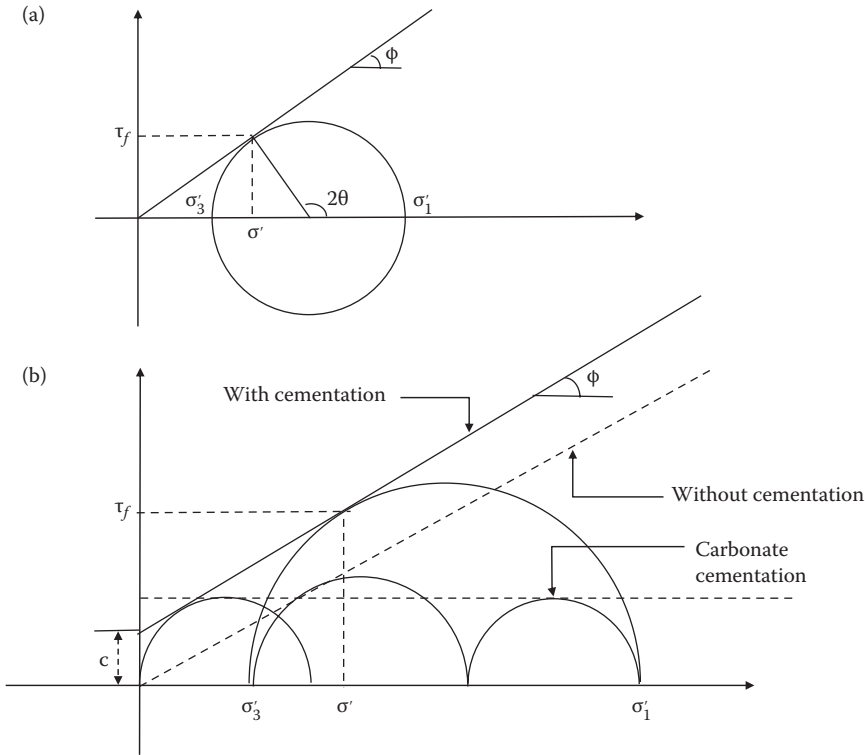
$$\tau_f = \sigma' \tan \phi \quad (12.14)$$

where σ' is the normal effective stress acting on the shear failure plane and ϕ is the angle of internal friction of the sand.

In the Mohr-Coulomb diagram for a sand with carbonate cementation shown Figure 12.12b, the shear strength of the cemented sand is expressed as

$$\tau_f = c + \sigma' \tan \phi \quad (12.15)$$

where c is the cementation strength of the carbonate binder.

**FIGURE 12.12**

(a) Failure criterion for sand without cementation. (b) Mohr's Coulomb failure criterion for cemented sand.

The cementation strength c —i.e., the strength contribution to the frictional strength by the cementation bonds—can be expressed as follows:

$$c = \frac{q_u}{2} \left(\frac{1}{\cos \phi} - \tan \phi \right) \quad (12.16)$$

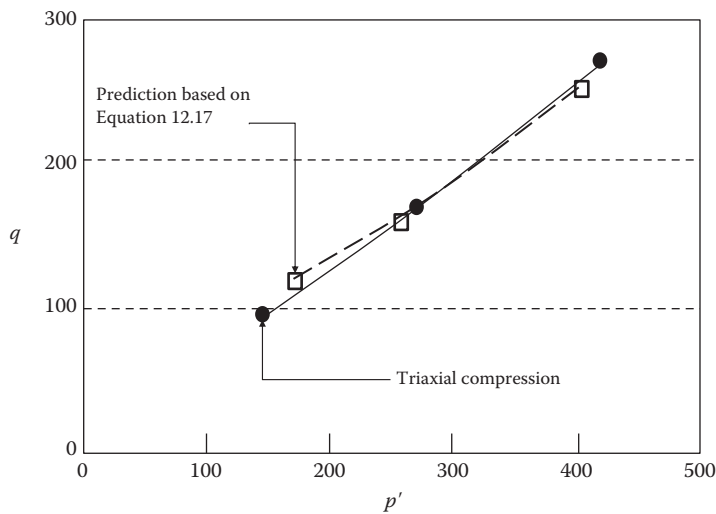
where q_u is the unconfined compressive strength of cemented soil (sand).

Figure 12.13 shows a comparison between the actual triaxial compressive strength and predicted strength in terms of p' and q using Equations 12.17 and 12.18, where p' and q are defined as

$$p' = \frac{\sigma'_v + \sigma'_h + q_u}{2} \quad \text{or} \quad = \frac{\sigma'_1 + \sigma'_3}{2} \quad (12.17)$$

$$q = \frac{\sigma'_v + q_u - \sigma'_h}{2} \quad \text{or} \quad = \frac{\sigma'_1 - \sigma'_3}{2} \quad (12.18)$$

The p' – q relation obtained from the approach shown in Figure 12.12b shows that p' and q agree well with the results obtained from triaxial compression tests, where p' and q are

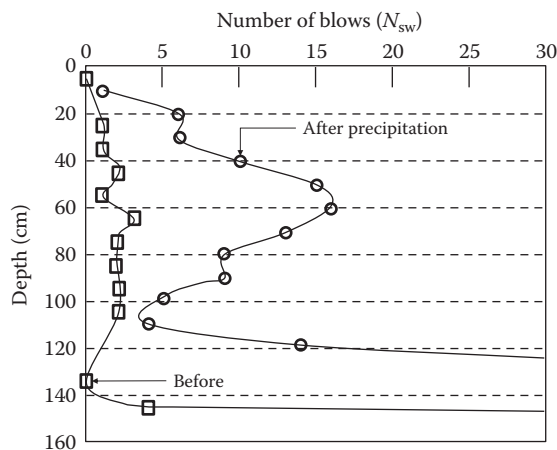
**FIGURE 12.13**

Relationships between p' and q for actual triaxial compression and prediction. Units for both axes are in kPa.

the center and radius of the largest Mohr's circle in Figure 12.12b, respectively. This p' – q relationship is a tool that can be used for design of soil improvement.

12.6.2.3 Cone Penetration Resistance

Figure 12.14 shows the change in cone penetration resistance (N_{sw}) as a result of microbial cementation (carbonate content about 0.5% at a soil depth of 60 cm) of loose medium sand. Figure 12.14 shows that penetration resistance increases because of carbonate cementation—i.e., the number of blows, N_{sw} —increases from approximately 10 to 70 at a soil depth of 60 cm, and as one would expect, the number of resistance blows depends on the carbonate content.

**FIGURE 12.14**

Results of the dynamic cone penetration test for sand with and without microbial cementation.

12.6.3 Concepts in Design

There are at least two approaches that one could take in designing application of artificial diagenesis. One approach, which one would consider as the conventional approach, is to use the desired soil or ground strength as the design target. The other approach seeks to improve the soil without any target strength in mind, i.e., “let us see how much improvement can be obtained from the treatment process.” It stands to reason that with this second approach, there is an implicit requirement that the capability of the improved ground must surpass anticipated design requirements.

12.7 Concluding Remarks

The discussion in this chapter dealt with an innovative concept of soil improvement that utilizes *diagenesis*, which can be defined as the carbonation process for soils. Carbonation is obtained with the hydrolysis of urea from strong ureolytic bacteria. Studies on sandy soils cemented with carbonates induced by microbes have shown significant increases in unconfined compressive strengths attributable to the cementation effect from the presence of carbonate in the soil.

Artificial diagenesis can be promoted by injecting the mixed solution of microbes and reactive agents into fine soils. The gain in strength can be governed by the numbers of injections, and the carbonate content obtained can be predicted from the concentrations of agents and the number of injection times. Success in obtaining diagenesis depends on whether or not the microbes are well distributed into the target zone. A useful technique for application in soft fine-grained soils is to install sand piles (sand columns) into the soft fine-grained soils, which can then be injected with the B–R solution (Figure 12.15) to allow for infiltration of the B–R solution from the sand piles into the pore spaces of the fine-grained soils.

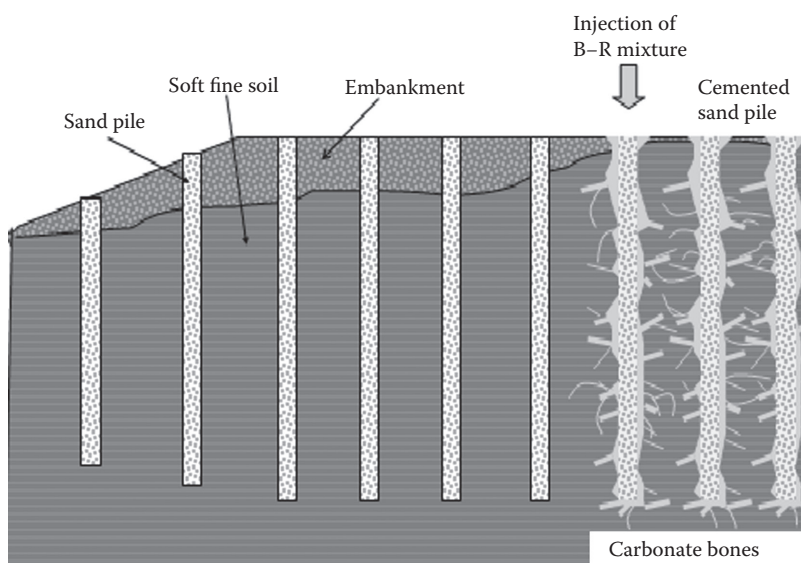


FIGURE 12.15

Application of artificial diagenesis into soft fine soil using sand piles.

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13

Sustainable Geoenvironmental Engineering Practice

13.1 Introduction

13.1.1 Undeniable Facts

The fact that humans require the various elements of a built environment for survival means that harvesting and exploitation of the natural resources and capital items of the geoenvironment are needed to support their needs. What is needed, in the face of this reality, is the implementation of

- Development and construction techniques, protocols, and activities in a built environment that accord with the objectives of protecting and maintaining optimal site functionality
- Harvesting, exploitation, and development techniques, procedures, plans, etc., that minimize adverse impacts on the geoenvironment
- Geoenvironmental engineering management practices that protect the geoenvironment from deleterious and adverse stressor impacts generated from sources associated with the efforts in support of the needs of humans, i.e., *sustainable geoenvironmental engineering practice*

In the face of the demands to support the needs of the human population, there are some undeniable facts and concerns that need to be confronted. These include

- Continued extraction of nonrenewable natural resources such as metal and mineral resources together with fossil fuels will not only result in their depletion, but will ultimately lead to their exhaustion
- Continued exploitation of renewable natural resources at a pace that does not permit them to fully replenish or regenerate themselves will also ultimately lead to their exhaustion
- Industrial activities such as farming, manufacturing, production, power generation, etc. In combination with activities in support of services' operations (government, civic, military, educational and medical institutions, etc.) and general human population activities, generate a variety of demands and stressors on the geoenvironment
- Continued human habitat construction and requirements for improvements and expansion of the built environment result in natural habitat encroachment and destruction

All the actions and activities associated with the preceding items and events serve as sources for mechanical, thermal, hydraulic, chemical, and biological stressors. The various stressors generated from all the aforementioned activities on the geoenvironment have been the subject of discussion in the preceding chapters of this book. Geoenvironmental engineering practice in support of all these activities and especially in respect to the management of stressor impacts on the geoenvironment needs to be applied in the context of protection of habitat and quality and health of the geoenvironment and its natural resources.

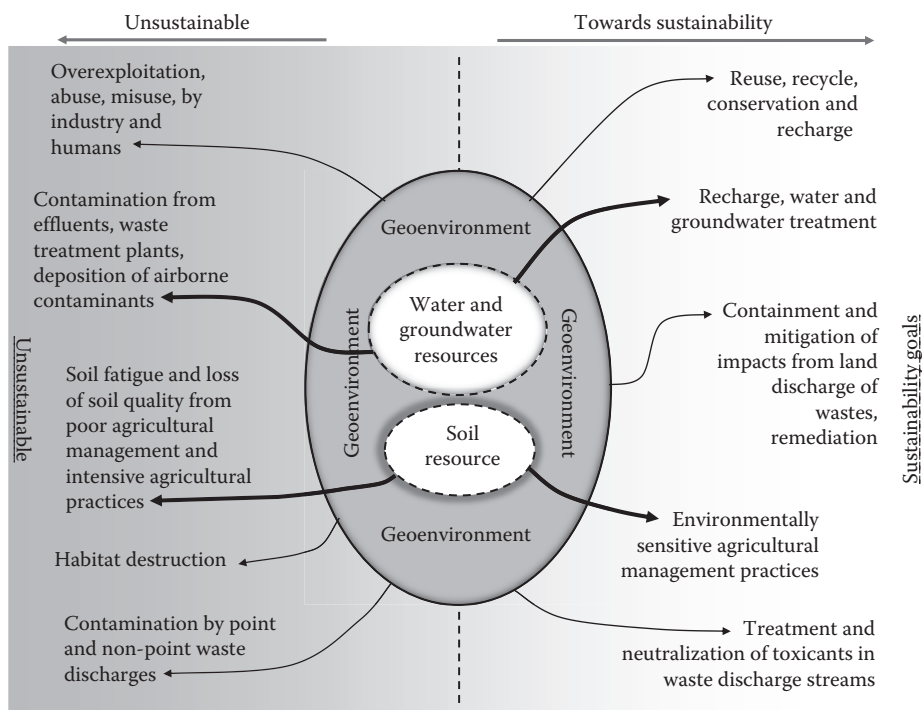
13.1.2 Geotechnical to Geoenvironmental Engineering Practice

Geotechnical engineering practice has historically addressed geoenvironmental mechanical and hydraulic stressor impacts through such actions as stabilization of slopes and embankments, control and/or elimination of piping of dams, building of flood prevention levees, slope erosion control measures, diversionary ditches and canals, soft soil stabilization in aid of constructed facilities, etc. Thermal stressor impact problems, especially in the permafrost regions of the world, were addressed by constructing habitable structures on stilts so as to allow the natural ground surface to maintain its previous ground cover and also allow for maintenance of natural ambient surface temperatures. These were measures to protect the permafrost—as were the use of thermopiles in the construction of the Alyeska (Trans-Alaska) pipeline in the mid-1970s. It is interesting to note that even at that time, geoenvironmental concerns were considered and considerable effort was made toward habitat protection including such factors as allowance for caribou crossings and protection of native fauna.

Chemical stressors and their impacts in and on the geoenvironment are more recent concerns, highlighted because of the greater awareness of the many health hazards posed by landfills, discharge of toxic or contaminated liquid waste streams, illegal dumping of noxious materials, etc. Protection of human health and other biotic receptors in the face of the impacts from chemical stressors required knowledge of the many different processes and interactions between the chemical contaminants and soils and their transport and fate in the affected soils. Geotechnical engineering perforce is now geoenvironmental engineering by virtue of the kinds of problems and challenges posed by present human activities. Protection of the soil and water resources of the geoenvironment as vital parts of the geoenvironment together with protection of the other natural resources of the geoenvironment are paramount requirements if survival of the human species is to be assured. This is the charge of *Sustainable Practices in Geoenvironmental Engineering*.

13.2 Unsustainable Actions and Events

Figure 13.1 illustrates some of the major issues involved in both unsustainable and sustainable activities that affect the geoenvironment and, in particular, the soil and water resources. Unsustainable actions refer to those actions and circumstances that generate adverse impacts to, or in, or on the geoenvironment. Discussions on many of these impacts or activities and events contributing to such impacts have been given in the previous chapters. The following brief discussion in this section provides a set of examples that demonstrate the problem at hand and also why the quality and health of the land and water resources are central issues.

**FIGURE 13.1**

The beetle diagram shows, on the left-hand side, some of the major stressor impacts in and on the geoenvironment, groundwater, water, and soil resources. An idea of what might be done to seek sustainability of the resources is shown on the right-hand side of the beetle.

13.2.1 Accidents and Unplanned Events

Accidents and unplanned events are at the root of many of the unsustainable actions shown in the left-hand side of the beetle diagram (Figure 13.1). Leaving aside the unplanned events and accidents in foundation and geotechnical engineering experiences, and focusing on geoenvironmental events, the 1966 major colliery spoil tip failure (slippage) at Aberfan that was responsible for the deaths of over a hundred individuals is an example of an unplanned geoenvironmental event (McLean and Johnes, 2000), not because of the failure of the slip itself, but also because of the leachates generated from such spoil tips. The height of the tips together with the slope of the tips and the weather conditions contributed to the disastrous slippage problems. These tips, heaps, and piles provided the source for leachates that threaten the groundwater and water resources. If and when the leachates reach these resources, without adequate protection of these resources from the chemical stressors, they will be impaired.

