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Environmental and Pollution Science
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Third Edition

Environmental and Pollution Science

MARK L. BRUSSEAU, IAN L. PEPPER, CHARLES P. GERBA

The much anticipated revision of this essential book on pollution and the environment, covering pollution in the air, in water or impacting the land from fundamental knowledge to sustainable options

Environmental and Pollution Science, Third Edition continues its tradition on providing readers with the scientific basis to understand, manage and mitigate pollution across the environment, be it air, land or water. Pollution comes from a wide variety of sources, both natural and anthropogenic, and in a wide variety of forms including, biological, chemical, particulate or even energy, making a multivariate approach to assessment and mitigation essential for success. This third edition has been updated and revised to include issues which have become more prominent when addressing pollution from sustainability of solutions to ecosystem services to environmental justice. Environmental and Pollution Science, Third Edition is designed to give readers the tools to be able to understand and implement multi-disciplinary approaches to help solve current and future environmental pollution problems.

Key Features:

- Emphasizes conceptual understanding of environmental impacts and can be used by students and professionals from a diversity of backgrounds focusing on the environment
- Covers many aspects critical to assessing and managing environmental pollution including characterization, risk assessment, regulation, fate and transport and remediation or restoration
- New topics to this edition include Urban Pollution, Household Pollution, Ecosystem Services, Sustainability, Pollution in the Global System, and the interrelation between Soil and Human Health as well as Environmental Health and Community Engagement
- Includes color photos and diagrams, chapter questions and problems, and highlighted key words

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THIRD EDITION

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Dedication

"I dedicate this to my Dad, Howard Brusseau"

Mark L. Brusseau

"My first viable memory is crawling in the dirt as an infant, in between rows of vegetables in my father's garden. Since then I have always been involved with earth, so I dedicate this book to soil."

Ian L. Pepper

"To Peggy, Peter, and Phillip for putting up with me all these years."

Charles P. Gerba

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Dr Mark Brusseau's work is focused on developing a fundamental understanding of the physical, chemical, and biological factors and processes influencing the transport and fate of contaminants in the subsurface environment. At the university he also teaches courses on Contaminant Transport in Porous Media as well as Soil and Groundwater Remediation. He has published over 250 works and is a fellow of the American Geophysical Union and the Soil Science Society of America.

Dr. Ian Pepper is currently Professor at the University of Arizona. He is also Director of the University of Arizona, Environmental Research Laboratory (ERL) and the NSF Water and Environmental Technology (WET) Center. Dr. Pepper is an environmental microbiologist specializing in the molecular ecology of the environment. His research has focused on the fate and transport of pathogens in air, water, soils, and wastes. His expertise has been recognized by membership on six National Academy of Science Committees and former memberships on an EPA FIFRA Science and Advisory Panel. Dr. Pepper is a Fellow of the American Association for the Advancement of Science, American Academy of Microbiology, the Soil Science Society of America, and the American Society of Agronomy. He is also a Board Certified Environmental Scientist within the American Academy of Environmental Engineers and Scientists. He is the author or coauthor of six textbooks, 40 book chapters, and over 180 peer-review journal articles.

Dr. Charles P. Gerba is a Professor at the University of Arizona. He conducts research on the transmission of pathogens through the environment. His recent research encompasses the transmission of pathogens by water, food, and fomites; fate of pathogens in land applied wastes; development of new disinfectants; domestic microbiology and microbial risk assessment. He has been an author on more than 500 articles including several books in environmental microbiology and pollution science. He is a fellow of the American Academy of Microbiology and the American Association for the Advancement of Science. In 1998 he received the A. P. Black Award from the American Water Works Association for outstanding contributions to water science and in 1996 he received the McKee medal from the Water Environment Federation for outstanding contributions to groundwater protection. He received the 1999 Award of Excellence in Environmental Health from National Association of County and City Health Officials.

Preface

This textbook focuses on (i) the continuum of the environment, namely, the lithosphere, hydrosphere, atmosphere, biosphere, and technosphere epitomized by the term "Environmental Science"; (ii) science-based aspects concerning pollution of and disturbances to the environment; and (iii) the human dimensions to pollution. The textbook is designed to provide the scientific knowledge necessary to understand complex pollution issues; to support sound decision-making; and to develop effective, sustainable solutions for managing, mitigating, and preventing environmental pollution.

In general, pollution can be defined as the accumulation and adverse interaction of contaminants within the environment. Pollution is ubiquitous and can occur on or within land, oceans, or the atmosphere. Contaminants can consist of chemical compounds/elements, biological entities, particulate matter, or energy, and they may be of natural or anthropogenic origin. In addition to pollution, environmental systems can be disturbed by other means, such as persistent drought or habitat destruction. Pollution and other disturbances of the environment can have numerous negative consequences for human health and well-being. Given the complexities of environmental systems and of the interactions between humans and the environment, multidisciplinary approaches are needed to address environmental pollution issues. This text provides a rigorous science-based integration of the physical, chemical, and biological properties and processes that influence the environment and that also affect the transport and fate of contaminants in the environment. It also incorporates the human dimensions, which are critical to a full understanding of pollution issues and the development of successful solutions.

Part I of the text covers the fundamental concepts of environmental and pollution science. Within that section, the properties of environmental systems are presented as well as the various processes that affect the transport and fate of pollutants within the environment. Part II covers the various types and sources of pollution. Part III is focused on the treatment and reuse of wastes, and the reclamation, remediation, and restoration of polluted and otherwise disturbed environments. Part IV highlights the human dimensions of pollution.

This text is designed for a science-based junior/senior-level undergraduate course or introductory graduate course. Students that will benefit from this text originate from a variety of science backgrounds, including environmental science, microbiology, hydrology, earth science, geography, social and political sciences, and environmental engineering. The text will also serve as an introductory text for those with nonscience backgrounds.

This third edition represents a continued evolution of "Pollution Science," which was published in 1996, and the second edition of "Environmental and Pollution Science," published in 2006. New and significantly revised material introduced in this third edition includes the following. Chapter 6, Ecosystems and Ecosystem Services, is a new chapter that presents the principles and concepts of ecology and the services that ecosystems provide. Chapter 20, Ecosystem Restoration and Land Reclamation, is greatly revised and expanded to cover the primary methods used for reclamation and restoration of terrestrial and aquatic systems. Chapter 25, Pollution and Environmental Perturbations in the Global System, is updated and expanded to focus attention on the interconnectedness of human activities and global-scale effects. Chapter 26, Environmental Human Health, is a new chapter focused on the impacts of pollution and other disturbances to human health and well-being. Chapter 27, Medical Geology and the Soil Health:Human Health Nexus, is a new chapter that illustrates how the natural environment can impact human health in both positive and negative ways. Chapter 31, Environmental Justice, is a new chapter highlighting how pollution and its many impacts are distributed unevenly among the human population, with the most vulnerable generally being impacted the greatest. Finally, Chapter 32, Sustainable Development and Other Solutions to Pollution and Global Change, is a new chapter focused on the various methods we have available to reduce, mitigate, and manage the impacts of human activities on the environment.

Ultimately, we hope this text will illustrate that the integration of physical, chemical, earth, and biological sciences with engineering, health, and social sciences can be successfully accomplished, thereby inspiring readers to implement inter-, multi-, and transdisciplinary solutions for past, present, and future environmental pollution issues.

Mark L. Brusseau,
Ian L. Pepper and Charles P. Gerba

Part I

Fundamental Concepts

Chapter 1

The Extent of Global Pollution

M.L. Brusseau, I.L. Pepper and C.P. Gerba

Pollution is ubiquitous, and can even cause beautiful sunsets. *Photo courtesy Ian Pepper.*

1.1 THE SCIENCE OF POLLUTION

Pollution is ubiquitous and takes many forms and shapes. For example, the beautiful sunsets that we may see in the evening are often due to the interaction of light and atmospheric contaminants, as illustrated in the photo above.

Pollution can be defined as the accumulation and adverse effects of contaminants or other constituents on human health and welfare, and/or the environment. But in order to truly understand pollution, we must define the identity and nature of potential contaminants. Contaminants can result from waste materials produced from the activity of living organisms, especially humans. However, contamination can also occur from natural processes such as arsenic dissolution from bedrock into groundwater or air pollution from smoke that results from natural fires.

The major categories of pollutants and their predominant routes of human exposure are illustrated in Fig. 1.1. Clearly, many of the agents identified in Fig. 1.1 are generated directly through human activities such as manufacturing, mining, or agriculture. However, pollution is also produced as an indirect result of human activity. For example, fossil fuel burning increases atmospheric carbon dioxide levels and increases global climate change. Global climate change, in turn, can create or exacerbate existing pollution.

Many contaminants are chemicals, either naturally occurring or synthetic (human made). Chemical contaminants can occur in the environment in the solid, liquid, or gaseous state. Some common chemical contaminants that find their way into the environment, with the potential to adversely affect human health and well-being, are presented in Table 1.1. Physical contaminants also exist, such as dust particles, heat, and noise. There are also biological contaminants, such as pathogenic microorganisms. Some examples of microbial pathogens and associated diseases are given in Table 1.2.

In this textbook, we will discuss the many different sources and types of pollution in a science-based context, hence the name: *Environmental and Pollution Science* (Information Box 1.1). Pollution in the environment, and the impacts on human health and environmental quality, is a very complex and challenging issue. The many diverse scientific disciplines needed to study pollution are shown in Fig. 1.2. It is the holistic integration of these diverse and complex entities that presents the means to understanding both Environmental and Pollution Science, and ultimately solving pollution issues.