Exploration, drilling, extraction, and production of petroleum can impact the environment at numerous points. Contamination of shores after oil spills can lead to oil that can remain for decades at beaches or marshes. Pressurized hoses with cold or hot water used for cleanup of spills on beaches, etc., may create more problems, for example, in the case of the *Exxon Valdez* spill where the more than 200,000 tonnes of disposable diapers, pads, clothing, and other waste materials used in washing individual stones on the cobble beaches required landfilling or burning (Graham, 1989). In addition, the hot spray used in the cleaning activities is reported to have caused damage to the benthic fauna.

Oil spills and pipeline leaks may also contaminate the soil and groundwater. Drilling mud stored in improperly lined pits may also leak into the soil. Well blowouts from overpressurized zones can lead to spreading of the petroleum on the surface of the land or water if at sea. On March 29, 1980, 468,000 tonnes of crude oil (the largest one in history) rushed into the Gulf of Mexico after a blowout, thereby affecting Mexican and Texas beaches. Approximately 0.8% of the oil reached the Texas shoreline, with about 5% of the original amount remaining after one year (Payne and Phillips, 1985).

Another more significant event in 2010, one the largest oil spills, known as the *Deepwater Horizon* oil spill, occurred in the Gulf of Mexico when 780,000 m³ of oil were released from an oil well blowout and explosion until the oil rig was capped after over 87 days. Despite the beach and wetland protection via floating booms, skimmer ships, controlled burners, and a dispersant addition, which has been anecdotally reported as seeming to increase oil toxicity substantially, marine wildlife, fishing, tourism, the economy, and human health were adversely affected.

At Lac Megantic in the Province of Quebec in Canada on July 6, 2013, a runaway freight train loaded with crude oil derailed and exploded, killing 47 people and destroying half of the downtown region. More than 30 buildings were destroyed from the fire including many irreplaceable historic buildings. Oil contamination of the land affected more than 31 ha (Beaudin, 2013). It has been estimated that more than 558,000 tonnes of soil will need to be decontaminated. More than 100,000 L of oil reached the Chaudiere River and traveled more than 80 km. The total cost is estimated at \$190 million for the remediation of water and soil in the area.

Tanacredi (1999) reports that as a result of human development, 115,000 ha of wetlands are removed each year, in the United States. Less than 40% of the area remains compared with preindustrial times. Depletion of peatlands alone causes emissions of up to 0.8 billion tonnes of carbon a year, much of which could be avoided through restoration (Environment Directorate-General and the Joint Research Centre [JRC] of the European Commission, 2010). A striking example of an unplanned event that occurred in Europe is the construction of a dam for energy purposes in Slovakia that caused the Szigetkoz marsh (500 m²) in Hungary to dry up, depriving 5000 species of flora and fauna of a habitat.

Another impact from human activity includes soil sealing, which is the covering of soil with an impermeable material. This leads to the loss of soil functions such as water filtration and storage, and food production. Over the 1990s, in the EU more than 1000 km² of soil were lost per year. From 2000 to 2006, the EU average loss increased by 3%, but in some countries the rate was higher such as in Ireland and Cyprus (14%), and in Spain (15%) (European Commission, 2014a). Nineteen EU member states lost a potential agricultural production capability equivalent to a total of 6.1 million tonnes of wheat (1990–2006) (Gardi et al., 2011). Soil biodiversity is another aspect that must be protected as it provides a release of nutrients for use by plants and other organisms, assists in the removal of contaminants and pathogens, and participates in the carbon cycle, and is a source of genetic and chemical resources (European Commission Joint Research Centre, 2013). Soil biodiversity is highly threatened in areas of high population density and/or areas of intense agricultural activity.

13.2.2 Wastes and Discharges

In the United States, medical wastes make up approximately 0.3% to 2% of the MSW stream (USEPA, 1990). The infectious waste is estimated by the EPA at 2 to 3 million tonnes/year (GGHC, 2008). High-income countries generate up to 0.5 kg of hazardous waste per person

per day compared with low-income countries, which produce an average of 0.2 kg of hazardous waste per person per day. In high income countries another 2 kg of waste is generated that is comparable to domestic waste. In low income countries hazardous and nonhazardous wastes are not usually separated (WHO, 2011).

Pathogen transport and survival is possible if these types of wastes are disposed as MSW. However, there is little experimental data available for the determination of pathogens in leachates or in runoff from a landfill. Approximately 15% of hospital waste is infectious. Medical waste incinerators are used by 70% of U.S. hospitals. There is little regulation of these incinerators due to their small size. As a result in some states, between 48% and 87% of the incinerators have no emission control equipment (Washington State Department of Ecology, 1989). Low level radioactive waste is generated through various medical procedures involving radiopharmaceuticals, radiology, and nuclear medicines. However, this type of waste from hospitals is less than 5% of the total waste in the United States (U.S. Congress OTA, 1989). Most of these wastes have a very short half-life and can be stored on site.

Between 220 and 380 m³ of water are required per tonne of paper produced (Badar and Farooqi, 2012). Effluent solids, biological oxygen demand, color, and toxicity are present in the wastewater. Approximately 30% to 70% of the contaminants are removed during treatment. The pulping and bleaching stages are the major sources of contaminants. Sludge generation is in the range of 14 to 140 kg/tonne of pulp. The generation of dry sludge is approximately 4.3% of the final paper product and in the case of recycled paper mills, increases to 20%–40% (World Bank, 2007).

In the United States, total sludge generation is about 2.5 million tonnes/year. Chlorinated organic compounds can be released from the sludge. Chlorine and compounds of chlorine are used in the bleaching of wood pulp particularly by the kraft or sulfite processes. Processes using elemental chlorine produce significant quantities of dioxins. However, by replacing elemental chlorine with chlorinedioxide, this procedure has reduced dioxin production substantially, and since 1990 elemental chlorine free (ECF) and totally chlorine free (TCF) processes have replaced element chlorine bleaching. Although these levels have been reduced, the pH of the sludge is typically still higher than 12.5.

Energy consumption trends have shifted in recent years. From 1972 to 1999, wood wastes, spent liquor solids and other internal sources of energy have increased from 41% of the energy used to 58%, thus relying less on fossil fuels. The U.S. Environmental Protection Agency has found that paper recycling instead of production of virgin paper has reduced water contamination by 35% and air contamination by 74% (USEPA, 2007).

In 1991, according to the U.S. Bureau of Mines, more than 1.15 billion tonnes of concrete were produced worldwide. According to the Strategic Development Council (2002), this amount has increased to more than 6 billion tonnes. Cement is the main ingredient of concrete. A typical mix is 12% Portland cement, 34% sand, 48% crushed stone and 6% water, all of which are abundant. However, transportation can be a main issue, and water requirements for washing and reduction of the impact of dust. Fly ash, a waste from coal-fired power plants, is now present at a proportion of about 9% in cement. Energy consumption is considerable in cement production. Addition of fly ash with concrete can make the process more energy efficient. Since coal is often used for energy emissions of carbon dioxide, sulfur, and nitrous oxide are high, carbon dioxide emissions are estimated at 1200 kg CO₂/tonne of cement, 60% from energy use and the other 40% from calcining. Dust emissions are also significant (180 kg/tonne of cement produced) but should be controlled as much as possible by water sprays, hoods, etc. Other contaminants include sulfur dioxide and nitrous oxide from both fuels and raw materials. Water contamination from washwater of

high pH is generated. Settling ponds are used to remove the solids. Reduction of the pH below 12 renders the wastewater not hazardous. Water usage has been reduced through recycling in the plant in a closed loop. Concrete has accounted for up to 40%–50% by weight of construction and demolition (C&D) waste (Sandler, 2003). More and more of this waste will be used in road aggregate. Precasting concrete at a central facility can reduce materials used and wastewater generated.

In the stone, and concrete products industries, more than 530 million tonnes of wastes were generated in 1993 (USEPA, 1995b). Approximately 96% was recycled, treated, or recovered for energy, whereas 2.3% was transferred off-site or released to the environment. Off-site disposal, underground injection, air, land, or water discharge accounted for 2.2% of the waste. The SDC (2002) indicates that the concrete industry wishes to continue to increase its use of recycled waste and by-product materials involved in concrete manufacturing, and thus, by 2030, zero net waste is the objective.

Waste generation and disposal demonstrate the problems of stressors and impacts. For example, waste production by industry and commerce in England for 1998 to 1999 (DEFRA, 2010) was estimated at 78 million tonnes. This does not include the 294 million tonnes produced by demolition, mining, quarrying, agricultural wastes, construction wastes and sewage sludge. In the Netherlands, 35 million tonnes more manure is produced than can be utilized by arable farming (Tirion, 1999).

More than 360,000 tonnes of waste were generated in 1993 by the fabricated metals industry (USEPA, 1995a). According to the Toxic Release Inventory (TRI), approximately 62% of the waste was either recycled or treated, or the energy was recovered on-site. Another 34% of the waste was either released to the environment or transferred off-site. Direct releases by air, water, land or underground injection or disposal accounted for 13.2% of the waste.

13.3 Renewable Geoenvironment Natural Resources

There are two specific classes of renewable geoenvironment natural resources, namely living and nonliving. Living renewable natural resources include land and aquatic animals, forests, native plants, etc., whereas nonliving renewable natural resources include water and soil. By definition, renewable natural resources refer to those resources that have the capability to regenerate, replenish, and renew themselves, either naturally or with human intervention within a reasonable time period. Sustainability as an objective requires that full regeneration–replenishment of renewable resources must be obtained. It is recognized that when consumption (use, exploitation, etc.) exceeds regeneration–replenishment rate, sustainability of the renewable resource is not obtained. This does not mean that the renewable resource will not or cannot renew itself. It simply means that the amount or rate of the resource that is renewed is insufficient to meet the demands placed on it. In recognition of this, we need to distinguish between (a) unsustainable renewable natural resources, i.e., renewable resources that by virtue of circumstances cannot be fully renewed or replenished, and (b) sustainable renewable natural resources, i.e., renewable resources that can be totally regenerated and replenished. When consumption rate is greater than the rate of regeneration and/or replenishment, etc., the amount or nature of the particular renewable natural resource will be depleted and may eventually become extinct. Striking examples of this are overfishing and overharvesting of groundwater and deep-seated aquifers.

Land and water resources are the principal physical capital items that constitute the geoenvironment. Their quality and health are vital issues because they provide the habitat and also the basis for life-support systems for plants, animals, and humans. These renewable resources have the capacity to maintain their natural quality through natural processes and/or through renewal and replenishment. A significant part of a sustainable geoenvironment is its land and water resources and sustainability is obtained when all the resource elements of the various land and water ecosystems are renewed, replenished, recharged, and restocked—to a level that will continue to meet the needs of those that depend on these resources. This will only occur when the health and quality of the land and water resources are protected, maintained, and allowed to flourish. Failure to do so will lead to a degradation of the quality of these two major capital resources and in turn will imperil and diminish the capability of these resources to allow the elements and inhabitants of the land and water ecosystems to renew and replenish themselves.

The primary sustainability concerns relating to industry and urban interactions with the land environment and its receiving waters are stressor impacts from

- Exploitation and extraction of renewable and nonrenewable resources. Acceptance of the need for these resources must be accompanied by responsible management of the many stressor sources associated with the activities of exploitation–extraction in a manner that minimizes the severity of their impacts on the geoenvironment.
- Destructive actions and noxious discharges from industrial operations and urban activities.

The severity of the impacts on the geoenvironment from stressors generated by these activities can be mitigated with proper and smart geoenvironmental engineering management, e.g., through engineering schemes and constructed facilities and through protective and treatment measures. For both sets of engineering disciplines, the primary responsibility is the protection of the geoenvironment and its natural capital through measures designed to obviate where possible, and/or minimize, relieve, ameliorate, and mitigate stressor impacts, and to provide and implement remediation technology for impacted sites and regions.

13.3.1 Sustainability of Renewable Nonliving Natural Resources

There is a further distinction or differentiation needed in discussing renewable natural resources. One needs to distinguish between *natural* and *developed* resources. Differentiation between renewable *natural* resources and renewable *developed* resources is necessary to distinguish between the renewable natural capital items (water, soil, land, and aquatic animals, native plants) and restocking and regeneration of man-made capital such as fish farms and agricultural output from farming. As has been noted previously, just because a resource is renewable does not make it sustainable. Two necessary, but not sufficient, conditions for sustainability of renewable natural resources are (1) replenishment and regeneration of the natural capital items in a reasonable time frame either through natural processes or through sound management practice, and (2) renewed natural resources are sufficient and will continue to be sufficient to meet the demands placed on these resources. Impediments to sustainability are due to (1) rate of recharge or regeneration or replenishment being outpaced by overexploitation of the natural resource and (2) corruption, degradation and/or contamination of the natural resource.

The renewable nonliving natural resources of prime importance are water and soil. They are in essence renewable dynamic resources—characterized by recharge and replenishment of these resources. However, when recharge and replenishment cannot overcome the deficits in the nonliving renewable resources, these resources are no longer sustainable. A good example of the preceding is the excessive use, overexploitation, and contamination of water resources. A full treatment of these and other issues relating to sustainable water use will be found in the textbooks dealing with this particular problem. The geoenvironmental concerns for water and soil are in respect to degradation in water and soil quality due to their misuse and also due to contamination of these capital items. Discussions in the previous chapters have shown that water and groundwater contamination, together with soil contamination and loss of soil quality are the major downfall of sustainability of water and soil resources—other than overuse, abuse, and misuse of these nonliving renewable resources by humans.

The beetle diagram in Figure 13.1 provides a very simple illustration of some of the major stressors on water, groundwater, and soil resources responsible for the unsustainable outcome of the nonliving renewable natural resources. Other than the use, misuse, abuse, etc., by industry and humans shown in the top left-hand side of the illustration, most of the stressors and their impacts have been identified and discussed in the previous chapters. Some of the key actions needed to drive the renewable natural resources of water, groundwater, and soil toward sustainability goals and objectives are shown on the right-hand side of the illustration. The major impact of contaminants on both water and soil resources is degradation of the quality of these resources. In the case of soils, for example, degradation of soil quality will lead directly to loss of productivity and lower agricultural yields. For water, degradation of water quality leads directly to loss of drinking water status at the upper end of water usage, to relegation for agricultural and industrial use, and finally to nonusable.

Contaminants are chemical stressors that can severely affect water, groundwater, and soil quality. These include land-based non point source contaminants such as herbicides, pesticides, fungicides, etc., and point source contaminants from effluents, waste treatment plants, and liquid discharges as wastes and spills from industrial plants (e.g., heavy metals, organic chemicals). Some of the methods and procedures for mitigating of the major impacts from contaminant stressors, together with treatment and remediation options have been discussed in the previous chapter. Undoubtedly, there will be more advanced and sophisticated methods developed in the very near future to meet the challenges posed by these stressors. Unsustainable renewable natural resources become nonrenewable, renewable natural resources, a condition that should not be allowed to happen.

13.3.2 Geoenvironmental Management of Soil and Water Resources

From a geoenvironmental perspective, the actions shown on both sides of Figure 13.1 are some of the more significant actions that detract from, or lead to conservation and recovery of nonliving renewable resources. The arrows that emanate from the total elliptical shell indicate actions affecting the total land environment, i.e., both soil and water-groundwater resources. Those arrows emanating specifically from the top or bottom resources (water-groundwater resources and soil resources) indicate actions affecting those specific resources. Not all the pertinent or necessary actions for all of these are shown. Only the more significant ones are depicted in the diagram.

13.3.2.1 Adverse Stressor Impacts

Many of the adverse stressor impacts arise from the unsustainable actions shown on the left-hand side of Figure 13.2. The points of note include (a) overexploitation, abuse, and misuse of water and soil resources by humans are actions requiring corrective measures that extend beyond the geoenvironmental sphere, and (b) contamination from effluents, waste treatment plants, deposition of airborne contaminants are both point and non-point sources of contaminants that degrade water quality and create contaminated ground. The extent and seriousness of health threats from the contaminants and the degree of degradation of both water and land resources are functions of both the quantity/concentration and toxicity of the discharges and atmospheric depositions on land. Runoffs over land surface and industrial chemical spills can severely pollute receiving waters and groundwaters. The Love Canal problem that surfaced in the 1970s is probably the first well-publicized hazardous waste dumping site in North America (Beck, 1979). Prior to this period, awareness of the problems and seriousness of indiscriminate dumping of toxic materials were not appreciated by the general public, and it was claimed that the Love Canal site was the recipient of such hazardous materials for a period of at least 20 years. Tests conducted by the New York Department of Environmental Concern showed severe contamination of ground and waters in the area, resulting in the declaration of a state of emergency by the governor of the State of New York, and the closing of schools and relocation of several

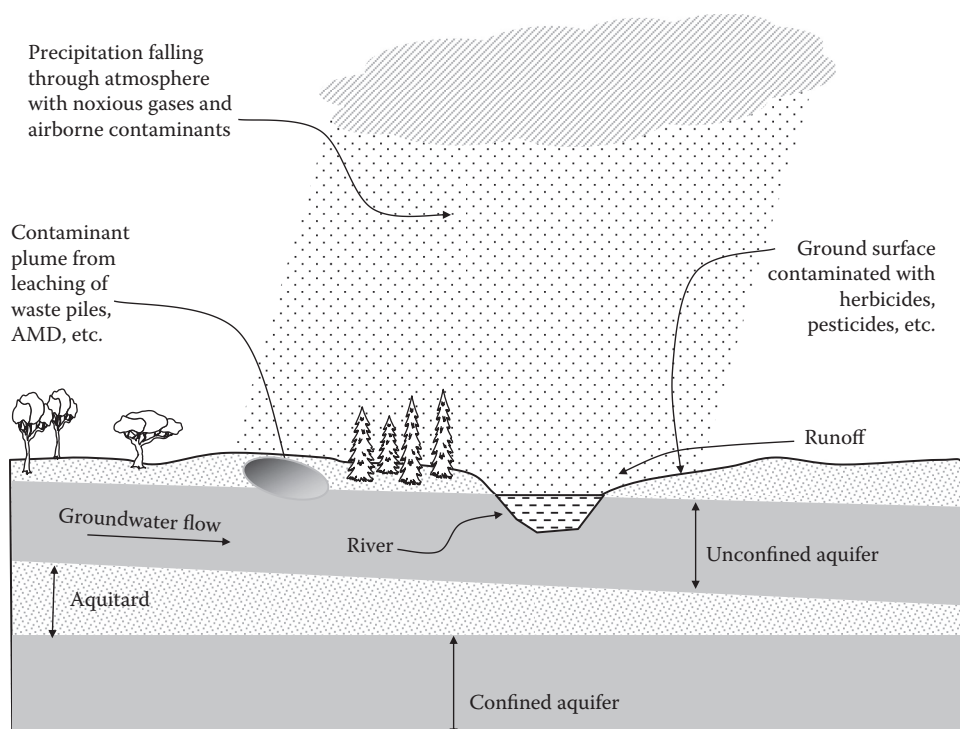


FIGURE 13.2

Some of the more prominent causes of contamination of recharge water for rivers, other receiving waters, and groundwater (aquifers). Contamination of the confined aquifer depends on whether communication is established with the unconfined aquifer.

families. There are other cases of contamination, however, that are indirectly caused by man-made activities. A good example of this is leaching of exposed sulfide ores and rocks (Chapter 5) and waste piles in landfills will also produce polluted recharge water. Other causes of contamination of water resources have been discussed in Chapter 3.

Soil fatigue and loss of soil quality can occur from natural causes such as those leading to aridification and desertification. Long periods of rainfall deprivation leading to aridification and finally desertification are conditions of nature. Desertification can also result from a prolonged process of degradation of a once-productive soil. The root causes for desertification are deemed to be a complex mix of various degradative actions. The present concern is soil fatigue and loss of soil quality from human activities leading to poor forest and agricultural management and intensive forestry and agricultural practice are conditions that will eventually render the soil useless for production of plants and crops. In respect to agriculture, as we have noted in Chapter 2, *soil quality* is a determinant of the capability of a soil to sustain plant and animal life and their productivity, and any diminution of soil quality will impact on its capability to provide the various functions such as plant and animal life support, forestry and woodland productivity, and will undoubtedly result in the loss of biological activity and biodiversity, and depletion of nutrients in the soil.

We should note that soil quality as a measure of the functionality or capability of a soil is not confined exclusively to the agricultural usage. Soil can also serve other kinds of functions. These include (a) containment and management of wastes and waste streams, (b) resource material for production of building blocks, and (c) sub-base support for structures and facilities. The determinants for soil quality for these types of functions will differ from the classic definition, which was developed for agricultural use. This is discussed further in Section 13.3.

13.3.2.2 Management for Sustainability Goals

For sustainability management of the land environment and particularly of the water and soil resources, a necessary requirement is for recharge materials and processes to be devoid of contaminants and other detrimental and degrading agents. This is particularly acute for reuse and recycle of process water. At all times, the quality of water and soil need to be maintained and even improved. For this to occur, we need to establish water and soil quality indices and to further establish baseline values for these indices. These indices will require analyses involving indicators—both status and material indicators—as will be discussed in more detail later in this chapter.

- *Recharge of Water Resources:* The sources of natural recharge of receiving waters and groundwater are direct precipitation (rain, snow, hail, and sleet) and snow-melt delivered as percolation and infiltration. The chemistry of precipitation that defines the quality of the precipitation is a function of the nature, chemistry, and concentration of airborne particulates through which precipitation occurs. As noted in Chapter 10, the noxious substances in the atmosphere derived from man-made activities include NO_x (nitrogen oxides), SO₂ (sulfur dioxide), CO (carbon monoxide), Pb and other metals such as Al, As, Cu, Fe, La, Mg, Mn, Na, Sb, V, and Zn, as airborne particulates, VOCs (volatile organic compounds), aromatic hydrocarbons such as benzene, toluene, and xylene and PAHs such as anthracene and naphthalene. The same holds true for the chemistry of the snowpack that serves as the storage for recharge as snowmelt. Thus, for example, Nanus et al. (2003) reports that high-elevation areas in the Rocky Mountains annually receive

large amounts of precipitation, most of which accumulates in a seasonal snow-pack. They maintain that all the accumulated atmospheric deposition is delivered in a very short period to the ground and receiving waters during spring snow-melt. The presence of the noxious gases together with other airborne particulates, ensures that the pH of rainfall onto the ground surface will be acidic. Spatial variations in atmospheric deposition of acid solutes are the result of precipitation amount in combination with concentration, and that deposition does not necessarily reflect variations in concentration alone (Nanus et al., 2003). Deposition of airborne particulates with rainfall will also ensure that these will be carried with the surface runoff and also with infiltrating water. The other causes of contamination of precipitation recharge water include (a) runoffs and from polluted land surfaces, as might be found on agricultural lands, and (b) infiltration into subsurface through land surface polluted with pesticides, fungicides, other surface wastes, organic debris, heaps, leach piles, sulfide rock piles, etc. The evidence shows that in regions where urbanization, industrialization, and exploitation are present, it is difficult to find precipitation recharge devoid of contaminants and airborne contaminants. Furthermore, in these regions, it is also difficult to rule out contamination of the receiving waters and groundwaters from contaminated runoffs and infiltration. For regions remote from the effects of industrialization and urbanization and also far remote from airborne contaminants, one would have better chances of finding uncontaminated recharge precipitation. Treatment of polluted or contaminated recharge precipitation is not generally practical since it is more than likely that contamination already exists in the water and land receptors in urbanized and industrialized regions. Instead, passive treatment using natural processes together with aggressive treatment of extracted water are used to provide safe drinking water (see Chapter 3).

- *Improvement of Soil Quality for a Sustainable Soil Resource:* Soil is an important resource material. It contains most of the nutrients required for plant growth and is rich with microorganisms. Besides being the most critical medium for agricultural food production and also production of other kinds of crops and trees such as cotton and palm trees, it is also a very important tool for management of wastes and waste discharges in the ground—as seen in the previous chapter. It serves as a dynamic resource not only for production of food and raw materials, but also for the soil microorganisms contained in the soil. These microorganisms not only play an important role in the natural bioremediation of harmful organic chemicals in the ground, they participate intimately in the recycling of carbon, nitrogen, phosphorus, and other elements in the soil. In essence, they are significant contributors to the control or management of greenhouse gases, water flow in soils, soil quality, and through all of these the life-support systems for humankind.

It is recognized that loss of nutrients, loss of biodiversity, loss of soil organics, salinization, acidification, and degradation of physical, chemical, and biological properties of soil occur with time—through leaching processes, intensive agricultural practice, erosion, and through overuse and poor land management. Natural and/or man-assisted recharge of soil as a resource material—i.e., recharge of soil quality—is required if sustainability of soil quality is to be achieved. We consider *recharge of soil quality* to consist of any or all of the types of physical, chemical, and biological amendments, methods, and processes that serve to increase soil quality. Figure 13.2 shows a schematic description of soil quality changes with time.

The ordinate shown in the diagram represents soil quality index (SQI). The SQI is a composite index that incorporates analyses that include consideration of the physical, chemical, and biological indicators relating to the soil resource application under review. Thus, for example, the specific component indicators for the physical, chemical, and biological indicators leading to calculations of the SQI for waste management would differ from those obtained for agricultural production, or for forestry. A more detailed discussion of the SQI and the various indicators will be found later in this chapter.

Artificial recharge—i.e., recharge through human intervention—involves the use of soil conditions, fertilizers, added nutrients, biological agents, and good agricultural land management practice. The term *soil amendments* is used as a general catch-all term to include all the preceding items and processes. These soil amendments, when introduced into a tired soil, are designed to improve the soil qualities through improvement of the physical, chemical, and biological properties of the soil—to allow for better use of the soil as a resource material. Improvements in soil permeability, infiltration, water retention, nutrient-holding capacity, and soil structure—on top of the addition of nutrients and fertilizers—constitute the artificial soil recharge process.

13.3.2.3 Protection of Soil and Water Resources

The impacts of significant consequence on the soil and water resources in the geoenvironment are due to physical disturbances of the land environment and direct and/or contamination of the soil and water resources, as shown in Figure 13.1. The various factors, conditions, and circumstances wherein impacts are generated have been discussed in the previous chapters. The three different categories for protection of the soil and water resources in the land environment are

1. Direct and specific protective measures to ensure no degradation of soil and water qualities. This category of actions and measures assumes that the soil and water qualities are at acceptable levels, and that with proper management, they will be sustainable.
2. Measures and actions to mitigate and minimize detrimental impact to both soil and water qualities. We assume that the impacts are managed to the extent that their effects do not degrade both soil and water qualities and also do not pose health threats to humans and other biotic receptors.
3. Application of treatment and remediation technologies to return soil and water qualities to levels acceptable for use. This category applies to situations where soil quality and/or water quality have degraded to the state that treatment and remediation are required to return them to the levels of quality required for use.

The actions included in the various measures undertaken for the three categories of protection and management of soil and water resources range from passive to aggressive. The physical and chemical buffering properties of the soil are central to the effectiveness of the passive protection technique. At the other end of the scale are physical protection barriers such as liner-barrier systems that prevent the migration of leachates and contaminants and treatment, and remediation techniques that require aggressive physical, chemical, and

even biotechnological intervention. Application of any of these techniques depends on (a) the nature and scope of the perceived threat, (b) the resource being threatened and its functions or use, (c) the predicted intensity and type of damage done to the resource by the impact, (d) the extent of resource protection needed, and (e) the economic impact. In Figure 13.2 for example, assuming the absence of noxious gases and airborne particles, the perceived source of threat is represented by the pesticides, insecticides, and other surface contaminants that will move toward the river and also infiltrate into the ground during periods of precipitation. The resources being threatened are the river, surface layer soil, and the unconfined aquifer. Assuming that the river and the unconfined aquifer serve as a drinking water sources, and further assuming that the soil is an agricultural soil resource, the need and extent of protection required for these resources will be evident.

13.4 Water and Soil Quality Indicators

The discussion in this section extends the discussion on indicators in Section 9.2 of Chapter 9. Figure 9.1 in Chapter 9 depicts the role of indicators in the situation created by precipitation falling through airborne noxious gases and particulates. The water and soil quality indicators identified as monitoring targets include both system status and material performance—or material property–status types. Water quality indicators and soil quality indicators are essentially material property–status indicators. They are meant to indicate the quality of the material (water or soil). The quality of the material under consideration or analysis is established with specific reference to its intended function. In regard to soil quality, for example, we have seen from the previous section that the classic definition developed for agricultural use needs to be broadened to encompass the use of soils for various other purposes—from waste management to building supplies and construction. This is also true for water quality indicators. The range of usage starts from the top with drinking water standards setting the height of the water quality bar. At the low end of water usage would be water for agricultural purposes and other similar functions. Indicators for all the various functions of both water and soil would vary both in form (type) and detail.

There are several levels of specificity (i.e., levels of detail) in prescription of water quality and soil quality indicators. These depend on (a) the intended function and management goals, for example, drinking water usage or irrigation purposes, (b) ability to obtain all the necessary data sets, (c) available and applicable remedial and/or corrective technological capabilities, (d) scale and risk tolerance, and (e) economic factors. Perhaps the overriding factors in all of these are *management goals* and *risk tolerance*.

13.4.1 Quality and Index

In Figure 13.3 and in the previous section, we talked about soil quality index (SQI) as a measure of soil quality. Similar to the different intended functions for water and soil, determination of soil quality index (SQI) and water quality index (WQI) will also depend on many of the same factors described in the preceding paragraphs. Development of indices requires full consideration of the many different properties and influences that ultimately combine to produce the material status. Since this is a dynamic process dependent on applications or processes being applied to the soil, internal soil reaction rates and elapsed time, the indices will also vary in accord with circumstances and time. Quantification of

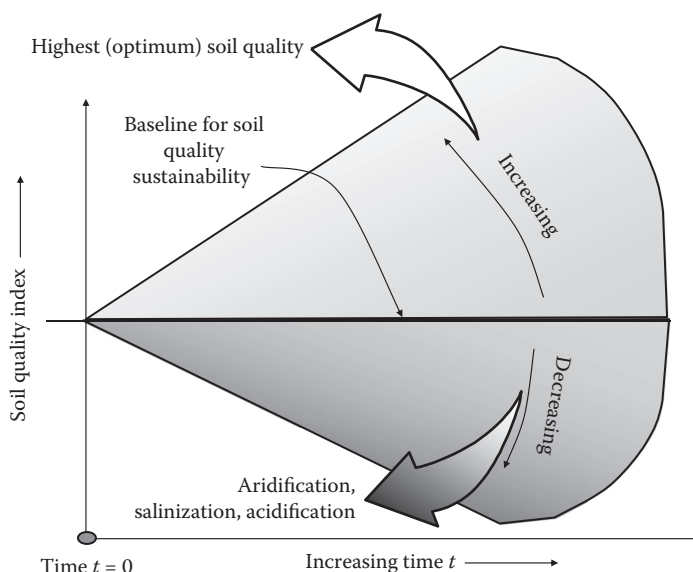
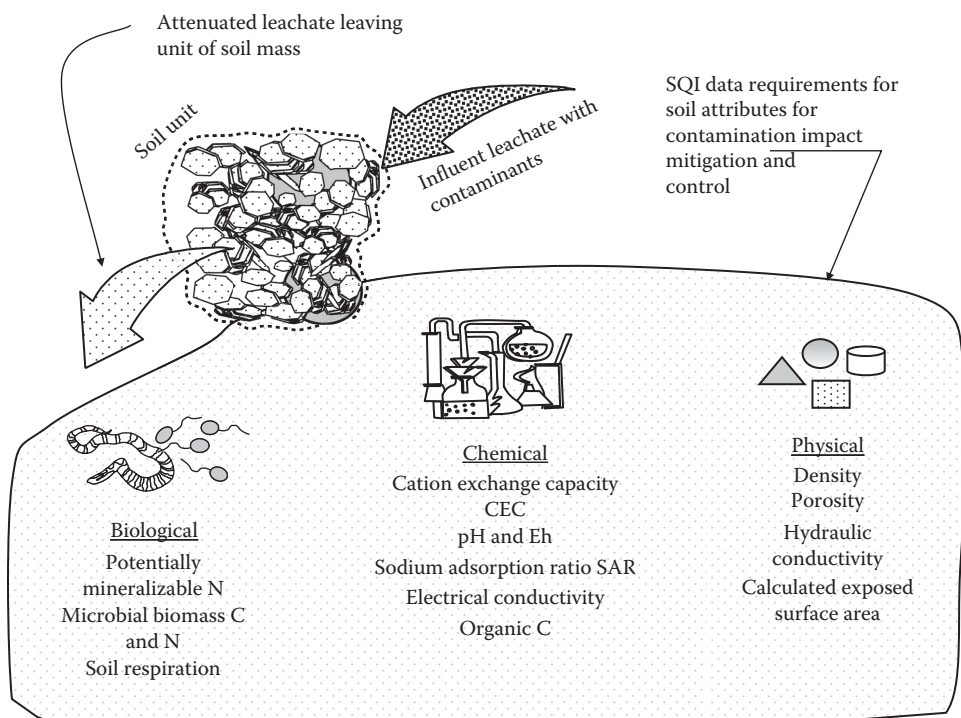
**FIGURE 13.3**

Illustration of increasing (enhanced) and decreasing (diminished) soil quality in relation to time. The soil quality index is a composite index determined on the basis of measures of achievement of levels required by prescribed physical, chemical, and biological indicators. Note that different soil quality indices are needed, depending on whether one is concerned with agricultural production or, for example, the use of soil for waste management.