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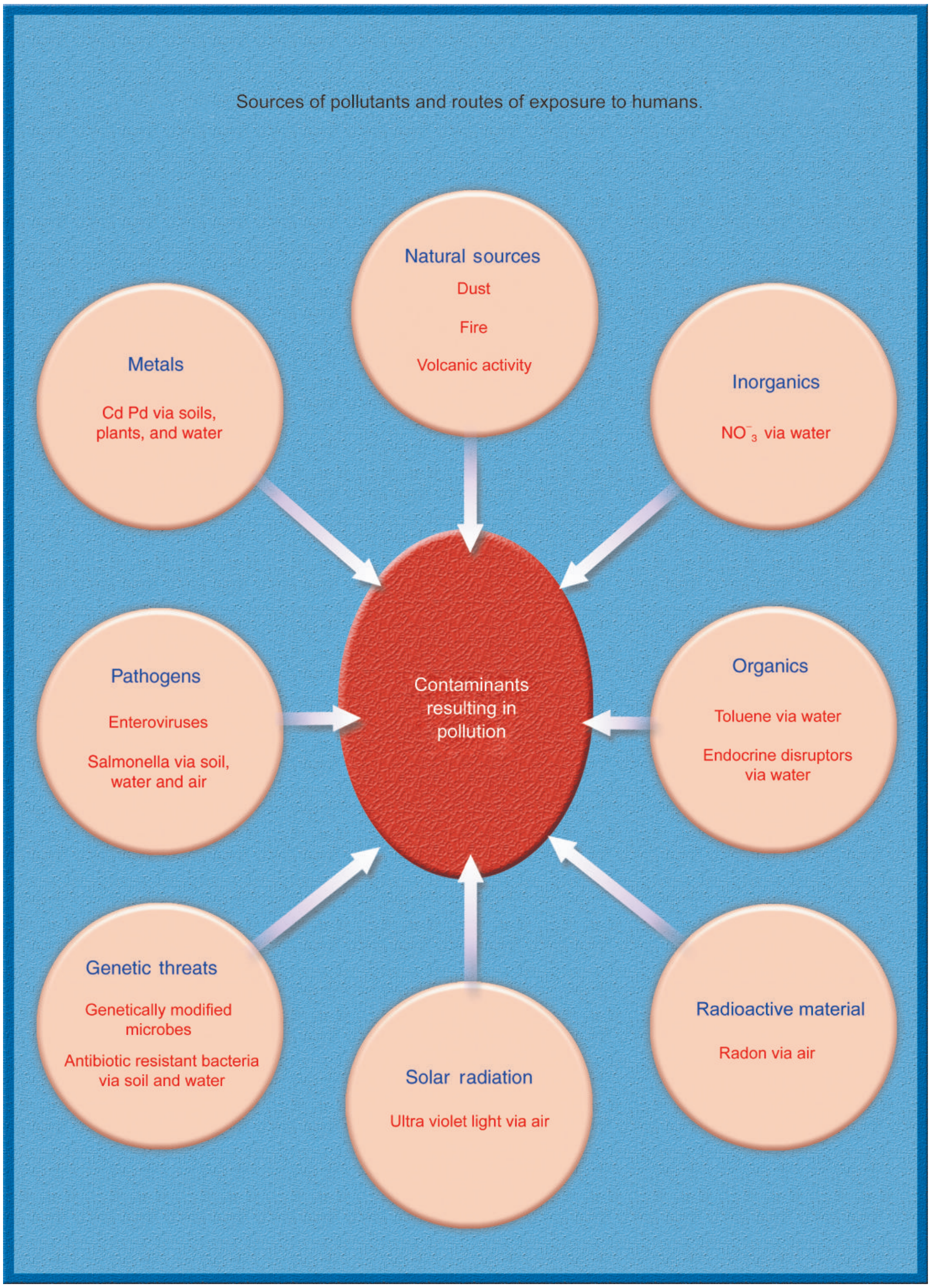

FIG. 1.1 Major sources of pollutants. *(From* Environmental and Pollution Science *© 2006, Academic Press, San Diego, CA.)*

1.2 ENVIRONMENTAL INTERACTIONS

We know that pollution can have negative impacts on environmental quality, producing for example, contaminated air or water. But, the environment itself plays a key role in the fate of pollutants, and thus mediates their impacts on the environment (and ultimately on humans). The environment consists of land, water, the atmosphere, and the biosphere. All sources of pollution are initially released into one of these phases of the environment. The environment thus acts as a receptacle into which all pollutants are placed. As

TABLE 1.1 Common Organic and Inorganic Contaminants Found in the Environment

Chemical Class	Frequency of Occurrence
Gasoline, fuel oil	Very frequent
Polycyclic aromatic hydrocarbons	Common
Creosote	Infrequent
Alcohols, ketones, esters	Common
Ethers	Common
Chlorinated organics	Very frequent
Polybrominated diphenyl ethers (PBDEs)	
Polychlorinated biphenyls (PCBs)	Infrequent
Nitroaromatics (TNT)	Common
Metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn)	Common
Nitrate	Common

From *Environmental Microbiology* © 2000, Academic Press, San Diego, CA.

TABLE 1.2 Microbes That Have had a Significant Impact on Human Health

Agent	Mode of Transmission	Disease/Symptoms
Rotavirus	Waterborne	Diarrhea
Legionella	Waterborne	Legionnaire's disease
Escherichia coli O157:H7	Foodborne Waterborne	Enterohemorrhagic fever, kidney failure
Hepatitis E virus	Waterborne	Hepatitis
Cryptosporidium	Waterborne	Diarrhea
	Foodborne	
Calicivirus	Waterborne	Diarrhea
	Foodborne	
Helicobacter pylori	Foodborne	Stomach ulcers
	Waterborne	
Cyclospora	Foodborne	Diarrhea
	Waterborne	

pollutants interact with the environment, they undergo physical and chemical changes, and are ultimately incorporated into the environment. The pollutants obey the conservation of mass law: matter cannot be destroyed; it is merely converted from one form to another. Thus, taken together, the manner in which pollutants are added to the environment, the rate at which these pollutants are added, and the subsequent changes that occur within the environment determine the ultimate impact of the pollutant on the environment, and concomitantly on humans and other organisms.

INFORMATION BOX 1.1

Environmental and Pollution Science is the study of the physical, chemical, and biological processes fundamental to the transport, fate, and mitigation of contaminants that arise from human activities as well as natural processes.

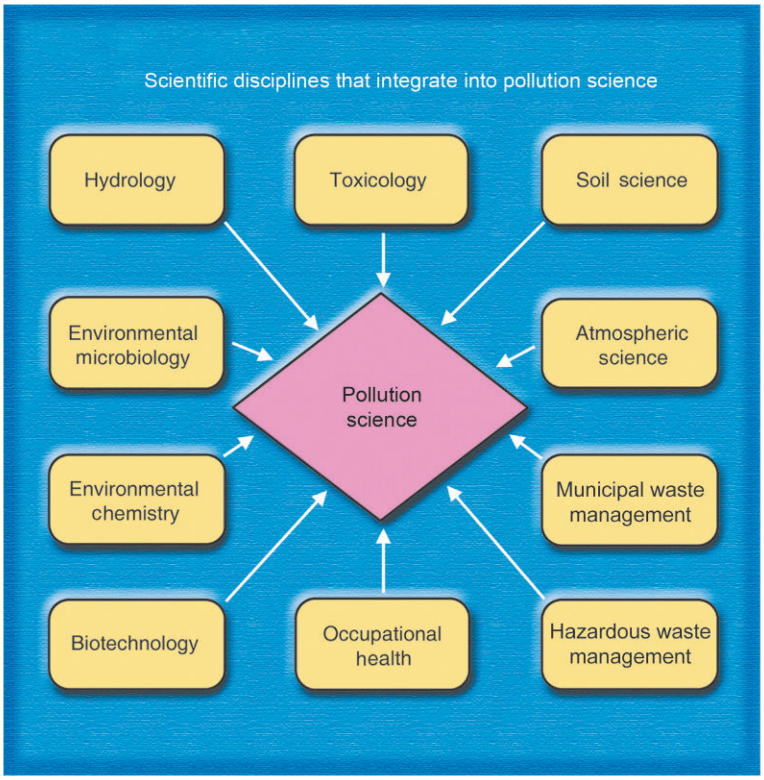

FIG. 1.2 The disciplines of pollution science. *(From* Environmental and Pollution Science *© 2006, Academic Press, San Diego, CA.)*

1.3 POLLUTION AND POPULATION PRESSURES

To understand the relationship between population and pollution, let us examine a typical curve for the growth of a pure culture of bacteria in a liquid medium (Fig. 1.3). Early on, the bacteria growing in the medium do not increase significantly in number, due to low initial population densities. Under these conditions, the organisms have minimal impact on each other or their environment. This initial low-growth phase is known as the *lag period*. Next, the number of organisms increases exponentially for a finite period of time. This phase of growth is known as the *exponential phase* or *log phase*. After this exponential phase of growth, a *stationary phase* occurs, during which the total number of organisms remains constant as new organisms are constantly being produced while other organisms are dying. Finally, we observe the *death phase*, in which the total number of organisms decreases. We know that bacteria reproduce by binary fission, so it is easy to see how a doubling of bacteria occurs during exponential growth. But what causes the stationary and death phases of growth? Two mechanisms prevent the number of organisms from increasing ad infinitum: first, the organisms begin to run out of nutrients; and second, waste products build up within the growth medium and become toxic to the organisms.