SQI and WQI permits one to arrive at determinations that show whether the material and, finally, the system itself, will be sustaining. Taking the SQI as an example and referring to Figure 13.3, when calculations show that the SQI at any one particular time is greater than the baseline value, we will have increasing soil quality, and we can be assured of sustainability of the function served by the soil. Evaluation and quantification of SQI is application or function-specific, i.e., they depend on management goals for the material (water and soil).

13.4.1.1 Example of SQI Development

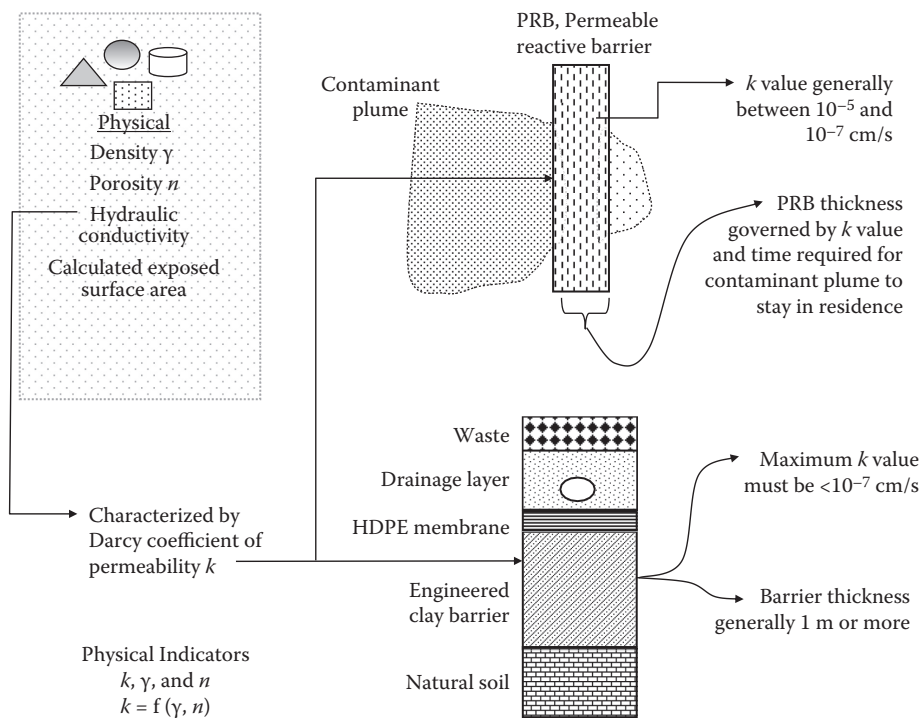
To illustrate the procedures that one would follow to evaluate and determine the appropriate SQI, we will use the role of soil as a resource material for management of the impacts from contaminant discharge into the ground. We recall from the previous chapters that the basic properties contributing to the development of the assimilative capability of soils are physical, chemical, and biological. From this starting point, determination of what pertinent attributes are significant and measurable is required. Furthermore, it needs to be determined whether or how these attributes vary with circumstances specific to the problem at hand, i.e., functions or use of the soil. Figure 13.4 is a schematic illustration of the physical, chemical, and biological properties that are considered to be significant in the development of the assimilative capability of the soil. If one were to compare the kinds of attribute data sets with the information given in Figure 9.19 in Chapter 9, it would be immediately evident that many of the basic interactions developed between contaminants and contaminants have been incorporated in the measured

**FIGURE 13.4**

Soil properties pertinent to use of soil as a management tool for mitigation of impact from contaminants discharged in the ground. Data from these attributes serve as input to determination of contamination mitigation soil quality index (SQI).

attributes. We use the term *attribute* in the discussion to mean the property or characteristic being measured.

The data obtained from tests and other kinds of measurements (field and laboratory) of the physical, chemical, and biological attributes can be used as (a) input to compare with individual attribute indicators, thus leading to immediate comparison of the sustaining capability of each individual attribute, and/or (b) input to statistical and analytical models developed to produce a *lumped* (combined or total) index parameter. Prescription of individual attribute indicators is performed once again on the basis of intended function of the soil. Take, for example, the set of attributes in the physical properties list in Figure 13.4. Density, porosity, calculated exposed surface area, and hydraulic conductivity have been chosen as the set of pertinent attributes. Consider two specific applications for the soil: (1) use as permeable reactive barrier (PRB) material, as in Figure 13.5, and (2) use as an engineered clay barrier (ECB) in the liner system shown in Figure 1.11 in Chapter 1. The primary controlling property in both the PRB and ECB applications is the hydraulic conductivity. For the PRB, one permits the transporting fluid to penetrate the PRB at a rate that allows for partitioning and transformation processes to occur. Residence time in the PRB is paramount. This is controlled by an appropriate soil permeability and thickness of the PRB. In general, one might want to design a wall thickness in conjunction with a Darcy coefficient of permeability k in the range of 10^{-5} to 10^{-7} cm/s, depending on the partitioning processes envisaged. In the case of the ECB application, a k value of considerably less than 10^{-7} cm/s is generally sought. The prescription of k indicators for desired objectives can

**FIGURE 13.5**

Prescription of hydraulic conductivity indicators based on intended function of soil. Since the k value determined is a function of density and porosity, the weighting factor for k is considerably larger than those for density and porosity. The calculated exposed surface area is a parameter of interest and may be neglected. The thicknesses of the PRB and ECB are determined by situation-specific conditions. Thickness of 1 m or more for the ECB is quite common for containment of MSW landfills.

now be obtained. The prescription of attribute indicators and their application can be seen in Figure 13.5 for the example of hydraulic conductivity. Given that hydraulic conductivity (as characterized by the Darcy k value) is a direct function of density and porosity—i.e., $k = f(\gamma, n)$ where γ refers to soil density and n refers to porosity—the *weighting* of data for γ and n becomes important. Application of weighting factors in such situations is to a large extent based on knowledge of previous behavior.

Determination of weighting factors to be used for all the data sets relating to the physical, chemical, and biological attributes can be a challenging task. Much depends on the experience and knowledge of the analyst. The results of the weighted data are used in a deterministic model that is designed to produce a lumped index known as the quality index. As stressed previously, the quality index will have a prefix that denotes the function of the material, for example, *drinking water quality index* and *contamination mitigation soil quality index*.

13.4.1.2 Water Quality Index WQI

Research and development of water quality indices have not received the same level of attention as for SQI in soil science. Instead, attention has been focused more on the establishment of national standards. Because of the very direct relationship between the

quality of drinking water and human health, drinking water quality standards are set by the regulatory bodies for most, if not all, of the countries in the world. As discussed in Section 3.3.1 in Chapter 3, the main parameters usually monitored for drinking water are BOD, color, turbidity, N, P, suspended solids, odor, heavy metals, VOCs, pesticides, bacterial level (such as coliform forming units, CFU), and perhaps other microorganisms. We should note that infectious diseases caused by pathogenic bacteria, viruses, and protozoa in drinking water are by far the greatest health threat.

Although these national standards set the basis for the water quality for the various countries, production of a national drinking water quality index for each and every country will require considerable effort in developing the relationships and weighting functions. To a large extent, this is because of the risk–benefit approach adopted by many responsible authorities in articulating quantitative values for the parameters chosen for monitoring. The risk–benefit consideration is not economically driven, at least not directly. Rather, it is driven by the need to provide acceptable drinking water to the most people without endangering public health. Setting standards that may be considered “too stringent” may on the one hand be prudent and safe, but on the other hand may make drinking water unavailable to a large percentage of the population—especially in regions of water deprivation. Because of these kinds of factors, development of drinking water quality indices becomes more than a challenge.

13.5 Sustainability Practice Examples

We will look at some case studies in this section. These are cases demonstrating sustainable practices and the implementation of methods to evaluate the sustainability of a project or process with regard to the geoenvironment. At least one case study is presented for each of the sectors, urbanization, resource exploitation, food production, industrial development, and the marine environment.

13.5.1 Rehabilitation of Airport Land

Between 150,000 and 350,000 m³ of soil in the contaminated site needed to be remediated at a former Norwegian airport (Ellefsen et al., 2001). A method was used to incorporate environmental effects into an evaluation of different remedial options. The environmental costs and benefits were determined, which became part of the decision assessment. One of the main environmental targets was the reuse of the treated soil for landscaping. Asphalt and concrete would also be reused. To perform the assessment, a model developed by the Danish National Railway Agency and the Danish State Railways was utilized. A life cycle approach for the remediation was used. Consumption of materials, fuel and energy, effects of noise, odor, and other annoyances to humans, and emissions to air, soil, and water were calculated.

The site (including soil and groundwater) was contaminated with diesel and heating oil between 3.5 and 5 m below the surface due to leaking storage tanks and runoff water. Free phase oil was also found. Two remedial options were chosen and compared. They were (a) excavation followed by biological treatment and (b) in situ treatment by biosparging and removal of six tanks.

Energy consumption for the excavation option was found to be five times higher than the in situ procedure. Additionally, emissions of greenhouse gases were estimated to be

three times more than the in situ option. For the in situ option, electricity consumption was considered to be the main environmental cost of the biosparging process. However, as hydroelectricity is the major source of electrical power, negligible amounts of CO₂ were emitted. Material consumption was equal in both cases but differed in origin. Iron and manganese were required for excavation machines, whereas nickel and copper were used for the air injection pipes and electrical materials. Biosparging was thus selected as the remedial option. The area is used for parking and storage facilities and will be used in the future for housing and parks. Other environmental assessments in the future will be performed using this approach.

A follow-up report by Ellefsen et al. (2005) indicated that the cleanup was completed in 2003. The area will become a green area with reserves for nature. Another challenge of the area was the management of the asphalt and sub-base contamination from PAHs from an old runway. Instead of transporting the waste to a hazardous waste facility, bitumen at a level of 3% was added to 20,000 tonnes of the soil via a cold mix process. The stabilized mixture was then used as a road foundation in the area. Leaching tests with water and road salt indicated that the material was appropriate for reuse. Another 80,000 tonnes of the contaminated soil were used without stabilization in the same road, whereas 60,000 m³ were used for other road construction and 80,000 tonnes for new terrain construction. In total 200,000 m³ of PAH contaminated soil were used with only 15,000 m³ requiring hazardous waste disposal.

Materials from the demolition were also used for recycling at an onsite recycling plant. The onsite plant enabled a reduction of 80,000 truckloads of materials during construction. A test road built with recycled asphalt and concrete showed better behavior than natural aggregates. Overall, 50,000 m³ of C&D waste, 120,000 m³ of old runways, 150,000 m³ of excavated material, and 300,000 m³ of blasted rock were used for 450,000 m³ of roads, buildings, and ditches. Another 60,000 m³ of composted sludge, 120,000 m³ of excavated materials, and 150,000 m³ of sand were for 400,000 m³ of new soil and green areas, whereas 888,000 m³ of the 1,050,000 m³ excavated material went to landfill. For energy, energy in seawater was exploited by heat pumps. The target was to supply 50% of the energy by renewable energy. Wetlands were conserved for migrant birds, and other landscaping for aesthetics and public recreation. Low impact transport such as public transportation, footpaths, and cycle paths was prioritized. The entire project is to be completed in 2015 (Statsbygg, Norwegian Directorate of Public Construction and Property [Statsbygg, 2014]).

13.5.1.1 Sustainability Indicators: Observations and Comments

There are several indicators that can be used to determine whether a remediation project meets the aims or principles of *sustainability*. These include

- *Land use*: The results show that if one uses the contaminated land as a starting point, the original plan for remediation and rehabilitation of the land to permit usage as parking and storage facilities is a step forward, i.e., better land use. The subsequent report indicating use of the rehabilitated land as green space is a positive step toward sustainability goals. We need to note that the land-use indicators here are not in reference to the initial airport land use. Because of the new intended green space land use, the sustainability indicators can now be cast in terms of “return to nature” indicators.

- *Energy utilization:* Conservative energy use as a target for remediation procedures does not always produce results that will support complete site remediation. Comparing two specific remediation procedures for energy use is a good procedure in minimizing depletion of energy resources, especially nonrenewable energy resources. Since the energy resource to be used for both remediation and rehabilitation procedures is hydroelectric based, and assuming that this is fully renewable, the sustainability feature here can be viewed more as a conservation measure. The energy indicators are referenced specifically to the remediation–rehabilitation processes and not to the production of hydroelectricity.
- *Noxious emissions:* The use of hydroelectricity as the source of power has essentially limited noxious emissions. Since the impact of CO₂ discharges has been minimized with the type of energy used, one will need to accept that emissions indicators for full sustainability cannot be realistically set. A set of realistic parameters and values for emissions indicators needs to be prescribed.
- *Nonrenewable and renewable resource materials:* The metals used are nonrenewable resources. Although reuse of the asphalt pavement material and the underlying and contiguous contaminated soil for road construction shows a positive approach to the principles of sustainability, there is a requirement for monitoring to ensure that these materials do not present future contamination problems to the immediate environment. As with the situation of emissions, a set of appropriate parameters and values for material and system status indicators is required.

The use of recycled products in construction of roads has also been recently demonstrated in a project in Finland designed to show that sensitivity to sustainability objectives in construction of roads (Lahtinen et al., 2005). New types of road construction materials based on the industrial by-products, fly ash, and fiber ash were evaluated in new roads. Fiber ash was evaluated in light traffic paths and for the widening of safety lanes. The pilot construction took place in 2002 and 2003. Monitoring of the road performance is underway until the end of 2005. The fly ash was obtained from the incineration of bark, peat, and/or sludge and the fiber ash is a fiber sludge from the paper industry with fly ash and cement binder. Up to now, the results of using the recycled materials in the road construction is positive both technically and economically and provides a potential way of saving virgin, nonrenewable resources.

13.5.2 Sustainable Mining Land Conversion

Mount Cenis was established as a coal mine near Herne in the Ruhr District of Germany in 1871 (Genske, 2003). Subsequent coal washing and coking facilities were then built. The mine was one of the largest in the area but it was closed in 1978 due to the coal and steel crisis in Europe. At the site, 26 ha of land were contaminated. There was subsidence, acid mine drainage, mine gas leakage, and many underground structures. However, in 1990, a large project was conceptualized to remediate and reuse the land for companies and enterprises. The main features of the project as shown in Figure 13.6 (EMC, 1998; <http://www.akademie-mont-cenis.de>) included

- An academy for the Ministry of Interior (the largest building)
- Various public service buildings such as a meeting hall, civic administration buildings, and a library

- Shops and services for a shopping mall that existed already
- 250 housing units
- Conference space, hotel, restaurant, and a recreation park

Wood was chosen for the structures due to resource efficiency as detailed in a report for the Club of Rome of 1995 (Weizäker et al., 1997). Forests close to the construction site were chosen as the source of the wood to reduce transportation requirements. Concrete buildings were chosen to reduce climate control requirements. Energy savings of 23% for heating enabled an 18% reduction of the CO₂ emissions. Approximately 10,000 m² (3800 PV cells) of solar cells covered the roof of the wood and glass structure for the academy, hotel, living quarters, and sports facilities. Natural ventilation was incorporated into the building. Energy consumption was reduced to 32 kW h/year. The power plant on the roof provides 1 MW of power, more than twice that needed by the center (EMC, 1998).

Approximately, 120 million m³ of methane are generated from the abandoned mines. The general practice of burning the methane releases approximately 8 million tonnes of CO₂. Therefore, it was decided to capture the gas containing 60% methane. This was converted to 2 million kW h of electricity and 3 million kW h of heat for the nearby buildings. The mine gas and solar panels generate energy for 130,000 homes. A power station is used for energy storage. A supplementary natural gas plant (1800 kW h) and a hot water storage tank were constructed to ensure adequate energy and heat due to the fluctuating nature

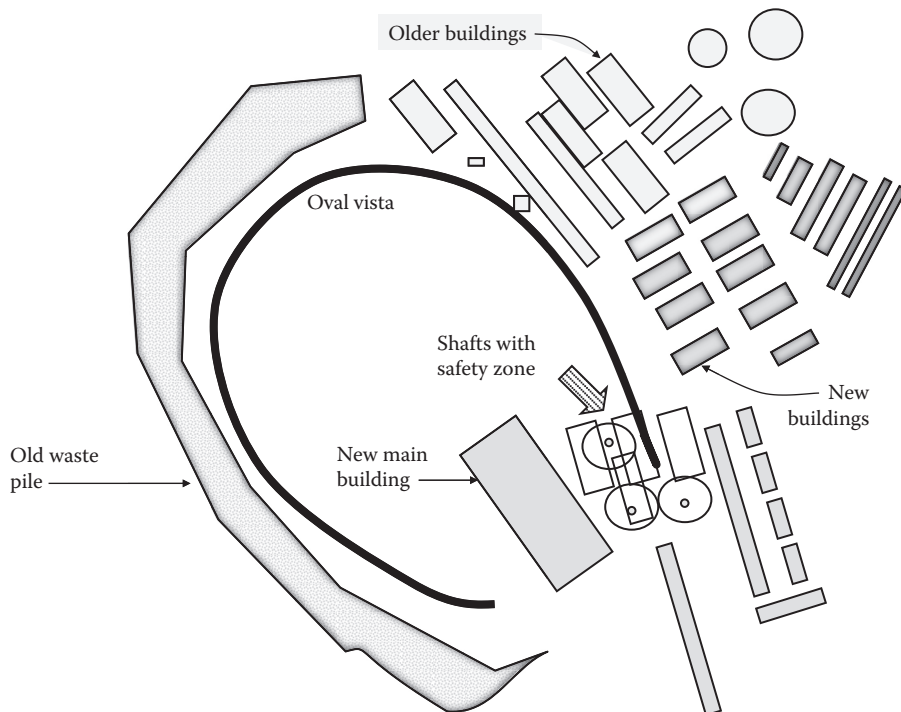


FIGURE 13.6

Redeveloped Mont Cenis site. New buildings are in gray and older buildings are in white. The three abandoned shafts (encircled with a safety zone) are used to recover energy. (Adapted from EMC, Mont-Cenis, *Report of the Entwicklungsgesellschaft*, Mont-Cenis, Herne D, 44 pp., 1998.)

of the methane production. As a backup, connection was made to the municipal energy system. This also was used for discharge of excess energy. Rainwater was collected in an underground cistern from buildings for use in toilets, showers, washing solar panels, and for watering gardens.

Infiltration of the water was allowed only where the soil was low in contamination. Excavation of the contaminated soil was not performed since this fills landfills and transfers the problem to another place. The soil was instead placed on clay liners or membranes to prevent leaching of the contaminants to the groundwater. Herb gardens are grown on top of the contaminated land. Gravel and sand filters are placed above the liners to collect the precipitation. The entire project cost 110 million euros and was shared between the community and private investors.

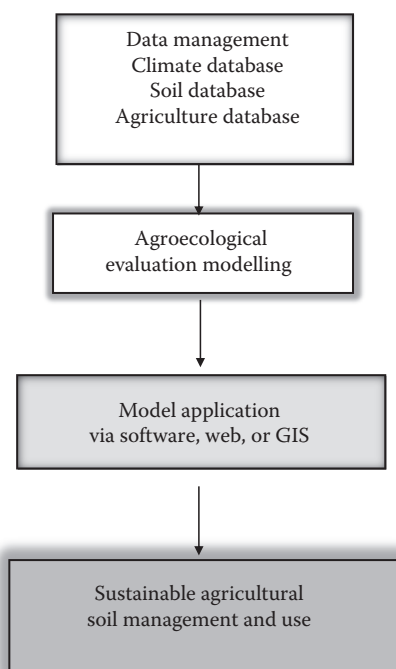
13.5.2.1 Sustainability Indicators: Observations and Comments

As with Section 13.4.1, there are several indicators that can be examined to evaluate whether sustainability or the path toward the goals of sustainability has been taken.

- *Land use:* Increased land-use capability has been achieved with the remediation–rehabilitation scheme. As with the land use case in Section 13.4.1, the land-use indicators chosen are in specific reference to the initial condition prior to remediation and rehabilitation and not before mining.
- *Energy sources:* The multisource energy input, from solar to methane gas capture and reuse, coupled with more efficient climate control in the buildings show good attention to energy conservation. This agrees with the requirement for reduction in depletion rate of nonrenewable energy resources as a goal toward *conservation for sustainability*.
- *Water use:* As with the conservation strategy for energy, utilization, and reuse of water show good accord with water sustainability indicators.
- *Remediation of contaminated land:* The concern for not dumping contaminated soil into another landfill as a reason for placing the contaminated soil on secure membranes and left on-site is a responsible attitude. One assumes that the appropriate requirements for (a) monitoring of the contaminated soil facility, (b) prescribing indicators for safety–recovery status of the contaminated soil facility, on the assumption that the contaminated soil will be remediated through intrinsic remediation processes, and (c) development of appropriate risk-management procedures.

13.5.3 Agriculture Sustainability Study

De la Rosa et al. (2003) have described soil quality decision support tools for the protection of agricultural zones, particularly in the Mediterranean region. Soil quality indicators are not sufficient for land management as soil, biological components, climate, water, and land use must all be considered. MicroLEIS is an agroecological decision support system available at <http://www.evenor-tech.com/microleis/microlei/microlei.aspx>. Databases, statistics, expert systems, neural networks, Web and GIS, and other technologies are integrated in the scheme (Figure 13.7). Information on the impact of soil use such as tillage on soil properties, soil quality and crop production is still needed. The concept of soil quality according to the Soil Quality Institute (U.S. Department of Agriculture [USDA],

**FIGURE 13.7**

Components of the MicroLEIS Decision Support System. (Adapted from de la Rosa et al., 2003.)

2006) is related to sustainable soil use and management. Some indicators are shown in Table 13.1. Physical, chemical, and biological factors are included in soil quality. Soil functions can be defined for crop growth, soil erosion or soil contamination, and thus other indicators must be added to address soil contamination in particular. For example, heavy metal contents as the result of sewage soil application or for contaminated site remediation are well defined by legislation. Biological indicators are less advanced. New

TABLE 13.1

Soil Quality Indicators

Group	Soil Quality Indicator
Physical	Aggregate strength and stability
	Bulk density
	Soil compaction
	Soil texture
	Soil structure
	Topsoil depth
Chemical	Plant nutrients
	Reaction pH
	Salinity
Biological	Organism population
	Respiration rate

Source: USDA, Soil Quality Institute, Natural resources conservation services. Available at <http://soils.usda.gov/sqi/>, 2009.

DNA extraction techniques or ribosomal RNA are developing (Thies, 2006). The soil assessment approach can be seen as Figure 13.7 as developed by de la Rosa et al. (2003). De la Rosa and Sobral (2007) have indicated that the general principles of sustainable agriculture practices should aim to

- Increase organic matter content
- Decrease erosion
- Improve water infiltration
- Decrease subsoil compaction
- Increase water holding capacity
- Decrease the leaching of agrochemicals in to the groundwater

A variety of innovated agroecological innovations could be employed (Uphoff et al., 2006) for sustainable agriculture. Some biological techniques include biorehabilitation of the soil, composting and vermicomposting and bioremediation of organic contaminants such as pesticides. For an area in Azarbaijan, six agroecological land evaluation models of the MicroLEIS DSS software were used to evaluate and compare strategies for land use (Shahbazi et al., 2008). Results from soil morphology and analytical data were studied. It was determined that 45% of the area was classified as suitable for agricultural use, whereas 12% must be reforested and not used for agriculture to minimize the land degradation. The crop rotation of wheat–alfalfa–soybean was selected as the best. Overall, the tool was appropriate for evaluation of sustainable agroecological systems in semiarid regions.

13.5.3.1 Sustainability Indicators: Observations and Comments

The use of *soil quality* as an indicator for sustainability in agricultural production has a history of almost 30 years. The use of soil quality as a tool for assessing the health of a soil with particular reference to agricultural purposes was first discussed in the late 1970s (Warkentin and Fletcher, 1977). The term *soil health*, which was (and may still be) used by farmers, refers to the functional capability of the soil to support crops and other plants. With the quantification procedures indicated in this section, it is seen that a structured effort is being made in agriculture to meet the goals and requirements for sustainable agriculture. The production of quantification techniques for soil quality provides the means for comparing the dynamic state of the agricultural soil, and offers the opportunity to develop the methodology for determination of soil quality indices. As with the other soil quality indices developed for the various soil function discussed in Section 13.3.1, these agricultural soil quality indices are the necessary constituents of the indicators for agricultural soil sustainability.

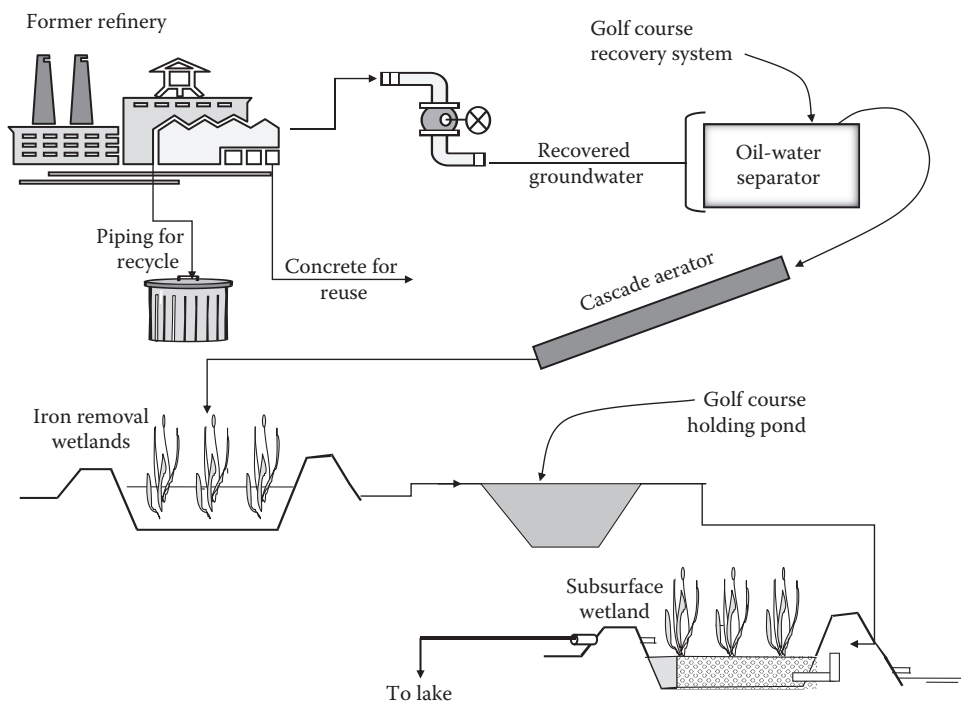
13.5.4 Petroleum Oil Well Redevelopment

The Damson Oil Site in California near Venice Beach is an abandoned oil well that stopped production in 1989 (CCLR, 2000). Damson deconstructed the facilities in 1991. However, after the oil wells were capped, the company filed for bankruptcy leaving soils contaminated with hydrocarbons, sumps with oil and sludge from the extraction process, vaults with oil, and several miles of pipeline. Further contamination occurred as a result of deliberate dumping of debris by passers by. Since it was deemed too expensive to restore the

site to a sandy beach, it was decided to establish an in-line skating facility. The oil site was to be capped with concrete and the remediation costs, and the improvements made would enable the facility to be economically viable. The plan consisted of (a) an environmental site assessment, (b) waste removal for all surface soils, liquid wastes and sludges, (c) demolition plan for the pipeline and other structures and tanks, (d) construction plan for a skating facility, (e) possible restoration of the beach, (f) establishment of other facilities, and (g) negotiation of a risk management plan with the Regional Board for remediation objectives and standards. By 2000, environmental assessments and cost estimates were completed and the construction of the boardwalks was initiated. The brownfield blocked the view of the ocean. The Department of Recreation and Parks acquired the site for public use and then the City's Brownfields Program provided the funds for the site remediation of \$100,000 for demolishing the structures, removing soil contaminated with metals and crude oil, completing lead and asbestos abatement, and installing groundwater monitoring wells. After remediation, the California Regional Water Quality Control Board performed quarterly groundwater monitoring. A skate park was built on some of the reclaimed land. The Brownfields Program provided funding for oil storage and drilling infrastructure cleanup, including underground storage tank removal. Besides the skate park, the multi-purpose recreation center includes picnic areas, play areas, sports fields, etc. (City of Los Angeles, 2014).

Another former oil refinery was converted to a business and recreational opportunity in Casper, Wyoming (Applegate et al., 2005; EPA, 2007). The refinery had operated since the early 1900s but closed in 1991 due to environmental liabilities related to oil spills, sludges, and underground pipelines. The cost of the site remediation was estimated at US\$350 million. Various risk assessments were undertaken. To protect the river and remediate the groundwater, a horizontal wall for air sparging and venting was designed and installed, in addition to a sheet-pile barrier wall. Pipes were also removed to eliminate the contamination source. Final remediation strategies included (a) removal of sediment from the lake, (b) removal of tanks, pipes, concrete, and other material from the refinery area. Cleaning of the groundwater involved oil recovery, sparging, venting, phytoremediation, and monitored natural attenuation in the refinery and tank farm areas. All concrete (nearly 272,000 tonnes) that was removed was crushed for reuse at the site and most of the pipes were sent to recyclers. Some examples of concrete reuse include (a) use as drainage in the water treatment system, (b) construction of a barrier that prevented animals from entering the waste depository near the lake, and (c) for construction of roads. It is estimated that oil recovery at the site will take approximately 25 years, on the basis of analysis of the mobility of the oil strongly adsorbed to the alluvium. As a golf course was also constructed at the site, oil recovery wells had to be designed so that they would not be placed in the fairways and greens.

Water at the site was also to be reused. Therefore a system (one of the largest engineered wetlands) was set up that included management of the stormwater, irrigation of the golf course, and pumping of the water into the lake for the migratory birds. The schematic of the water management system is shown in Figure 13.8 and can handle between 1890 and 5670 L/min. It is mainly hidden and integrated in the golf course. Nearby Soda Lake was also contaminated and thus 150,000 m³ of contaminated sediment had to be removed and efforts were made to promote the bird and wildlife population. Institutional controls were necessary to manage the remaining contamination. A kayaking course was also placed in the river. To implement phytoremediation, 2000 trees were planted. There have been numerous awards for this project.

**FIGURE 13.8**

Golf course water treatment system for recovered groundwater from former refinery and tank farm. (Adapted from Applegate, D. et al., *Civil Engineering*, 75, 44–49, 2005.)

13.5.4.1 Sustainability Indicators: Observations and Comments

From a land-use sustainability perspective, the ongoing project in the first example together with remediation of the contaminated site in the second example and use of recycled materials, it appears that improved land use has been obtained. The remediation–rehabilitation plan in the first example provides opportunities for prescription of indicators for sustainability. It appears that site restoration will be performed in a fashion that will return the site to conditions and usage beyond initial sandy beach conditions. From a land-use standpoint, the remediation–rehabilitation scheme is a positive step. One presumes, however, with the initial environmental site assessment that a proper accounting has been given to avoidance of negative impacts from the development and operation of all the new facilities. Prescription of *facilities-operation indicators* would be useful.

13.5.5 Mining and Geoenvironmental Sustainability

The Sullivan Mine in Kimberley, British Columbia, Canada, was discovered in 1892 (Teckcominco, 2001). Although the community was previously dependent on a single industry (mining), since 1990, the community became more diversified and the area is now a resort destination. To determine the viability of the community, a set of indicators was developed based on the following guidelines: (a) Canadian Mining Association Guidelines for Sustainable Development, (b) Australian Minerals Industry, (c) the Global

Reporting Initiative, and (d) the World Business Council for Sustainable Development. These indicators were divided into economic, environment, and social categories for several components. The environment indicators for sustainability were (a) ecosystem health based on soil erosion and species diversity, (b) the availability of natural resources such as minerals, (c) the effect of the company on the ecological amenity, and (d) sustainability. The features included for the environment sector were a tailings pond reclamation, and a drainage water treatment plant. Reuse, recycling, and safe handling of all products are practiced. The Mark Creek is now been carefully landscaped with a golf course. A Sullivan Mine Public Liaison Committee was formed to ensure public participation in the process.