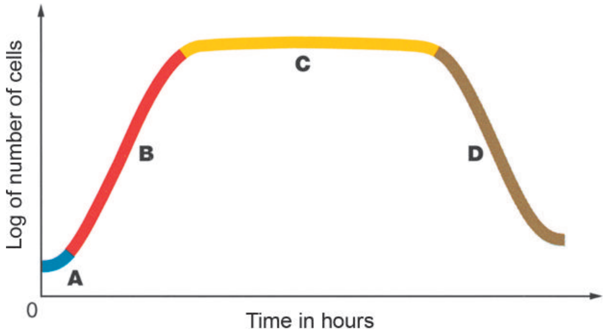

FIG. 1.3 Typical growth curve for a pure culture of bacteria. A = lag period, B = exponential phase, C = stationary phase, D = death phase. *(From* Pollution Science *© 1996, Academic Press, San Diego, CA.)*

An analogous situation exists for humans. Initially, in prehistoric times, population densities were low and population numbers did not increase significantly or rapidly (Fig. 1.4.). During this time resources were plentiful; thus the environment could easily accommodate the numbers of humans present and the amount of wastes they produced. Later, populations began to increase very rapidly. Although not exponential, this phase of growth was comparable to the log phase of microbial growth. During this period then, large amounts of resources were used, and wastes were produced in ever-greater quantities. This period of growth is still under way. However, we seem to be approaching a

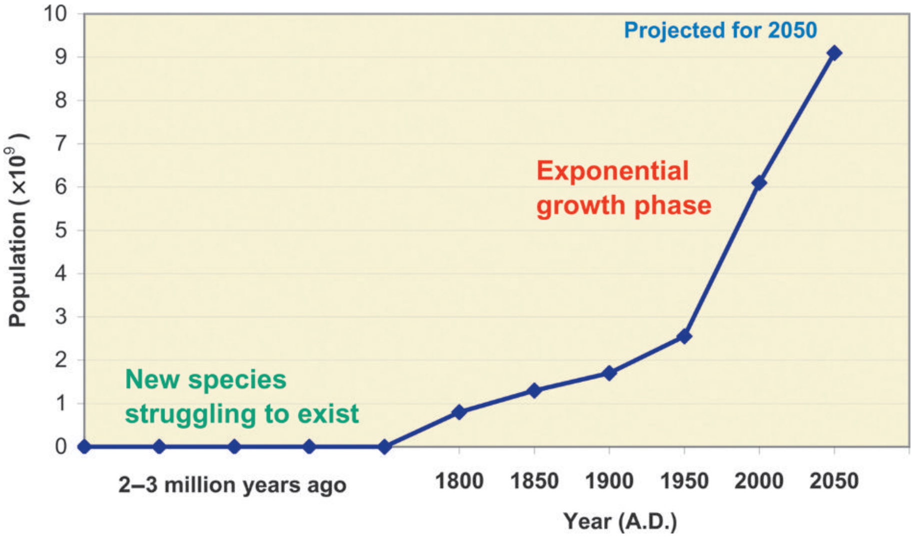

FIG. 1.4 World population increases from the inception of the human species. *(From Population Reference Bureau, Inc., 1990. Adapted from* Pollution Science *© 1996, Academic Press, San Diego, CA.)*

period in which lack of resources or buildup of wastes (i.e., pollution) will limit continued growth—hence the great interest in recycling materials as well as in controlling, managing, and cleaning up waste materials—what is termed sustainable development. To do this, we must have a clear understanding of the biotic and abiotic characteristics of the environment and the hydrobiogeochemical processes occurring therein.

Currently, the world population is 7.6 billion and increasing rapidly. This population pressure has caused intense industrial, resource extraction, and agricultural activities that produce hazardous contaminants in their own right. In addition, increased populations result in the production of greater amounts of wastes. Finally, note that as the world population increases, people tend to relocate from sparsely populated rural areas to more congested urban centers or "mega-cities." Typically, urbanized areas consume more natural resources and produce more waste per capita than rural areas. The continued trend toward mega-cities will intensify this problem.

1.4 THE HUMAN DIMENSIONS TO POLLUTION

Poor management of waste materials, overuse of resources, and uncontrolled development all have negative impacts on the environment. These impacts reverberate throughout the environment, leading to impaired soil, water, and air quality; damaged habitats; and stress to wildlife populations. These impacts, in turn, have a myriad of direct and indirect effects on humans. The presence of pollutants may cause illness and even death for some members of an exposed population. This is a direct consequence of pollution. The presence of pollution in a particular environmental medium reduces the quality of that medium, which makes it less available and usable for humans, possibly leading to scarcity of that resource. This in turn may affect human well-being, which is an indirect consequence. Similarly, overuse of a particular resource can lead to scarcity, and hence indirect effects on human health and well-being.

For example, consider people living in a small town that uses groundwater as their sole potable water source. If that groundwater is unknowingly contaminated with a carcinogenic compound, some of the population may develop cancer after a long period of groundwater use. Once the contaminant is identified, its presence may prevent further use of that water source if it is too difficult or costly to treat the contamination. This contamination then reduces the availability of potable water, which may lead to water scarcity, depending upon the availability of alternate water sources. Let us say that the town switches to a local surface water reservoir for their potable water. If they use the water at a rate greater than it is replenished, they will eventually arrive at a condition where their only other source of potable water is depleted, possibly affecting the very viability of that town.

From the above we see that human activities that create pollution and resource-scarcity issues are posing direct and indirect threats to their own health and well-being. Thus it is in our own best interests to reduce our impacts on the environment. The impacts of humans on the environment, the resultant effects on humans of these impacts, and how humans respond to these issues constitute what we may call the *human dimensions to pollution*.

1.5 ORGANIZATION OF TEXTBOOK AND NEW MATERIAL

The focus of the text will be to identify the basic scientific processes that control the transport and fate of pollutants in the environment. We will also define the potential for adverse effects to human health and well-being. Finally, we will present and discuss various approaches for mitigating the effects of pollution and cleaning up contaminated environments.

Part I of the text covers the fundamental concepts of pollution science. Within that section, the properties of environmental systems are presented as well as the various processes that affect the transport and fate of pollutants within the environment. Part II covers the various types and sources of pollution. Part III is focused on the treatment and reuse of wastes, and the reclamation, remediation, and restoration of polluted and otherwise disturbed environments. Part IV highlights the human dimensions of pollution.

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We hope that the revised and expanded third edition enhances the contributions of the text to improved understanding of environmental systems and the development of innovative solutions to pollution issues in the 21st century.

Chapter 2

Physical-Chemical Characteristics of Soils and the Subsurface

I.L Pepper and M.L. Brusseau

Cover Art: Photograph of top soil. *Source: (https://en.wikipedia.org/wiki/Topsoil)*

2.1 SOIL AND SUBSURFACE ENVIRONMENTS

The human environment is located at the earth's surface and is heavily dependent on the soil/water/atmosphere continuum. Ultimately, this continuum moderates all of our activities, and the physical, chemical, and biological properties of each component are interactive. Soil is the thin veneer of material that covers much of the earth's surface. This fragile part of the earth's skin is frequently less than a meter thick, yet is absolutely vital for human life. It has a rich texture and fragrance and teems with plants, insects, and microorganisms. Young and Crawford (2004) described it as "the most complicated biomaterial on the planet." The complexity of soil is driven by two components: the abiotic soil architecture; and biotic diversity, which is driven and supported by large amounts of energy from the sun through photosynthesis. Bacterial diversity in soil ranges from 2000 to 8.3 million per gram of soil depending on the measurement methods used (Roesch et al., 2007). This diversity results in bacterial populations of 10^8–10^{10} per gram of soil (Pepper et al., 2015). Integrated together these components result in amazing physical, chemical, and biological heterogeneity among soils globally. The geological zone between the land surface and groundwater consists of unsaturated material and is known as the *vadose zone*. A subset of the vadose zone is the near-surface *soil* environment, which is in direct contact with both surface water and the atmosphere. Since pollutants are often disposed of into surface soils, the transport of these contaminants into both the atmosphere and groundwater is influenced by the properties of soil and the vadose zone. In addition, since plants are grown in surface soils, the potential for uptake of contaminants such as heavy metals by plants is also controlled by soil properties.

Soil is an intricate, yet durable entity that directly and indirectly influences our quality of life (Pepper, 2013). Colloquially known as dirt, soil is taken for granted by most people, and yet it is essential to our daily existence. It is responsible for plant growth, for the cycling of all nutrients through microbial transformations, for maintaining the oxygen/carbon dioxide balance of the atmosphere; it is also the ultimate site of disposal for most waste products. Soil is a complex mixture of weathered rock particles, organic residues, water, and billions of living organisms. It can be as thin as six inches or it may be hundreds of feet thick. Generally, most soils are 2–3 ft in depth. Because soils are derived from unique sources of parent material under specific environmental conditions, no two soils are exactly alike. Hence, there are literally thousands of different kinds of soils just within the United States. These soils have different properties that influence the way soils are used optimally.

Soil is the weathered end-product of the action of climate and living organisms on soil parent material with a particular topography over time. We refer to these factors

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INFORMATION BOX 2.1 The five soil forming factors

- *Parent Material*: The risk and mineral base from which soil is formed through weathering.
- *Climate*: Precipitation and temperature and particularly important in weathering of parent material.
- *Organisms*: Plants, animals, and microbes add organic matter and aid in decomposition and nutrient cycling that are part of the weathering process.
- *Topography*: In particular the site slope angle and length.
- *Time*: Essential for the soil weathering process, soils generally form more rapidly in warm environments than in cold ones.

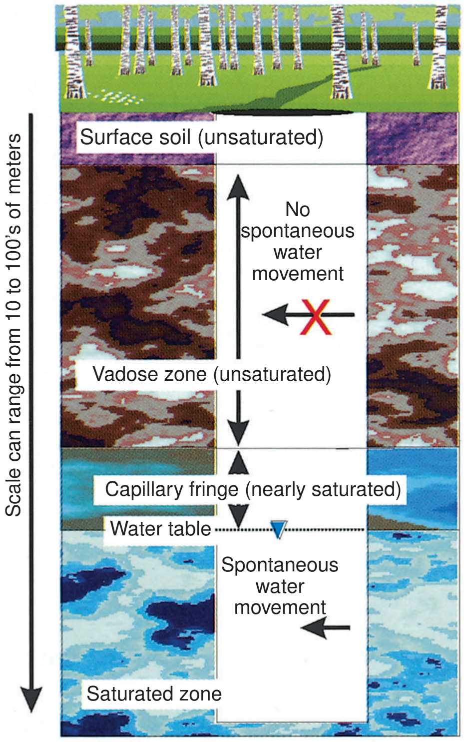


FIG. 2.1 Cross section of the subsurface showing surface soil, vadose zone, and saturated zone. *(Adapted from Environmental Microbiology, © 2000, Academic Press, San Diego, CA.)*

as the five *soil-forming factors* (Information Box 2.1). The biotic component consists of both microorganisms and plants. The *vadose zone* is the water-unsaturated and generally unweathered material between groundwater and the land surface. The major difference between a surface soil and a vadose zone is the fact that the vadose zone parent material has generally not been recently modified by climate. A model of a cross section of a typical subsurface environment is shown in Fig. 2.1.

2.1.1 Vadose Zone

The *vadose zone* is defined as the subsurface unsaturated oligotrophic environment that lies between the surface soil and the saturated zone. The vadose zone contains mostly unweathered parent material and has a very low organic carbon content (generally $<0.1\%$). Thus the availability of carbon and micronutrients is very limited compared with that of surface soils. The thickness of the vadose zone varies considerably. When the saturated zone is shallow or near the surface, the unsaturated zone is narrow or sometimes even nonexistent, as in a wetland area. In contrast, there are many arid or semiarid areas of the world where the unsaturated zone can be hundreds of meters thick. These unsaturated regions, especially deep unsaturated regions, may receive little or no moisture recharge from the surface, and normally have limited microbial activity because of low nutrient and/or moisture status. However, these regions are receiving more attention from a biogeochemical and site-remediation perspective because pollutants that are present from surface contamination must pass through the vadose zone before they can reach groundwater (Fig. 2.2).

There are several parameters of soil that vitally affect the transport and fate of environmental pollutants. We will now discuss these parameters while providing an overview of soil as a natural body as it affects pollution.

2.2 SOLID PHASE

2.2.1 Soil Profiles

The process of soil formation generates different horizontal layers, or *soil horizons*, that are characteristic of that particular soil. It is the number, nature, and extent of these horizons that give a particular soil its unique character. A typical soil profile is illustrated in Fig. 2.3. Generally, soils contain a dark organic-rich layer, designed as the O horizon, then a lighter colored layer, designated as the A horizon, where some humified organic matter accumulates. The layer that underlies the A horizon is called the E horizon because it is characterized by *eluviation*, which is the process of removal or transport of nutrients and inorganics out of the A horizon. Beneath the E horizon is the B horizon, which is characterized by *illuviation*. Illuviation is the deposition of the substances from the E horizon into the B horizon. Beneath the B horizon is the C horizon, which contains the parent material from which the soil was derived. The C horizon is generally unweathered or minimally weathered parent material. Although certain diagnostic horizons are common to most soils, not all soils contain each of these horizons.

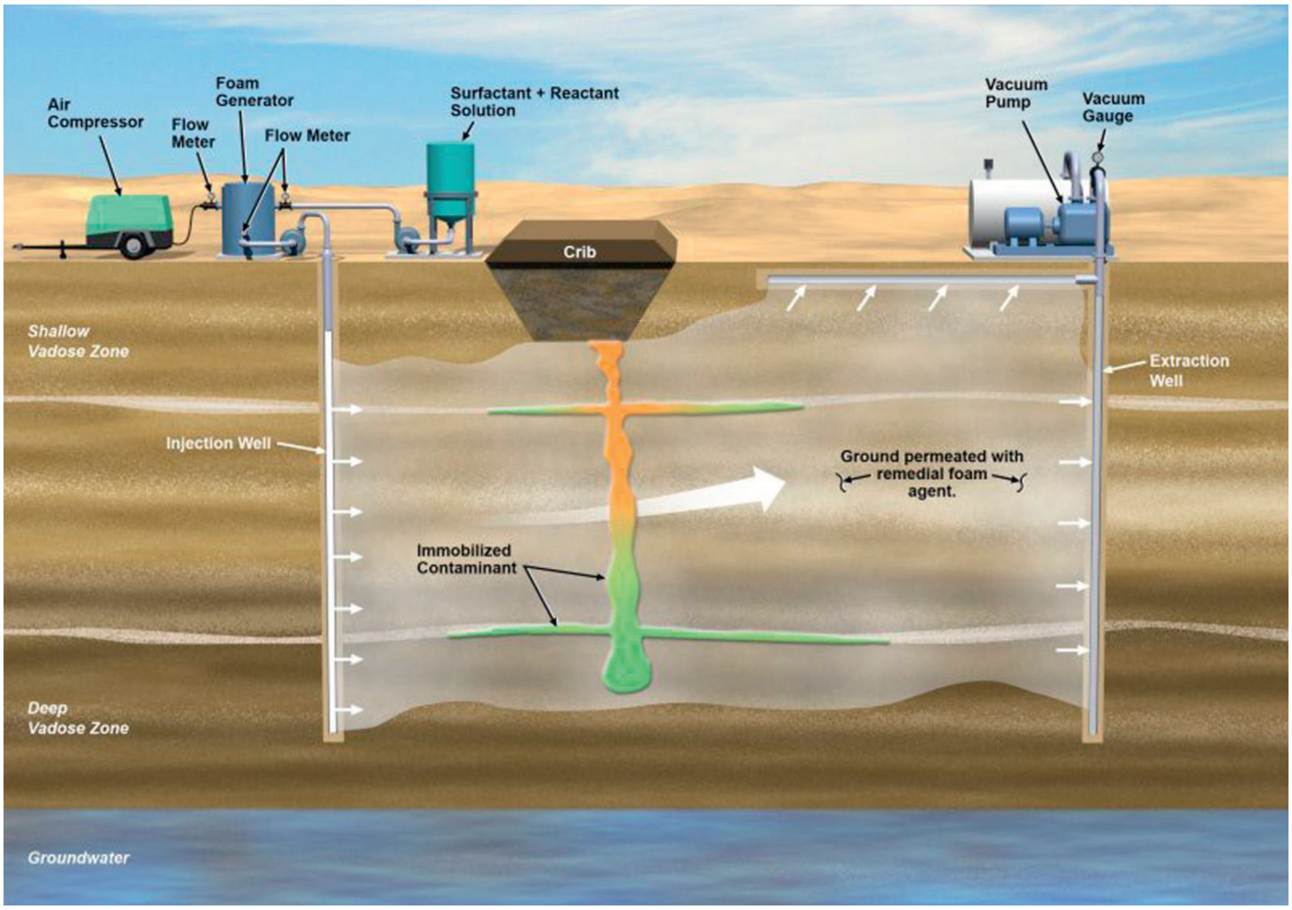


FIG. 2.2 Delivery of remedial solutions through a heterogeneous deep vadose zone to remove contaminants. *(Source: Pacific Northwest National Laboratory. From Environmental Microbiology, © 2015, Academic Press, San Diego, CA.)*

2.2.2 Primary Particles and Soil Texture

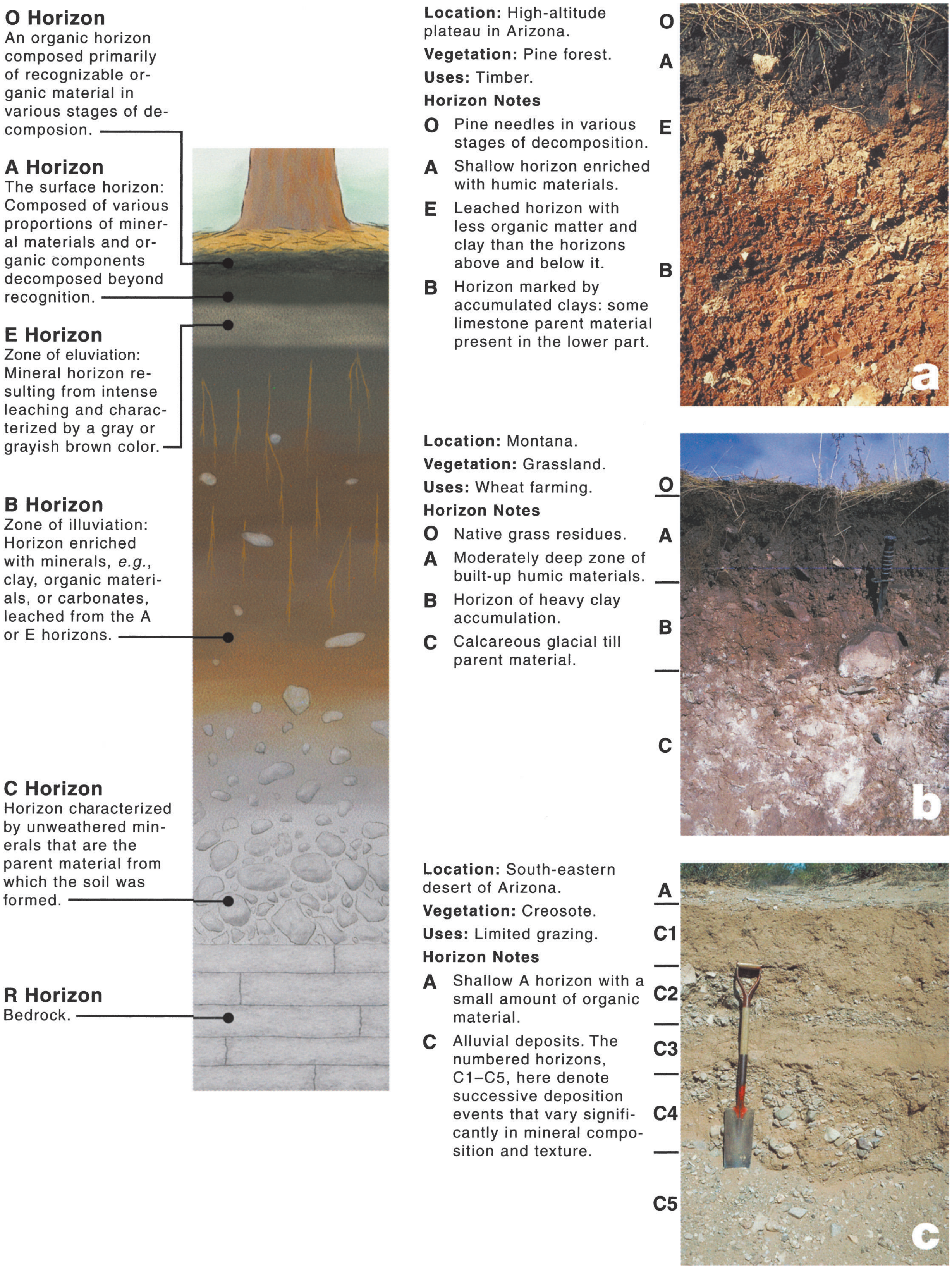
Typically, a soil contains 45%–50% solids on a volume basis (Fig. 2.4). Of this solid fraction, 95% to >99.9% is the mineral fraction. Silicon (47%) and oxygen (27%) are the two most abundant elements found within the mineral fraction of the earth's crust. These two elements, along with lesser amounts of other elements, combine in a number of ways to form a large variety of minerals. For example, quartz is SiO_2 and mica is $K_2Al_2O_5[Si_2O_5]_3Al_4(OH)_4$. These are primary minerals that are derived from the weathering of parent rock. Weathering results in mineral particles that are classified on the basis of three different sizes: sand, silt, and clay (Information Box 2.2). The distribution (on a percent by weight basis) of sand, silt, and clay within a porous medium defines its *texture*. Soils predominated by sand are considered coarse textured while those with higher proportions of silt and clay are known as fine textured.