Four fatalities occurred at this site in May 2006 in a seepage monitoring station that was hydraulically connected to an acid generating waste rock. Various studies were completed to determine the cause of the asphyxiation deaths in the shed (Hockley et al., 2009). Reactions occur within the waste piles that lead to hazardous gas production. Gas flows are induced due to temperature differences and depletion of oxygen and moisture in the pore spaces. Therefore, physical and chemical factors must be considered for storage of waste rock.

Another example of the practice of sustainability (Stanton-Hicks, 2001) can be found in an iron industry at another site in Australia (Pilbara). A theoretical model (CSIRO)

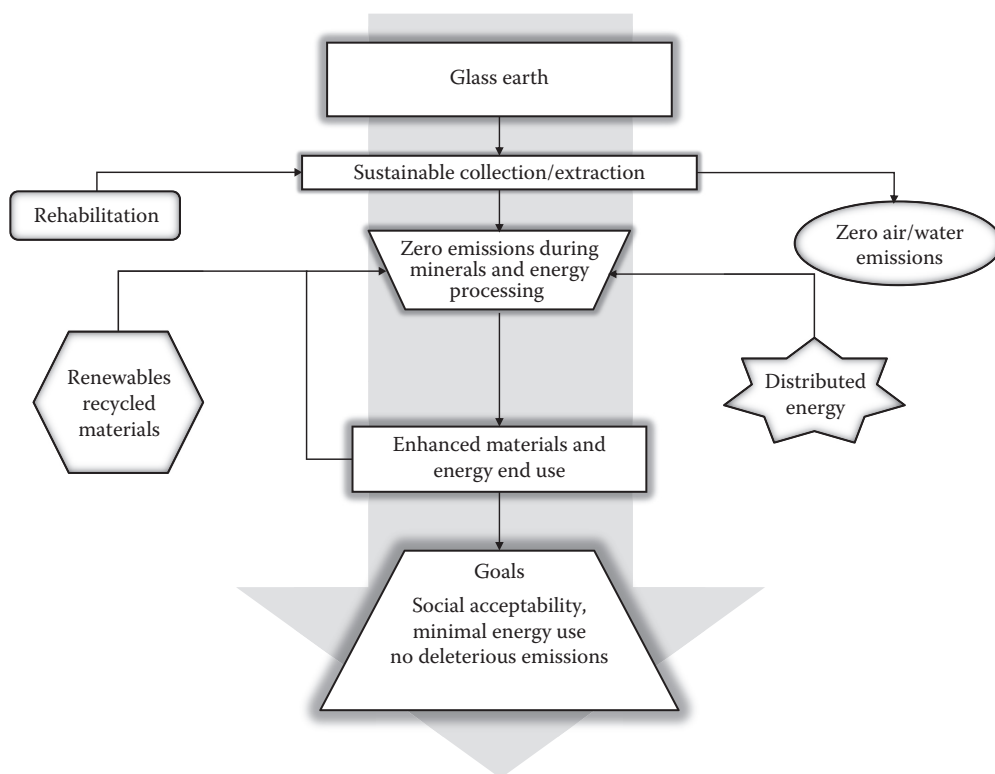


FIGURE 13.9

Concept of the CSIRO model. (Adapted from Stanton-Hicks, E., *Sustainability and the Iron Ore Industry in the Pilbara: A Regional Perspective*. *Sustainability and Mining in Western Australia*, Institute for Sustainability and Technology Policy, Murdoch University, 2001.)

as shown in Figure 13.9 has been incorporated. Mining was initiated in the region in the 1960s with large-scale technology and inland mining operations. A number of programs have been established since 1990 to train and work with the indigenous employees and contractors in the area. The life cycle cost approach is being used with eventual rehabilitation of the site to be considered at an early stage. Fugitive dust is a particular issue for mine dumps. In addition to using wind block and conveyor coverings, the appropriate amount of water must be added to ensure that dust does not become airborne.

Moller et al. (2006) presented an approach for sustainable development during mine closure for the Western Australia to minimize impact on humans and the environment. The four stages included understanding the aspects related to closure, evaluation of land-use options, development of the strategy and finally development of the management plan. The principles are shown in Figure 13.10.

Hamersley Iron has developed the HIs melt Technology (Rio Tinto, 2014), which enables the use of more feedstocks and subsequently more recycling and high-quality recycled products from the high phosphorus iron ore. Phosphorus is no longer problematic due to the reduction process, which replaces the conventional oxidation one. Heat energy can be recaptured, and scrubbing reduces the release of toxins and particulates in addition to greenhouse gases. The process is under development. The area still has many challenges including ensuring the maintenance of the small ecosystems (desert, mountain, and coastal) in the areas. The HIs melt process improves the environmental aspects of ironmaking by incorporating high process efficiency and eliminating coke and sinter production.

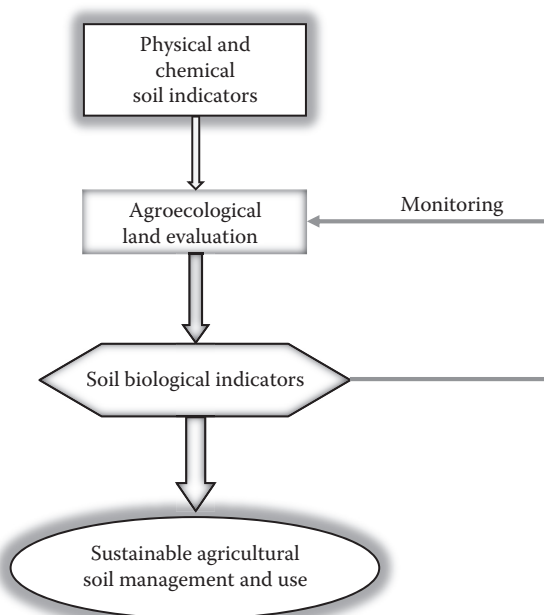


FIGURE 13.10

Schematic of agroecological approach for sustainable agricultural soil use and management. (Adapted from Moller, M. et al., *Pilbara Iron's Approach to Sustainable Development during Mine Close—The Case Study of Greater Tom Price and Pannawonica Operation*, unpublished report, Sinclair Knight Merz, Australia, pp. 1–6, 2006.)

Emissions of CO₂, SO₂, and NO_x are lower than other processes and dioxin, furan, tar, and phenol products are eliminated and steel plant wastes can be recycled. Through a collaboration with ULCOS/Tata Steel, the HIsarna process has been developed to reduce the emissions of greenhouse gases significantly (Rio Tinto, 2011).

13.5.5.1 Sustainability Indicators: Observations and Comments

The aspects of sustainability include

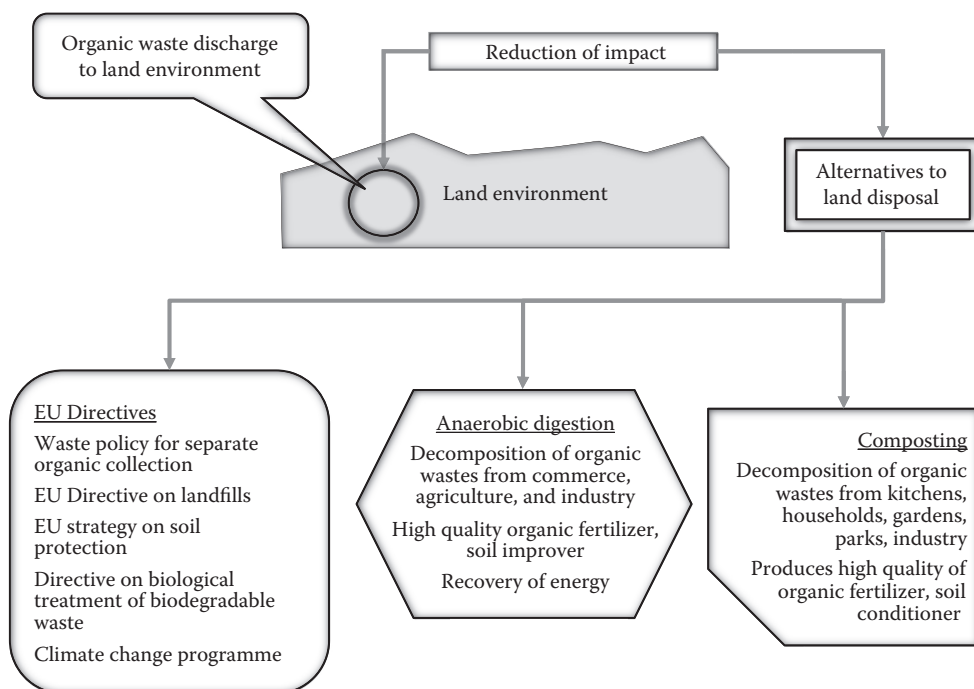
- Maximization of economic, ecological, and sociocultural efficiencies through integration
- Extension of mine life through new techniques and development of new markets
- Land-use agreements to benefit economic and socioeconomic sustainability
- Pastoral management practices to improve environmental management and cooperation with land management agencies.

13.5.6 Organic Urban Waste Management in Europe

In Europe, more than 40% of all waste is biologically treated via composting or anaerobic digestion (Barth, 2005). In the EU, this amounts to a potential organic waste of around 50 million tonnes of food and garden residues. Forty-two percent of this waste can be easily source separated. The composts can serve as an organic fertilizer or soil improver. Open windrows are the main technology for European countries. Another technology, anaerobic digestion, meanwhile, is divided into 46% dry digestion and 49% wet digestion, with many treating more than 40,000 tonnes/year of waste. Commercial and food waste is Germany and Austria is increasing, as well as mixed municipal waste in Spain. Denmark digests household biowaste in agricultural digestion sites. The aim is also to produce organic fertilizers and soil improvers.

Various policies with the EU Commission also will promote biological treatment directly or indirectly (Figure 13.11). The Landfill Directive (The Council of the European Union, 1999) states that fermentable waste must be reduced by 25% by 2006 and 65% by 2016. This will improve landfill structures and reduce biogas production in landfills and to introduce methods to collect and treat biowaste. According to the *Eurobserv'er*, The State of Renewable in Europe 2011 (Eurobserv'er, 2011), the production of biogas for electricity increased by 31% for 2009 to 2010. Its aim is to promote recycling of biowaste and to promote certified compost that prevents contamination. A green paper was issued on the management of biowaste in the European Union (SEC [2008] 2936 discusses composting and anaerobic digestion as means of reducing biowaste in landfills) (European Commission, 2008). In Italy, for example, more than 18 waste treatment plants have been established since 2005 that treat source segregated waste that treat 600,000 tonnes of biowaste in 2009. Almost all anaerobic digestion plants employ composting to treat the digestate, and thus producing a product (Mainero, 2011).

The European Soil Protection Strategy (European Commission, 2006) promotes the sustainable protection of soil by mitigating the three threats to soil including decreased organic matter, soil contamination, and erosion due to desertification and includes prevention soil degradation. The addition of composts and residues of organic matter to soil can clearly enhance organic matter and restore the agronomical and microbiological properties of soil. In addition, the addition of these types of organic matter to the soil can mitigate

**FIGURE 13.11**

European initiatives for managing organic waste. (From Barth, J., *From Waste to Valuable Product—15 Years of Successful Experiences with Recycling of Organic Waste in Europe*, presented at AMERICANA 2005, Montreal, April 6–8, 2005.)

climate change by providing a carbon sink in the soil. Since the adoption of the strategy in 2006, a report was issued in 2012 from the Commission to the European Parliament, the Council, the European Economic and Social Committee, and the Committee of the Regions to implement the Soil Thematic Strategy and ongoing activities (European Commission, 2012). This report also presents trends in soil degradation both in Europe and worldwide and challenges for the future protection of the soil.

The four pillars include raising awareness, research, integration, and legislation. With regard to research around 25 research projects on soil have been funded under the Seventh Framework Programme for Research (European Commission, 2014b). The European Climate Change Programme (ECCP) (European Commission, 2014c) promotes the buildup of carbon in the soil by organic fertilizers, which can thus serve as a carbon sink (via the process of carbon sequestration) of up to 2 gigatonnes of carbon per year. This is compared with 8 gigatonnes of carbon per year that are emitted in to the atmosphere. Therefore, the practice of biological waste treatment of separated wastes that is developing in Europe is clearly more sustainable than landfilling solid waste. The first ECCP ran from 2002 to 2004. ECCP (II) was initiated in 2005. It focuses on implementing aspects highlighted in ECCP (I). Some of the aspects being investigated are particularly relevant to the geoenvironment such as carbon capture and geological storage, agriculture, and the sinks-subgroup on agricultural soils and forest-related sinks.

13.5.7 Sediment Reuse: Orion Project, Port of New York and New Jersey

Sediments must often be removed by dredging to maintain waterways and ports. Approximately 5% to 10% of these sediments are contaminated (Urban Harbors Institute, 2000). Management of these materials must be planned carefully with environmental protection and economic viability. An initial draft report was of a Dredged Material Management Plan (DMMP) was prepared in 1999 and finalized with Environmental Impact Statement in 2008. The Port of New York and New Jersey has to dredge approximately 0.8 to 1.6 million m³ of sediment every year. Since one third of the sediments do not meet standards, alternate uses are required. More than 1.2 million m³ have been used as foundation fill for a parking lot. The sediments were dredged, transported to a screening facility and then pumped on to the shore for mixing with cement kiln dust to improve compressive strength. The mixture was placed on a 24-ha lot and asphalt was used to cover the fill. No virgin material was required for the lot foundation. In the DMMP, numerous options are considered for dredged sediments (U.S. Army Corps of Engineers, 2008). They include

- Contaminant remediation, removal, treatment of containment by capping
- Use of dredged material to remediate the ocean site of Historic Area Remediation Site (HARS)
- Use of dredged materials for restoration and creation of wetlands, benthic, and bird habitats, reefs for marine life
- Remediation of abandoned mines, quarries, and landfills with dredged materials
- Reuse of treated dredged materials, for construction grade cement, light weight aggregate, and manufactured soil
- Confined aquatic disposal

13.6 A Case Study Scheme for Sustainable Geoenvironment Practice: Remediation of Cesium-Contaminated Surface Soils

13.6.1 Introduction and Problem Setting

The techniques for cleaning or decontamination of contaminated soils has been well discussed in the previous chapters. However, when extensive areas of surface layer soils are contaminated, the kinds of remediation technology will likely be different—to a very large extent because of the areal extent of surface soil contamination, and also because the depth of the surface soil layer precludes application of subsurface soil treatment techniques. Such a case of extensive surface layer soil contamination is the farmlands in the Tohoku area of Japan. The discussion in this section uses the radioactive cesium-contaminated surface layer soils of the area as an example of what might be used as an applicable technology for remediation of the surface layer soils—drawing its experience from the successful remediation of contaminated sediments in Fukuyama Harbor, Hiroshima Prefecture, Japan.

A special note: The discussion in this section should not be construed as promoting the use of the discussed technique, procedures, and technologies previously applied for remediation of Fukuyama Harbor for the soils in the Tohoku area. Instead, it is the intent

of this section's discussion to introduce the concepts of soil attributes and their ability to respond to cleanup techniques as integral to the practice of sustainable geoenvironment management.

The soils in Tohoku area have been contaminated by the radioactive substances discharged from the Fukushima Daiichi Nuclear Power Plant accident. The power plant buildings, which were damaged by the March 11, 2011, east Japan great earthquake and accompanying tsunami, suffered hydrogen explosions on March 12, 14, and 15, which destroyed the upper portions of the nuclear power plant buildings. This resulted in the release of radioactive nuclides consisting of Kr, Xe, I, Cs, Ce, Sr, Ru, etc. (Nakano and Yong, 2013). The resultant fallout onto the surrounding regions is extensive and presents the geoenvironmental science and engineering professions with the problem of how to remediate the soils contaminated with radioactive cesium (Ebihara et al., 2012; Akai et al., 2013; Nakano and Yong, 2013). The fallout remains mainly in the surface soil layer, sediments, and surface water, with some penetration into the subsurface soil (Vray et al., 2003; Lusa et al., 2009). Of great concern are ^{134}Cs and ^{137}Cs since they possess strong photon energies and long half-lives. The radioactive cesium shows relatively high sorption properties in soils and sediments (Akai et al., 2013). The sorption characteristics of radioactive cesium depend on pH (Poinssot et al., 1999; Koarashi et al., 2012), types of minerals, and organic matter content (Nakano et al., 2003).

According to the Japanese tentative regulation, the soils with radioactive cesium concentrations higher than 8000 Bq/kg have to be removed and strictly controlled. Lower concentrations are also detrimental to human health and other living things. This situation holds not only for the Fukushima accident, but to other places under similar circumstances. It is a significant challenge and responsibility for geoenvironmental engineers to undertake to decontaminate the affected regions—taking note of the fact that more than 20% of the ^{137}Cs radioactive nuclides released were deposited on land surfaces in areas between 60 and 400 km from the power plant site (Nakano and Yong, 2013). Reduction of the volume of moderately contaminated soils over a widely spread area may be an approach. The present target is to produce remediated soils with radioactive concentrations lower than 8000 Bq/kg. By rehabilitating these soils, a wide area around the center of the accident can be readied for reconstruction and many victims can return. To achieve this, it may be necessary to remediate the contaminated soils and to reuse some of the remediated soils.

13.6.2 Rehabilitation Schemes

There have been several schemes proposed for remediation of contaminated soils. However, when it comes to large areas of land surface soils, many of these schemes are not practical—to a large degree because of the vast expanse of land surface and also because the techniques proposed are not economically practical and/or suitable for thin surface layers. Such a case is the problem posed by the cesium-contaminated farmlands in the Tohoku region. Nakano and Yong (2013) have estimated that the total volume of surface soil to be removed for treatment in the 80 km affected zone is about $34.23 \times 10^6 \text{ m}^3$ —meaning that if the farmlands are to be returned to their original site and regional functionality, efficient, and robust treatment techniques for handling such large quantities of contaminated material are required. The following discussion details the underlying rationale for the application of a set of procedures that has been applied to treatment–remediation of vast areas of contaminated sediments. The basic elements of the technique show that this technique is applicable for treatment and rehabilitation of vast areas of contaminated surface layer soils, and is a prime example of sustainable geoenvironmental engineering practice.

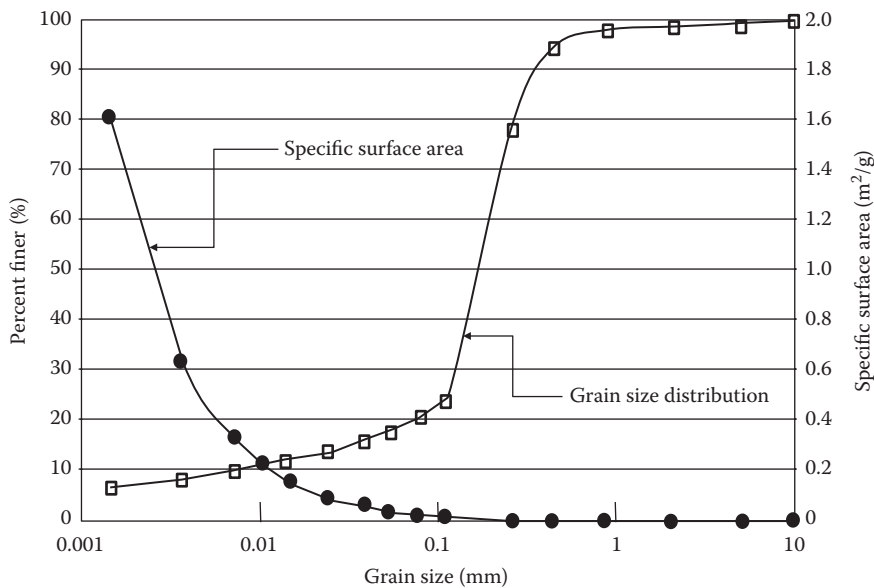


FIGURE 13.12

Grain size distribution and ideal specific surface area of the sample soil.

It is well known that more radioactive cesium can be adsorbed on the finest soil particles such as montmorillonite clay than on coarse soil particles (Maes et al., 1985) due to the surface characteristics and specific surface area of the particles. The sorption characteristics of the particles can be used for removing radioactive cesium (Karamanis and Assimakopoulos, 2007). If the sorption characteristics of radioactive cesium are similar to other metal ions, the sorption quantity is thus considered to be function of the specific surface area. In the example shown in Figure 13.12, the relationship between specific surface area and grain size distribution is obtained by calculating the ideal specific surface area of spherical particles with a density of 2.65 g/cm^3 . The graph shows that specific surface area increases rapidly with a decrease in grain size, and that specific surface area of particles greater than 0.1 mm can be neglected (for this sampled soil). Furthermore, the specific surface area of particles smaller than D_{10} , grain size (10% finer), possesses approximately 90% of the total specific surface area. Therefore, if we remove the particles smaller than D_{20} (grain size that is 20% finer; approximately 0.07 mm in Figure 13.12), most adsorbates can be removed. It is noted that this can be achieved by removing the silt and clay fractions.

13.6.3 Segregation of Particles in Water

Smaller particles can be segregated by suspension of soil particles in water under forced convectional flow, as explained by Stoke's law.

$$v_w = \frac{D^2(\rho_p - \rho_w)g}{18\eta} \quad (13.1)$$

where v_w is the forced convectional upward flow velocity, D is the diameter of the spherical particle (m), ρ_p is the density of the particle (kg/m^3), ρ_w is the density of water (kg/m^3), g is

the gravity (m/s^2) and η is the viscosity of water (Pa s). To suspend a spherical particle with a diameter of D , the condition required is expressed by

$$v_w \geq \frac{D^2(\rho_p - \rho_w)g}{18\eta} \quad (13.2)$$

or

$$D \leq \sqrt{\frac{18\eta v_w}{(\rho_p - \rho_w)g}} \quad (13.3)$$

Thus, under a given convective upward velocity, particles smaller than a given size (weight) can be suspended and most of them can be transported with the convective water flow. From Equation 13.2, the approximate v_w value against $D = 0.075$ mm, can be estimated to be $v_w = 4.4$ mm/s. This can provide the approximate upward flow velocity necessary to suspend particles smaller than 0.075 mm. Field trials will allow for fine-tuning of the flow velocity requirements. In the case of particles larger than the anticipated maximum size, these will remain at the bottom. In a given water column system, convective flow can segregate the suspended particles, as demonstrated in Figure 13.13 and smaller suspended particles can be removed from a given water depth. The diameters of the particles in Figure 13.13 are expressed as $D_s < D < D_g$ at steady state. It is noted that the specific gravity of particles and the viscosity of water will affect the result, as shown in Equation

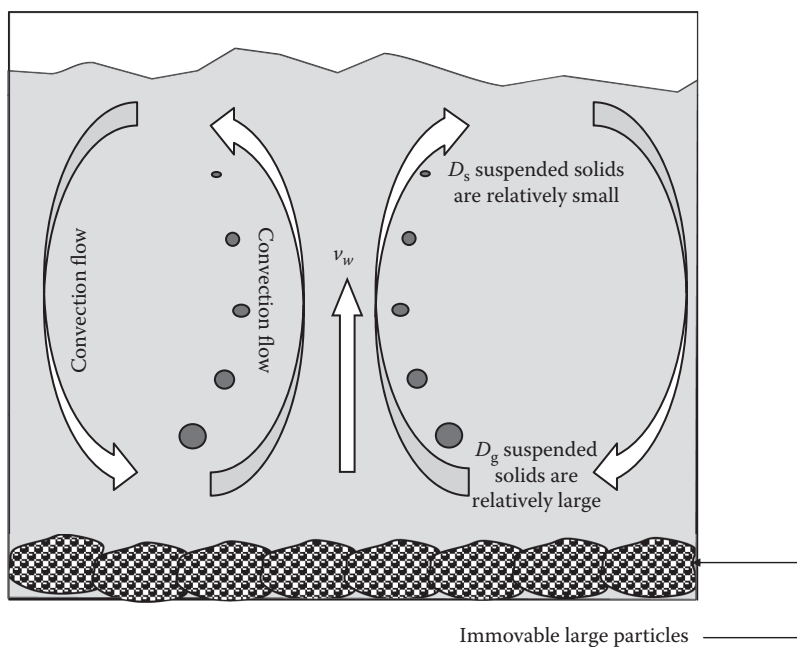


FIGURE 13.13

Concept for suspending smaller particles by forced convection flow.

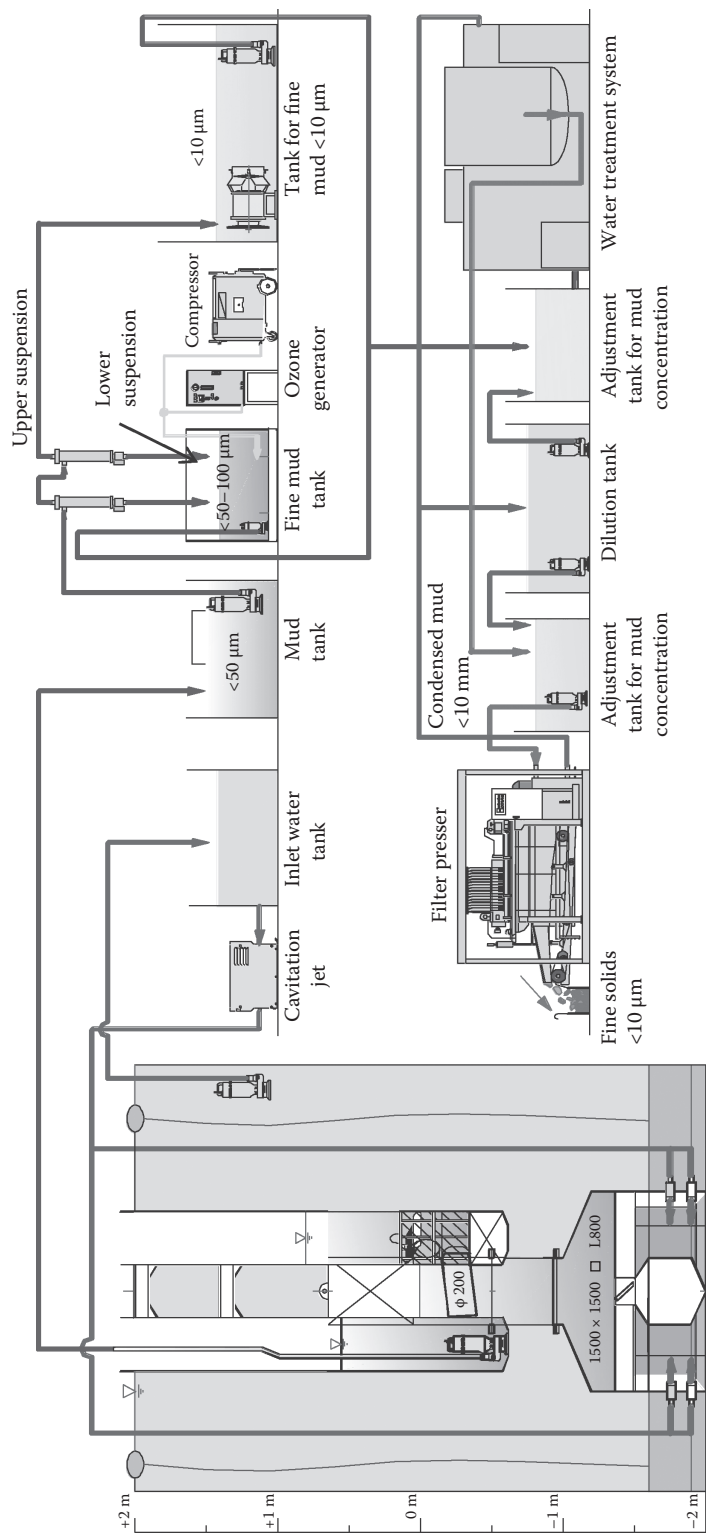


FIGURE 13.14 Schematic of remediation for vast quantities of contaminated soils and sediments used by Aomi Construction of Japan. (Adapted from Fukue, M. et al., *Marine Georesources and Geotechnology*, 30, 222–233, 2012.)

13.3. Energy will be required to separate the smaller particles from the coarse particles to disperse them. Experience showed that cavitation is much more effective than water jetting for the separation of particles. This may be because cavitation acts as a tensile force for the detachment of particles (Fukue et al., 2012).

13.6.4 Technological Images

For vast surface areas and for vast volumes of contaminated soils, a primary objective for remediation of the affected soils is to reduce the volume of contaminated soils. The same holds for contaminated sediments. To achieve this we need to separate contaminated fractions from the noncontaminated fractions. The schematic rendering of the elements of the remediation system, developed by Aomi Construction, Japan (Figure 13.14) shows the technology consisting of four types of activities: separation, segregation, filtration, and dilution (when required). The technology has been successfully applied for removal of organic matter and fine particles from the bottom sediments in Fukuyama Port, Japan (Fukue et al., 2012). For soils contaminated with radioactive substances, a closed system is required together with the proper monitoring system to ascertain complete removal of health-threatening issues.

13.6.4.1 Demonstration Pilot Tests on Contaminated Sediments and Soils

The techniques used in the demonstration pilot tests on contaminated sediments are instructive inasmuch as they serve to inform one on how the system shown in Figure 13.14 would perform with contaminated soils. In the pilot tests that used a prototype of the system shown in Figure 13.15, the contaminated sediments were placed in the segregation tank and for dispersion by water jets that induced cavitation (116 L/min). In the siphon typed rod, smaller particles (less than 75 μm) were pumped in to the separation tank to remove floating material from the pumped mud water. To separate floating material, a 0.5 mm mesh was used, as shown in Figure 13.15. The suspension with particles greater than 10 μm was separated by the cyclone (120–250 L/min) and was moved into the tanks for fine mud. The supernatant was reused for water jetting. These procedures were repeated and the sediments in the segregation tank were segregated into very fine or fine mud by sedimentation process in the fine mud tank.

The grain size distribution curves for the suspended solids at various stages are shown in Figure 13.16. The original sample soil was silty sand. The sediment after cavitation treatment was sand without a fine fraction. Suspensions at a low level in the cyclone contained silt fractions with a little amount of clay fractions. The suspension at the top of the cyclone consisted of clayey silt without sand and gravel fractions. Thus, the pumped suspension—i.e., upper and lower suspensions in the cyclone—contained only clay and silt fractions. Thus, fine and coarse fractions of the sampled soil were well separated by the cavitation and the cyclone treatments.

The effects of cavitation and supersonic separation were examined independently in the laboratory. For cesium-contaminated soils, the procedures for measuring ^{134}Cs and ^{137}Cs of different samples are shown in Figure 13.17, where sample A is the original contaminated soil and sample B is obtained from the sediments after the treatment by cavitation. The sediments in the cavitation treatment tank were moved into the ultrasonic treatment tank. Samples C to G were obtained from the sediments at different times (3, 6, 9, 12, and 15 min) during the ultrasonic treatment. Sample H consists of fine fractions settled in the flocculation tank following flocculant addition and sample W was obtained from the solution in