The differences in the size of the particles are due to the weathering of the parent rock. Table 2.1 presents the size fractionation of soil constituents including mineral, organic, and biological constituents. This figure also illustrates the effect of size on specific surface area.

Soil texture affects many of the physical and chemical properties of the soil. Various mixtures of the three primary components result in different textural classes (Fig. 2.5). Of the three primary particles, clay is by far the dominant factor in determining a soil's properties. This is because there are more particles of clay per unit weight, than sand or silt, due to the smaller size of the clay particles. In addition, the clay particles are the primary soil particles that have an associated electric charge (see Chapter 8). The predominance of clay particles explains why any soil with >35% clay has the term *clay* in its textural class. In addition, because increases in soil clay concentrations result in increased surface area, this also increases the chemical reactivity of the soil (see Chapter 8).

2.2.3 Soil Structure

The three primary particles do not normally remain as individual entities. Rather, they aggregate to form secondary



O Horizon
An organic horizon composed primarily of recognizable organic material in various stages of decomposion.

A Horizon
The surface horizon: Composed of various proportions of mineral materials and organic components decomposed beyond recognition.

E Horizon
Zone of eluviation: Mineral horizon resulting from intense leaching and characterized by a gray or grayish brown color.

B Horizon
Zone of illuviation: Horizon enriched with minerals, *e.g.*, clay, organic materials, or carbonates, leached from the A or E horizons.

C Horizon
Horizon characterized by unweathered minerals that are the parent material from which the soil was formed.

R Horizon
Bedrock.

Location: High-altitude plateau in Arizona.
Vegetation: Pine forest.
Uses: Timber.
Horizon Notes

- **O** Pine needles in various stages of decomposition.
- **A** Shallow horizon enriched with humic materials.
- **E** Leached horizon with less organic matter and clay than the horizons above and below it.
- **B** Horizon marked by accumulated clays: some limestone parent material present in the lower part.

Location: Montana.
Vegetation: Grassland.
Uses: Wheat farming.
Horizon Notes

- **O** Native grass residues.
- **A** Moderately deep zone of built-up humic materials.
- **B** Horizon of heavy clay accumulation.
- **C** Calcareous glacial till parent material.

Location: South-eastern desert of Arizona.
Vegetation: Creosote.
Uses: Limited grazing.
Horizon Notes

- **A** Shallow A horizon with a small amount of organic material.
- **C** Alluvial deposits. The numbered horizons, C1–C5, here denote successive deposition events that vary significantly in mineral composition and texture.

FIG. 2.3 Typical soil profiles illustrating different soil horizons. These horizons develop under the influence of the five soil-forming factors and result in unique soils. (Source*: Pepper et al. (2006). From* Environmental Microbiology*, © 2015, Academic Press, San Diego, CA.)*

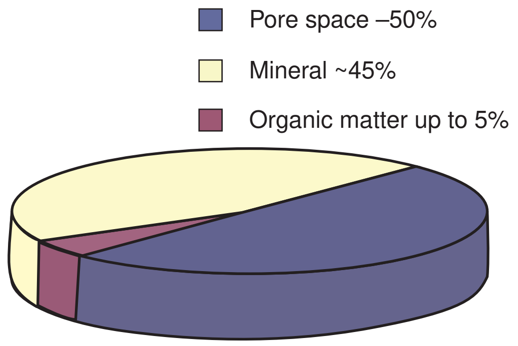


FIG. 2.4 Three basic components of a porous medium, such as a typical surface soil, on a volume basis. *(From* Environmental Microbiology, © *2015, Academic Press, San Diego, CA.)*

INFORMATION BOX 2.2 Primary mineral size classifications

Sand	0.05–2 mm
Silt	0.002–0.05 mm
Clay	< 0.002 mm (2 μm)

structures, which occur because microbial gums, polysaccharides, and other microbial metabolites bind the primary particles together. This results in soil architecture (Fig. 2.6). In addition, particles can be held together physically by fungal hyphae and plant roots, or chemically by precipitates (e.g., cementation). These secondary aggregates, which are known as *peds* (Fig. 2.7), can be of different sizes and shapes, depending on the particular soil. Soils with even modest amounts of clay usually have well-defined peds, and hence a well-defined *soil structure*. These aggregates of primary particles usually remain intact as long as the soil is not disturbed, for example, by plowing. In contrast, sandy soils with low amounts of clay generally have less well-defined soil structure.

The phenomenon of soil structure has a profound influence on the physical properties of the soil. Because its particles are arranged in secondary aggregates, a certain volume of the soil includes voids that are filled with either air (the soil atmosphere) or soil water. Soils in which the structure has many voids within and between the peds offer favorable environments for soil organisms and plant roots, both of which require oxygen and water. Soils with no structure, that is, those consisting of individual primary particles are characterized as *massive*. Massive soils have very small void spaces and therefore little room for air or water.

TABLE 2.1 Size Fractionation of Soil Constituents

Specific Surface area Using a Cubic Model	Soil		
	Mineral Constituents	Size	Organic and Biologic Constituents
$0.0003\,m^2/g$	Sand Primary minerals: quartz, silicates, carbonates	2 mm	Organic debris
$0.12\,m^2/g$	Silt Primary minerals: quartz, silicates, carbonates	50 μm	Organic debris, large microorganisms Fungi Actinomycetes Bacterial colonies
$3\,m^2/g$	Granulometric clay Microcrystals of primary minerals Phyllosilicates Inherited; illite, mica Transformed: vermiculite, high-charge smectite Neoformed; kaolinite, smectite Oxides and hydroxides	2 μm	Amorphous organic matter Humic substances Biopolymers
$30\,m^2/g$	Fine clay Swelling clay minerals Interstratified clay minerals Low range order crystalline compounds	0.2 μm	Small viruses

From *Environmental Microbiology*, © 2000, Academic Press, San Diego, CA.

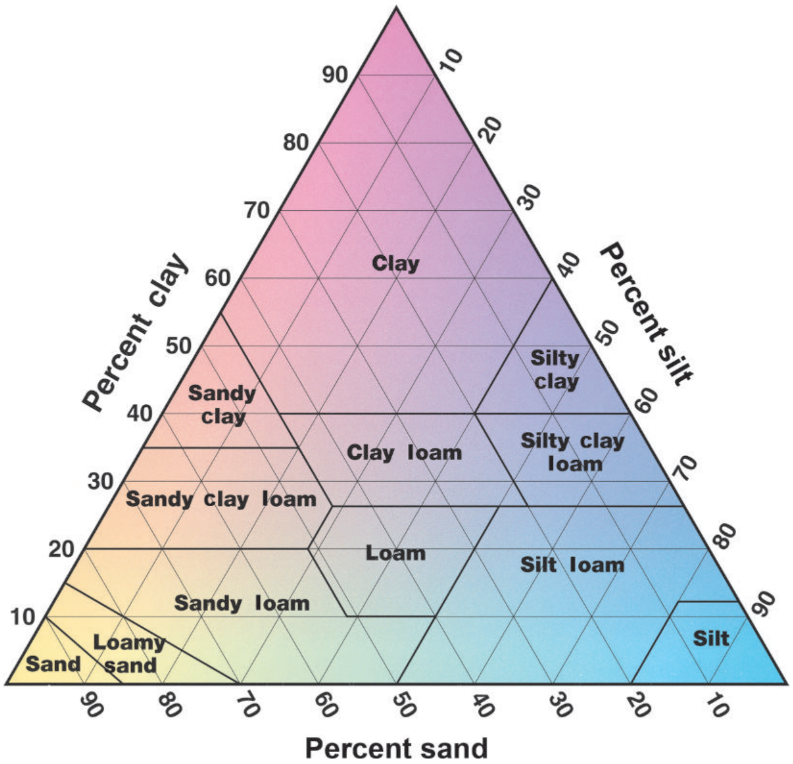


FIG. 2.5 A soil textural triangle showing different textural classes in the USDA system. These textural classes characterize soil with respect to many of their physical properties. *(From* Pollution Science, *© 1996, Academic Press, San Diego, CA.)*

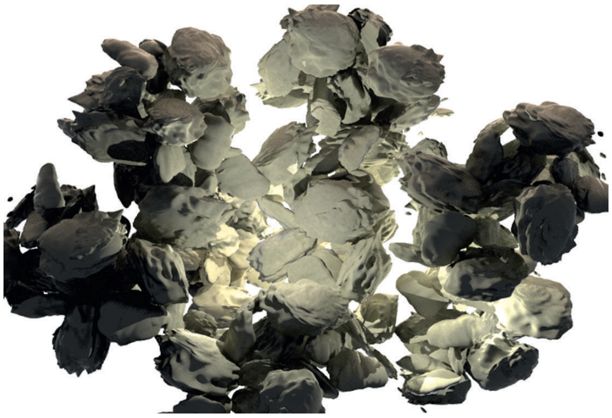


FIG. 2.6 Soil architecture resulting from secondary aggregate formation with intraaggregate and interaggregate pore space. *(Source: Pepper (2014). From* Environmental Microbiology, *© 2015, Academic Press, San Diego, CA.)*

FIG. 2.7 Soil structure results from secondary aggregates known as peds. *(From* Environmental Microbiology *© 2015, Academic Press, San Diego, CA.)*

Void spaces are known as *pore space* which is made up of individual pores. These pores allow movement of air, water, and microorganisms through the soil. Pores that exist between aggregates are called *interaggregate pores*, whereas those within the aggregates are termed *intraaggregate pores* (Fig. 2.8). Although the average pore size is smaller in a clay soil, there are many more pores than in a sandy soil, and as a result, the total amount of pore space is larger in a fine-textured (clay) soil than in a coarse-textured (sandy) soil (Fig. 2.9). However, because small pores do not transmit water as fast as larger pores, a fine-textured soil will slow the movement of any material moving through it, including air, water, and microorganisms (see Chapter 3). Sometimes fine-textured layers of clay known as *clay lenses* can be found within volumes of coarser materials resulting in heterogeneous environments. In this case, water will move through the coarser material and flow around the clay lens. This has implications of remediative strategies such as pump and treat,

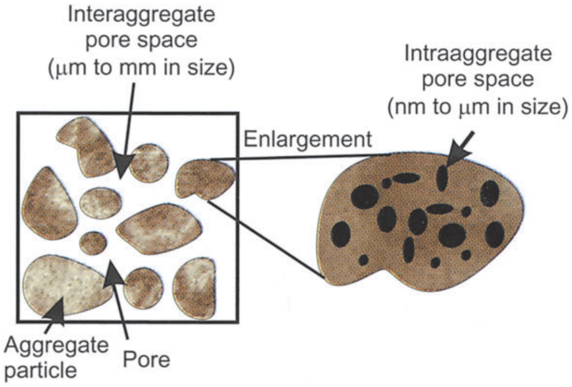


FIG. 2.8 Pore space. In surface soils, mineral particles are tightly packed together and even cemented in some cases with microbial polymers forming soil aggregates. The pore spaces between individual aggregates are called interaggregate pores and vary in size from micrometers to millimeters. Aggregates also contain pores that are smaller in size, ranging from nanometers to micrometers. These are called intraaggregate pores. *(From* Environmental Microbiology*, © 2015, Academic Press, San Diego, CA.)*

oxides. Substitution of a divalent magnesium cation (Mg^{2+}) for a trivalent aluminum cation (Al^{3+}) can result in the loss of one positive charge, which is equivalent to a gain of one negative charge. Other substitutions can also lead to increases in negative charge.

(II) *Ionization*: Hydroxyl groups (OH) at the edge of the lattice can ionize, resulting in the formation of negative charge:

$$Al + OH = Al + O^{-} + H^{+}$$

These are also known as *broken-edge bonds*. Ionizations such as these usually increase as the pH increases and are therefore known as *pH-dependent charge*. The functional groups of organic matter, such as carboxyl moieties, are also subject to ionization and can contribute to the total pH-dependent charge. The total amount of negative charge is usually measured in terms of equivalents of negative charge per 100 g of soil and is a measure of the potential CEC of the soil. A milliequivalent (meq) is one-thousandth of an equivalent weight. Equivalents of chemicals are related to hydrogen, which has a defined equivalent weight of 1. The equivalent weight of a chemical is the atomic weight divided by its valence. For example, the equivalent weight of calcium is 40/2 = 20 g. A CEC of 15–20 meq per 100 g of soil is considered to be average, whereas a CEC > 30 is considered high. Note that it is the clays and organic particles that are negatively charged. Due to their small particle size, they are collectively called the *soil colloids*. The existence of CEC allows the phenomenon of cation exchange to occur (see also Chapter 8).

How does the process of cation exchange work? Common soil cations such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and H^{+} that exist in the soil solution are in equilibrium with cations on exchange sites. If the concentration of a cation in the soil solution is changed, for example, increased, then that cation is likely to occupy more exchange sites, replacing existing cations within the site (Fig. 2.10). Thus

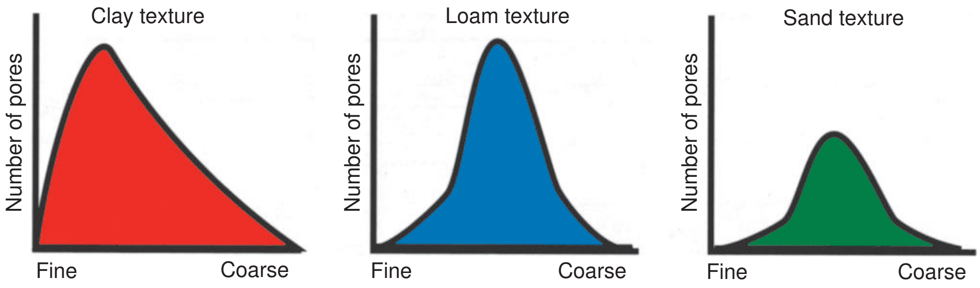


FIG. 2.9 Typical pore size distribution for clay-, loam-, and sand-textured horizons. Note that the clay-textured material has the smallest average pore size, but the greatest total volume of pore space. *(From* Environmental Microbiology*, © 2015, Academic Press, San Diego, CA.)*

which is used to remove contaminants from the saturated zone. Pore space may also be increased by plant roots, worms, and small mammals, whose root channels, worm holes, and burrows create macro openings. These larger openings can result in significant aeration of surface and subsurface soils and sediments, as well as *preferential flow* of water through the soil.

Together texture and structure are important factors that control the movement of water, contaminants, nutrients, and microbes through soils, and hence affect contaminant transport and fate.

2.2.4 Cation-Exchange Capacity

The parameter known as cation-exchange capacity (CEC) arises because of the charge associated with clay particles and other soil components. Normally, this is a negative charge that occurs for one of two reasons:

(I) *Isomorphic substitution*: Clay particles exist as inorganic lattices composed of silicon and aluminum

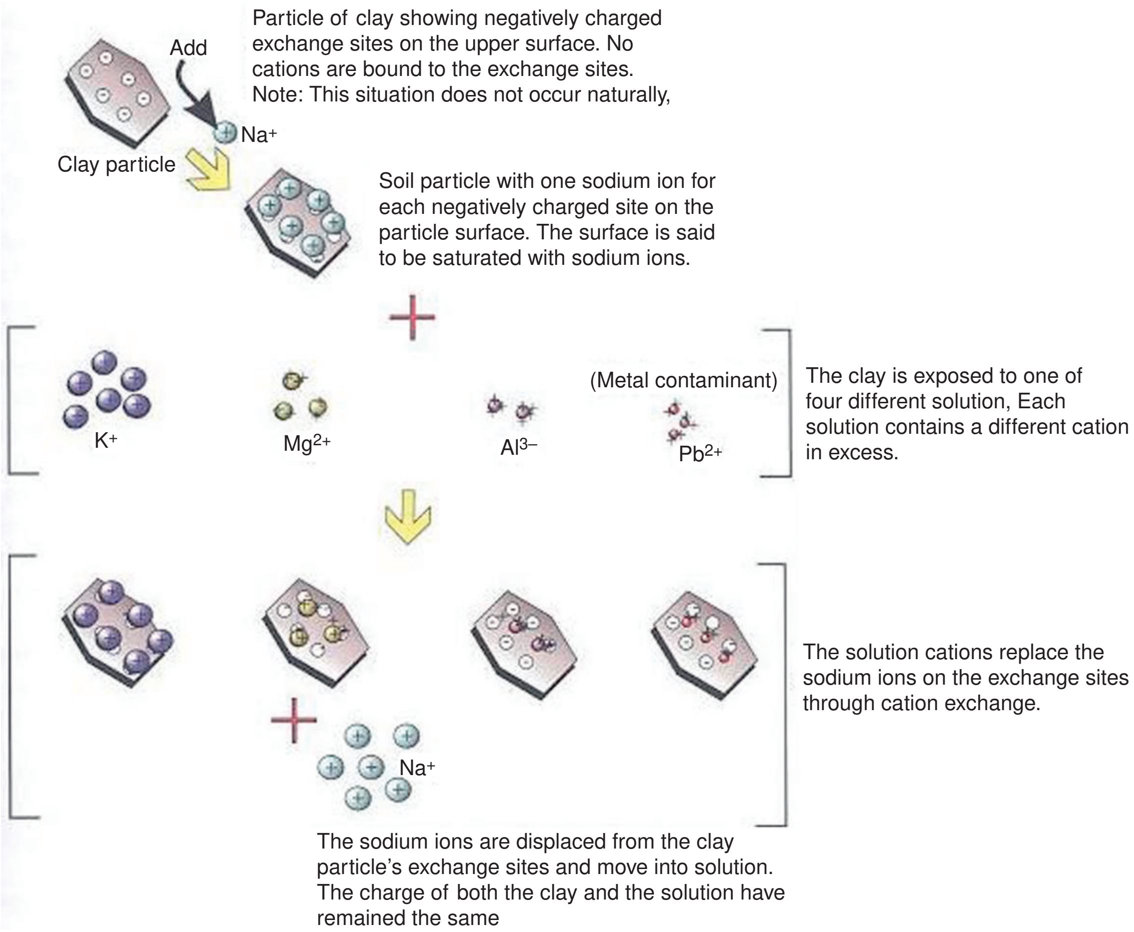


FIG. 2.10 Cation exchange on clay particles. *(Adapted from Pepper et al. (2006). From* Environmental Microbiology*, © 2015, Academic Press, San Diego, CA.)*

a monovalent cation such as K^+ can replace another monovalent cation such as Na^+, or two K^+ can replace one Mg^{2+}. Note however, that when working with charge equivalents, one milliequivalent of K^+ replaces one milliequivalent of Mg^{2+}. Cation exchange ultimately depends on the concentration of the cation in soil solution and the *adsorption affinity* of the cation for the exchange site. The adsorption affinity of a cation is a function of its charge density, which in turn depends on its total charge and the size of the hydrated cation. The adsorption affinities of several common cations are given in the following series in decreasing order:

$$Al^{3+} > Ca^{2+} = Mg^{2+} > K^+ = NH_4{}^+ > Na^+$$

Highly charged small cations such as Al^{3+} have high adsorption affinities. In contrast, monovalent ions have lower affinities, particularly if they are highly hydrated such as Na^+, which increases the effective size of the cation. The extensive surface area and charge of soil colloids (clays +organic material) are critical to microbial activity since they affect both binding or sorption of solutes and microbial attachment to the colloids.