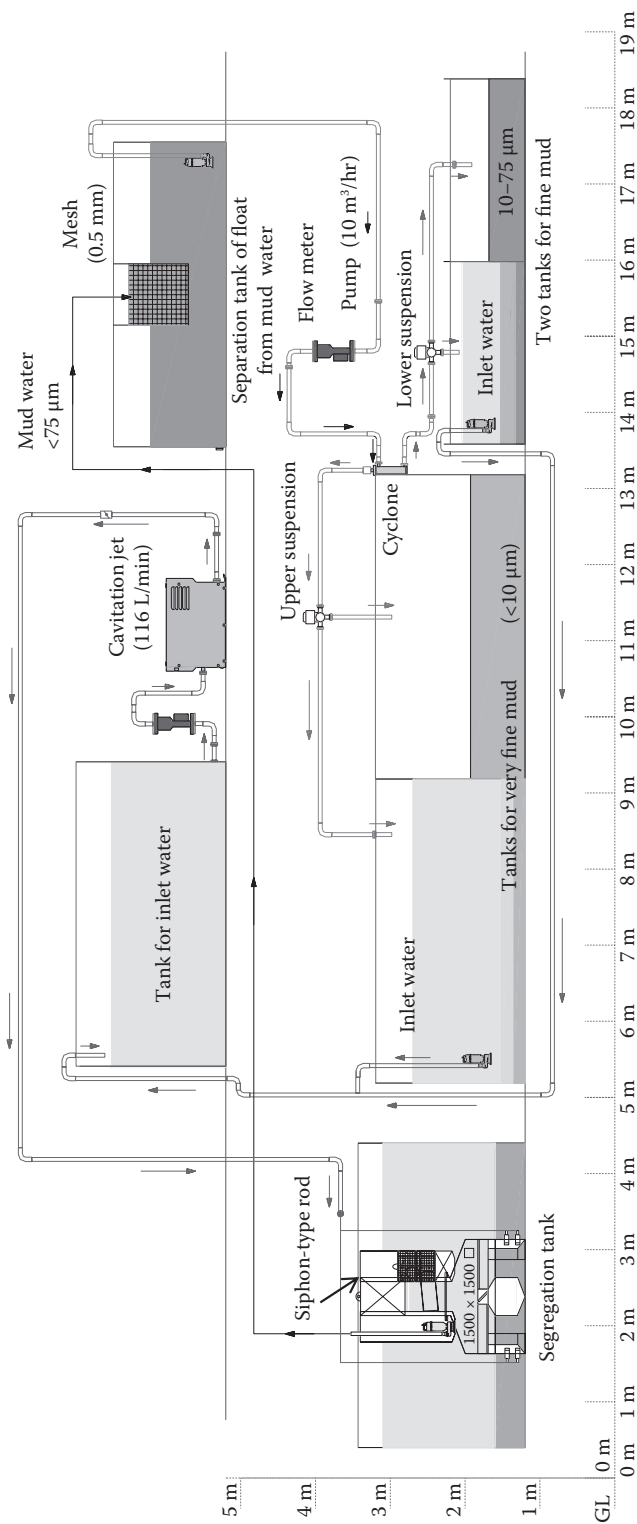
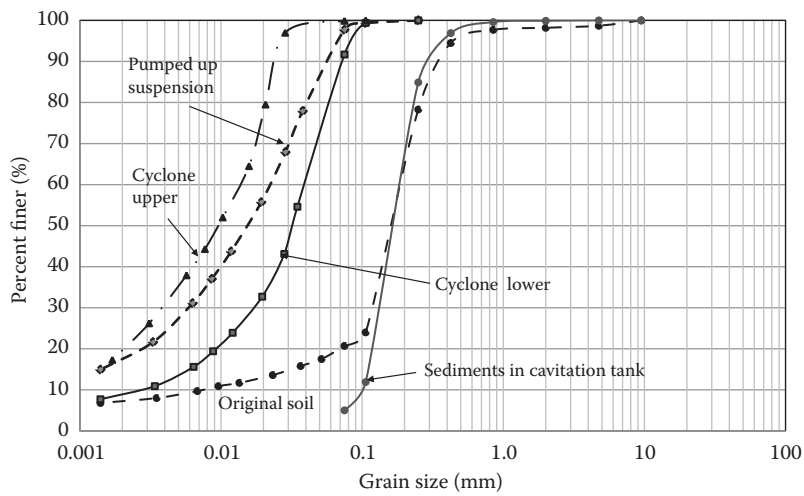
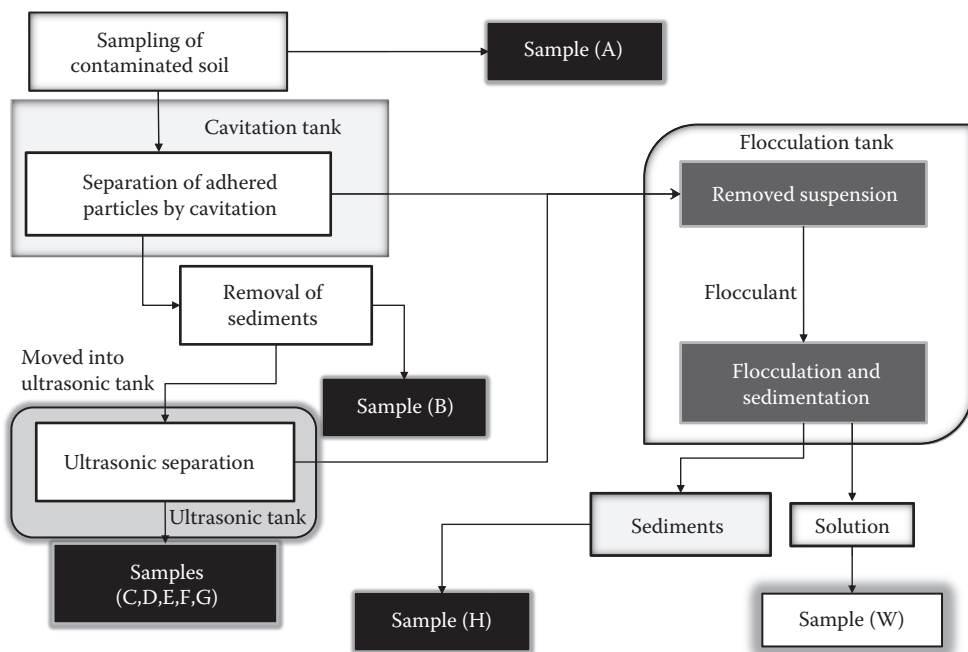


FIGURE 13.15
Elements of prototype system used for treatment of contaminated sediments.

**FIGURE 13.16**

Grain size distribution curves at various stages of pilot test treatment.

**FIGURE 13.17**

Measurement procedures for obtaining samples following cavitation and ultrasonic treatments.

the flocculation tank. This sample (sample W) was found to consist primarily of water, with concentrations of ^{134}Cs and ^{137}Cs in the undetectable range ($<10\text{ Bq/L}$).

The results shown in Figure 13.18 indicate that the concentrations of ^{134}Cs and ^{137}Cs for the various samples obtained at different treatment stages, cavitation treatment and removal of fine fractions could effectively decrease the concentrations of the radioactive cesium (Sample B). The decrease of radioactive concentrations resulting from the removal of fine suspended solids after cavitation treatment was 90.3% for both the ^{134}Cs and ^{137}Cs . The effects of ultrasonic treatment followed by cavitation treatment for the coarse fractions are not as effective (Samples from C to G).

13.6.4.2 Full-Scale Application

In full-scale application, carrying on from the pilot tests into actual performance, the procedure will consist of separating fine particles from the coarser materials, by cavitation, ultrasonic treatment, deposition using the flocculants, and pressing. As far as cesium-contaminated surface soils are concerned, water treatment is not necessary when the deposition of suspended solids is performed using flocculants. The pilot study shows that approximately 20% of the original sample in weight was separated from the original soils, and that the separated fine fractions maintained a high concentration of radioactivity, meaning that the residual sand and gravel fractions in the original soil material were remediated. However, the concentrations of radioactive cesium in the remaining fine particles after cavitation and ultrasonic treatments showed approximately 200 Bq/kg in ^{134}Cs and 350 Bq/kg in ^{137}Cs .

13.6.4.3 Assessment of Sustainable Practice Success

The goal of remediating vast surface areas of contaminated surface layer soils requires one to reduce the huge quantities of contaminated material as part of the treatment process

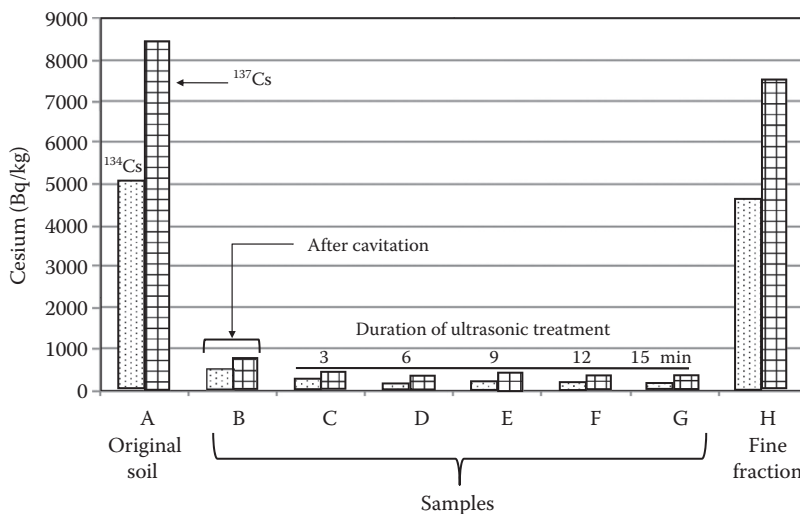


FIGURE 13.18

Results of the cavitation and ultrasonic treatments of samples contaminated with ^{134}Cs and ^{137}Cs .

that will remove the contaminants in the soil. Reduction of the huge quantities must be accompanied by removal or remediation of the removed quantities, meaning that the material removed must meet regulatory requirements for “clean” soils. This kind of process can be applied as an *ex situ* treatment procedure for contaminated soils from all kinds of locations and depths, namely, a process to remove the finer fractions that will likely have greater concentrations of contaminants attached to the particles from a contaminated soil while leaving the coarser fractions relatively clean. In other words, volume reduction of contaminated soil can be achieved. The question of whether the remaining fine particles are still contaminated (partially or completely) will depend on the nature of the fine particles and also the kind of contaminants adsorbed by the fines.

13.7 Concluding Remarks: Sensible Practice for a Sustainable Geoenvironment

It is clear that so long as depletion of the nonrenewable natural resources contained within the geoenvironment occurs, sustainability of the geoenvironment cannot be attained. When one adds the burden of natural catastrophic disasters and their consequences together with physical, chemical, and biological impacts to the geoenvironment from the various stressors described in the previous chapters, it becomes all the more evident that geoenvironmental sustainability is an impossible dream. One has two simple choices: (1) to concede that the sustainability of the geoenvironmental resources that provide society with its life-support systems cannot be realized and prepare to face the inevitable or (2) to correct those detrimental elements that can be corrected and to find substitutes, and alternatives to replace the depleting geoenvironmental resources. The material in this book is a first step in a long series of required steps in adoption of the second choice.

It has been argued that if the global population were to be reduced to some small limiting size, say in the order of just over a billion people, and if replacements or substitutes for the nonrenewable resources can be found, sustainability can be achieved. Working on the assumption that this will not likely happen, we have chosen to address the problem of protection of the geoenvironmental base that provides society with its life-support systems. The need to protect the environment and especially the natural resources that provide the basis for the sustenance and well-being of society is eminently clear. The subject addressed in this book is a difficult one, not only from the viewpoint of the basic science–engineering relationships involved in ameliorating adverse impacts on the geoenvironment, but as much or more so from the fact that many crucial elements contributing to the generation of these same impacts could not be properly addressed. This is a fact and a realization that many of these elements were either not within the purview of this book (especially the critical subject of biological diversity) or were elements that were dictated by forces influenced by business, public awareness, and political will. Prominent among these are (a) social–economic factors and business–industrial attitudes and relationships, (b) public attitudes, awareness, sensitivity, and commitment, and (c) political awareness and will.

In adopting the second choice, we have focused on the importance of the geoenvironment as a resource base for (a) provision of the required sustenance of the human population and (b) production of energy and goods. We have attempted to develop a better understanding of the stressors on the geoenvironment and to lay emphasis on the need

to better manage the geoenvironmental natural renewable and nonrenewable resources. Again, the absence of discussion relating to the direct primary sources of stressors such as the decision-makers responsible for the upstream and downstream industries, means that this book can only provide the geoenvironmental perspective on results of the main impacts resulting from these stressors. The oceans and the coastal marine environments are also significant resource bases, and are essential components of the life support for the human population and must not be neglected.

Outside of the calamitous natural events in the very recent years, in the form of earthquakes, hurricanes, landslides, floods, etc., that have caused death and severe distress to countless numbers of unfortunate humans, it is seen that contamination of air, land, and water resources is the greatest anthropogenic threat to the human population and the geoenvironment. The various discards, spills, and loss of materials (chemicals, etc.) and discharge of wastes, either in liquid form or as solids, are common to all types of human activities within (a) the built urban environment, (b) mineral and hydrocarbon exploitation, (c) agricultural ecosystem, and (d) industries. Some of these activities include wastewater discharges, use of nonrenewable resources as energy input and also as raw materials for the industries, injection wells, leachates from landfills and surface stockpiles, open dumps, illegal dumping, underground storage tanks, pipelines, train accidents, irrigation practices, gaseous and noxious particulate airborne emissions, production wells, hydraulic fracking, use of pesticides and herbicides, urban runoff, mining activities, etc. These pose significant threats to the land environment and the receiving waters, and to the inhabitants of these environments.

The degree of environmental impact due to contaminants in a contaminated ground site is dependent on (a) the nature and distribution of the contaminants, (b) the various physical, geological and environmental features of the site, and (c) existent land use. Through management and education, the sources of contamination must be controlled to maintain water quality and supply for future generations. Environmental management including various remediation and impact assessment and avoidance tools have been developed that technology can develop such as the development of renewable resources replacements for the nonrenewable resources that are being depleted. Mitigation and management of contaminants in the subsoil should seek to reduce and eliminate the presence of contaminants in the soil. Engineering the natural attenuation capability of soils, through enhancements of the attenuation capability with geochemical, biological, and nutrient aids will provide greater management options. Considerable attention needs to be paid to many of these issues by researchers, policy makers, and other professionals to alleviate the stresses to the geosphere and seek sustainability and innovative and non-conventional ways are needed for society to live in harmony with the environment now and in the future.

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FIGURE 3.4
Iron runoff from a coal mine into canal area.

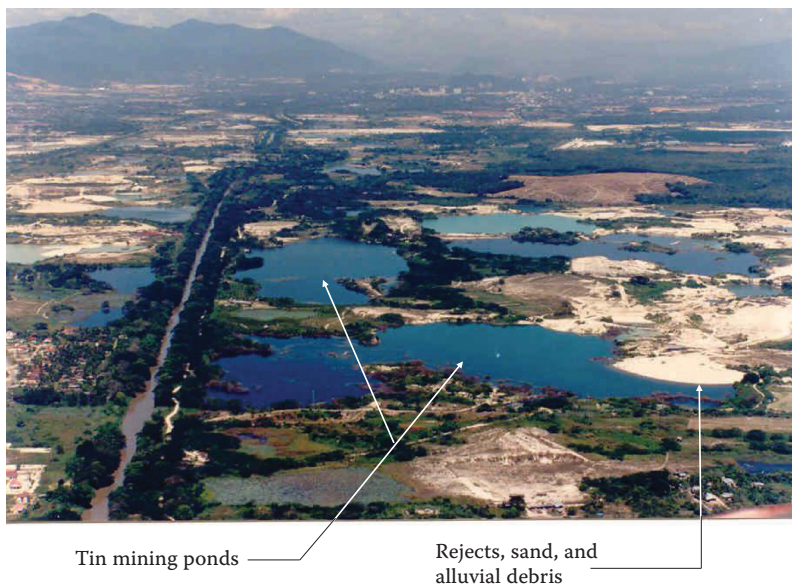


FIGURE 5.15
Tin mining slurry ponds obtained as a result of hydraulic dredging and pumping. Reclamation of ponds is necessary to accommodate expansion of housing units seen at left of the picture (and left of the canal).

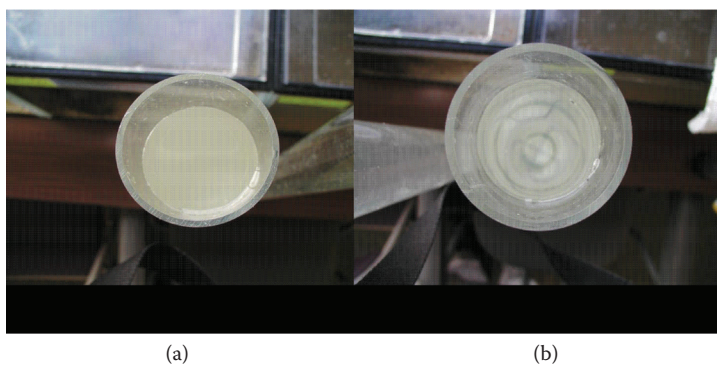


FIGURE 8.15

Plastic cylinders showing (a) nonfiltered and (b) filtered seawater obtained with purification units in the purification vessel.



FIGURE 12.7

Calcirudite cemented with calcite as a result of the precipitation of carbonate.

Sustainable Practices in Geoenvironmental Engineering

In the seven years since the publication of the first edition of ***Sustainable Practices in Geoenvironmental Engineering***, the combination of population growth and increased exploitation of renewable and non-renewable natural resources has added increased stresses on the quality and health of the geoenvironment. This is especially true when viewed in the context of the growing demand for food and shelter, energy and mineral resources, and their resultant effects on the natural capital of the geoenvironment. Completely revised and updated, this second edition of a bestseller introduces and discusses the concept of “stressors” and their impacts on the geoenvironment.

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The authors explore the technologies that take into account targets, exposure routes (if applicable), future land use, acceptable risks, legislation, and resultant emissions/discharges in establishing the criteria and tools for evaluating technologies and protocols for environmental management of the impacted land. They then discuss how to choose the correct ones to use in different situations to protect the quality and health of natural resource and capital of the geoenvironment and ensure that these geoenvironmental natural resources and capital remain available for future generations and to develop innovative and sustainable techniques to make land more stable and safer.



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