Sorption is a major process influencing the movement and bioavailability of essential compounds and pollutants in soil. The broadest definition of *sorption* is the association of organic or inorganic molecules with the solid phase of the soil. For inorganic charged molecules, cation exchange is one of the primary mechanisms of sorption (Fig. 2.10). Generally, positively charged ions, for example, calcium (Ca^{2+}) or lead (Pb^{2+}), participate in cation exchange. Since sorbed forms of these metals are in equilibrium with the soil solution, they can serve as a long-term source of essential nutrients (Ca^{2+}) or pollutants (Pb^{2+}) that are slowly released back into the soil solution as the soil solution concentration of the cation decreases with time.

Attachment of microorganisms can also be mediated by cation bridging (Fig. 2.11) or by the numerous functional groups on clays (Fig. 2.11). Although the clay surface and microbial cell surface both have net negative charges, clay surfaces are neutralized by the accumulation of

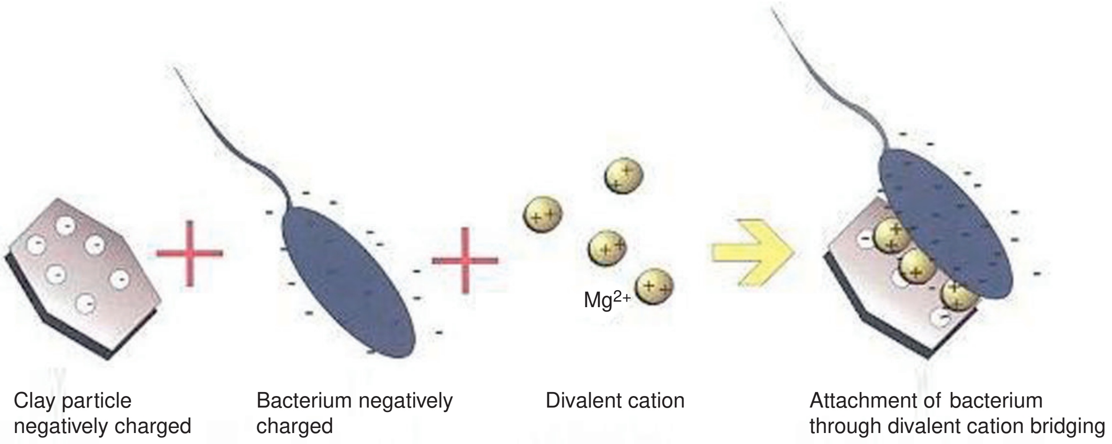


FIG. 2.11 Attachment of a bacterial cell to a clay particle via cation bridging. *(From* Environmental Microbiology, *© 2015, Academic Press, San Diego, CA.)*

positively charged counterions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}. Together, these negative and positive surface charges form what is called the *electrical double layer*. Similarly, microbes have an electrical double layer. The thickness of the clay double layer depends on the valence and concentration of the cations in solution. Higher valence and increased cation concentrations will shrink the electrical double layer. Because the double layers of the clay particles and microbial cells repel each other, the thinner these layers are, the less the repulsion between the clay and cell surfaces. As these repulsive forces are minimized, attractive forces such as electrostatic and van der Waals forces allow the attachment of microbial cells to the surface (Gammack et al., 1992). As a result, most microbes in terrestrial environments exist attached to soil colloids, rather than existing freely in the soil solution.

2.2.5 Soil pH

In areas with high rainfall, basic cations tend to leach out of the soil profile; moreover, soils developed in these areas have higher concentrations of organic matter, which contain acidic components and residues. Thus such soils tend to have decreased pH values and are acidic in nature. Soils in arid areas do not undergo such leaching, and the concentrations of organic matter are lower. In addition, water tends to evaporate in such areas, allowing salts to accumulate. These soils are therefore alkaline, with higher pH values.

Soil pH affects the solubility of chemicals in soils by influencing the degree of ionization of compounds and their subsequent overall charge. The extent of ionization is a function of the pH of the environment and the dissociation constant (pK) of the compound. Thus soil pH may be critical in affecting transport of potential pollutants through the soil and vadose zone.

We define pH as the negative logarithm of the hydrogen ion concentration:

$$pH = -\log[\mathrm{H}^+]$$

Usually, water ionizes to H^+ and OH^-:

$$HOH = \mathrm{H}^+ + OH^-$$

The *dissociation constant* (K_{eq}) is defined as

$$K_{eq} = \frac{[\mathrm{H}^+][OH]}{[HOH]} = 10^{-14}\ \mathrm{mol\ L^{-1}}$$

Since the concentration of HOH is large relative to that of H^+ or OH^-, it is normally given the value of 1; therefore

$$[\mathrm{H}][OH^-] = 10^{-14}\ \mathrm{mol\,L^{-1}}$$

For a neutral solution

$$[\mathrm{H}^+] = [OH^-] = 1 \times 10^{-7}$$

and

$$pH = -\log[\mathrm{H}^+] = -(-7) = 7$$

A pH value of <7 indicates acidity whereas a pH value >7 indicates alkalinity (or basicity) (Table 2.2).

2.2.6 Organic Matter

Organic compounds are incorporated into soil at the surface via plant residues, such as leaves or grassy material, and microorganisms. These organic residues are degraded microbially by soil microorganisms, which utilize the organics as food or microbial substrate. The main plant constituents, presented in Table 2.3, vary in degree of complexity and ease of breakdown by microbes. In general, soluble constituents are easily metabolized and break down rapidly, whereas lignin, for example, is very resistant to

TABLE 2.2 Soil pH Regimes

Soil	pH Regime
Acidic	>5.5
Neutral	6–8
Alkaline	>8.5

From *Pollution Science*, 8, 1996, Academic Press, San Diego, CA.

TABLE 2.3 Major Constituents of Plant Residues

Constituent	% Dry Weight
Cellulose	15–60
Hemicellulose	10–30
Lignin	5–30
Protein and nucleic acids	2–15
Soluble substances, for example, sugars	10

From *Pollution Science*, 8 1996, Academic Press, San Diego, CA.

microbial decomposition. The net result of microbial decomposition is the release of nutrients for microbial or plant metabolism, as well as the particle breakdown of complex plant residues. These microbial modified complex residues are ultimately incorporated into large macromolecules that form the stable basis of soil organic matter. This stable organic matrix is slowly metabolized by indigenous soil organisms, a process that results in about 2% breakdown of the complex materials annually. Owing to the slow but constant decomposition of the organic matrix and annual fresh additions of plant residues, an equilibrium is achieved in which the overall amount of soil organic matter remains constant. In humid areas with high rainfall, soil organic matter contents can be as high as 5% on a dry-weight basis. In arid areas with high rates of decomposition and low inputs of plant residues, values are usually <1%. The formation of soil organic matter is illustrated in Fig. 2.12, and terms used to define soil organic matter are given in Table 2.4.

The release of nutrients that occurs as plant residues degrade has several effects on soil. The enhanced microbial activity causes an increase in soil structure, which affects most of the physical properties of soil, such as aeration and infiltration. The stable humic substances contain many moieties that contribute to the pH-dependent CEC of the soil. In addition, many of the humic and nonhumic substances can complex or chelate heavy metals, and sorb organic contaminants. This retention affects their availability to plants and soil microbes as well as their potential for transport into the subsurface (see Chapter 6).

2.2.7 Vadose Zone Solid Phase

The *vadose zone* is defined as the unsaturated environment that lies between the surface soil and the saturated zone (groundwater). Physically, the vadose zone parent material may be very similar to that of the surface soil above it, except that it is less weathered and has very low organic matter content. In terms of texture, vadose zones normally contain larger rocks and cobbles than surface soils, but still have high amounts of sand, silt, and clay. The low organic content is due to the fact that organic material added to surface soils as vegetative leaf litter is usually degraded within the surface soil. Therefore the organic carbon content of vadose zones is usually very low. This leads to *oligotrophic* (low nutrient) conditions. Hence, microbial activity in vadose zones is normally lower than in surface soils (see also Chapter 5). This may affect the fate of subsurface organic contaminants since there may be decreased rates of biodegradation (see also Chapter 8).

2.3 GASEOUS PHASE

2.3.1 Constituents of Soil Atmosphere

Soil and the atmosphere are in direct contact; therefore most of the gases found in the atmosphere are also found in the air

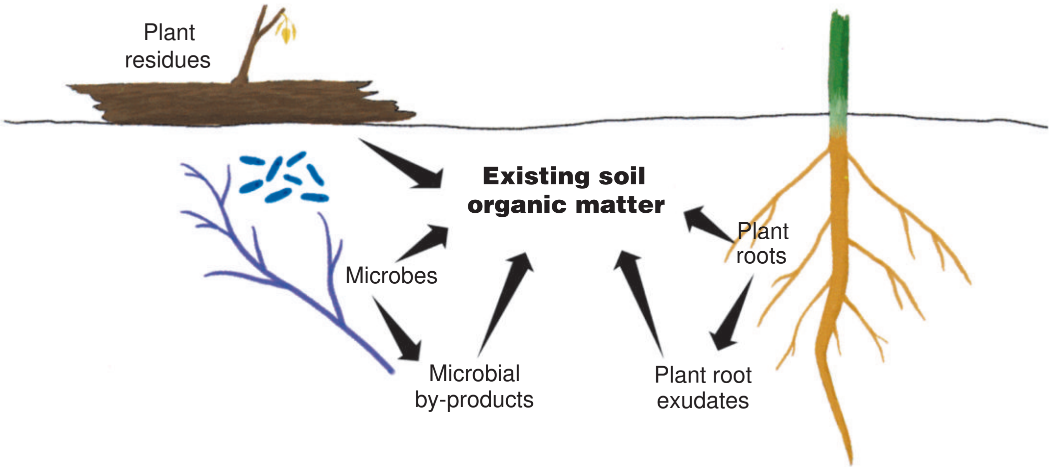


FIG. 2.12 Schematic representation of the formation of soil organic matter. *(From* Pollution Science, *© 1996, Academic Press, San Diego, CA.)*

TABLE 2.4 Terms Used to Define Soil Organic Matter

Term	Definition
Organic residues	Undecayed plant and microbial biomass and their partial decomposition products
Soil biomass	Live microbial biomass
Soil organic matter or humus	All soil organic matter, except organic residues and soil biomass
Humic substances	High-molecular-weight complex stable macromolecules with no distinct physical or chemical properties. These substances are never exactly the same in any two soils because of variable inputs and environments. This is the stable backbone of soil organic matter and is degraded only slowly (2% per year)
Nonhumic substances	Known chemical materials such as amino acids, organic acids, carbohydrates, or fats. They include all known biochemical compounds and have distinct physical and chemical properties. They are normally easily degraded by microbes

From *Pollution Science*, 8, 1996, Academic Press, San Diego, CA.

phase within the soil (called the soil atmosphere), but at different concentrations. The main gaseous constituents are oxygen, carbon dioxide, nitrogen, and other volatile compounds such as hydrogen sulfide or ethylene. The concentrations of oxygen and carbon dioxide in the soil atmosphere are normally different than in the atmosphere (Table 2.5). This variable reflects the use of oxygen by aerobic soil organisms and subsequent release of carbon dioxide. In addition, the gaseous concentrations in soil are normally regulated by diffusion of oxygen into soil and of carbon dioxide from soil.

2.3.2 Availability of Oxygen and Soil Respiration

The oxygen content of soil is vital for *aerobic microorganisms*, which use oxygen as a terminal electron acceptor during degradation of organic compounds (see Chapter 9). *Facultative anaerobes* can utilize oxygen or combined forms of oxygen (such as nitrate) as a terminal electron acceptor. *Anaerobes* cannot utilize oxygen as an acceptor. Strict anaerobes are lethally affected by oxygen because they do not contain enzymes that can degrade toxic peroxide radicals. Since microbial degradation of many organic compounds in soil, including xenobiotics, is carried out by aerobic organisms, the presence of oxygen in soil is necessary for such decomposition. Oxygen is found either dissolved in the soil solution or in the soil atmosphere, but soil oxygen concentrations in solution are much lower than in the soil atmosphere.

The total amount of pore space depends on soil texture and soil structure. Soils high in clays have more total pore space, but smaller pore sizes. In contrast, sandy soils have larger pore sizes, allowing more rapid water and air

TABLE 2.5 Characteristics of the Soil Atmosphere

	Composition (% volume basis)		
Location	Nitrogen (N_2)	Oxygen (O_2)	Carbon dioxide (CO_2)
Atmosphere	78.1	20.9	0.03
Well-aerated soil surface	78.1	18–20.5	0.3–3
Fine clay or saturated soil	>79	~0–10	Up to 10

From *Environmental Microbiology*, 8, 2000, Academic Press, San Diego, CA.

movement. In any soil, as the amount of soil structure increases, the total pore space of the soil increases. Aerobic soil microbes require both water and oxygen, which are both found within the pore space. Therefore the soil moisture content controls the amount of available oxygen in a soil. In soils saturated with water, all pores are full of water and the oxygen content is very low. In dry soils, all pores are essentially full of air, so the soil moisture content is very low. In soils at *field capacity*, that is, soils having moderate soil moisture, both air (oxygen) and moisture are readily available to soil microbes. In such situations, soil respiration via aerobic microbial metabolism is normally at a maximum. It is important to note, however, that low-oxygen concentrations may exist in certain isolated pore regions, allowing anaerobic microsites to exist even in aerobic soils, thereby supporting transformation processes carried out by facultative anaerobes and strict anaerobes. This is an excellent example of how soil can function as a discontinuous environment of great diversity.

2.3.3 Gaseous Phase Within the Vadose Zone

Vadose zones generally are primarily aerobic regions. However, due to the heterogeneous nature of the subsurface, anaerobic zones can occur particularly in clay lenses. Thus both aerobic and anaerobic microbial processes may occur.

At contaminated sites, volatile organic compounds can be found in the gaseous phase of the vadose zone. For example, chlorinated solvents, which are ubiquitous organic contaminants (see Chapters 12 and 15), are volatile and are often found in the vadose zone gaseous phase below hazardous waste sites. In such cases, soil venting is often used to remove the contamination (see Chapter 19). The porosity, structure, and water content of the vadose zone is critical to effective application of soil venting.

2.4 LIQUID PHASE

Water is, of course, essential for all biological forms of life, in part because of the unique nature of its structure. The fact that the oxygen moiety of the molecule is slightly more electronegative than the hydrogen counterparts results in a polar molecule. This polarity, in turn, allows water to hydrogen bond both to other water molecules and to other polar molecules. This capacity to bond with almost anything has a profound influence on biological systems, and it explains why water is a near-universal solvent (see Chapter 3). It also explains the hydration of cations and the adsorption of water to soil colloids (see Chapter 8).

By definition, the vadose zone is unsaturated and contains low moisture content. However, whenever rainfall or irrigation events occur at the soil surface, some moisture leaches into the vadose zone. Other avenues by which moisture can reach the subsurface is through burrowing animal holes or worm holes which results in preferential flow. Even so, significant moisture in the vadose zone is the exception rather than the rule. Basic properties of water in both surface and subsurface environments are discussed in Chapter 3.

2.5 BASIC SOIL PHYSICAL PROPERTIES

2.5.1 Bulk Density

Soil bulk density is defined as the ratio of dry mass of solids to bulk volume of the soil sample:

$$\rho_b = \frac{M_s}{V_T} = \frac{M_s}{V_s + V_w + V_a}$$

where:

ρ_b = Soil bulk density [M L^{-3}]
M_s = Dry mass of solid [M]
V_s = Volume of solids [L^3]
V_w = Volume of water [L]
V_a = Volume of air [L^3]
V_T = Bulk volume of soil [L^3]

The bulk volume of soil represents the combined volume of solids and pore space. In SI units, bulk density is usually expressed in $\mathrm{g\,cm^{-3}}$ or $\mathrm{kg\,m^{-3}}$. Bulk density is used as a measure of soil structure. It varies with a change in soil structure, particularly due to differences in packing. In addition, in swelling soils, bulk density varies with the water content. Therefore it is not a fixed quantity for such soils.

2.5.2 Porosity

Porosity (n) is defined as the ratio of void volume (pore space) to bulk volume of a soil sample:

$$n = \frac{V_v}{V_T} = \frac{V_v}{V_w + V_s + V_a}$$

where:

n is the total porosity [n];
V_v is the volume of voids [L^3];
V_T is the bulk volume of sample [L^3].

It is dimensionless and described either in percentages with values ranging from 0 to 100%, or as a fraction where values range from 0 to 1. The general range of porosity that can be expected for some typical materials is listed in Table 2.6.

Porosity of a soil sample is determined largely by the packing arrangement of grains and the grain-size distribution. Cubic arrangements of uniform spherical grains provide the ideal porosity with a value of 47.65%. Rhombohedral packing of similar grains presents the least porosity with a value of 25.95%. Because both packings have uniformly sized grains, porosity is independent of grain size. If grain size varies, porosity is dependent on grain size as well as distribution. Total porosity can be separated into two types, primary and secondary, as discussed in Section 2.2.3. The porosity of a soil sample or unconsolidated sediment is determined as follows. First, the bulk volume of the soil sample is calculated from the size of the sample container. Next, the soil sample is placed into a beaker containing a known volume of water. After becoming saturated, the volume of water displaced by the soil sample is equal to the volume of solids in the soil sample. The volume of voids is calculated by subtracting the volume of water displaced from the bulk volume of the bulk soil sample.

In a saturated soil, porosity is equal to water content since all pore spaces are filled with water. In such cases, total porosity can also be calculated by weighing the saturated sample, drying it, and then weighing it again. The difference in mass is equal to the mass of water, which, using a water density of $1\ \mathrm{g\ cm^{-3}}$, can be used to calculate the volume of void spaces. Porosity is then calculated as the ratio of void volume and total sample volume.

Porosity can also be estimated using the following equation:

$$n = 1 - \frac{\rho_b}{\rho_d}$$

where ρ_b is the bulk density of soil [ML^{-3}], and ρ_d is the particle density of soil [ML^{-3}].

A value of $2.65\,\mathrm{g\,cm^{-3}}$ is often used for the latter, based on silica sand as a primary soil component. Void ratio (e),

TABLE 2.6 Porosity Values of Selected Porous Media

Type of material	*n* (%)
Unconsolidated media	
Gravel	20–40
Sand	20–40
Silt	25–50
Clay	30–60
Rocks	
Karst Limestone	5–30
Sandstone	5–30
Shale	0–10
Fractured crystalline rock	0–20
Dense crystalline rock	0–10

From *Environmental Monitoring*, 8, 2004, Academic Press, San Diego, CA.

which is used in engineering, is the ratio of volume of voids to volume of solids:

$$e = \frac{V_V}{V_s}$$

The relationship between porosity and void is ratio is described as:

$$e = \frac{n}{1-n}$$

It is dimensionless. Values of void ratios are in the range of 0–3.

2.5.3 Soil Water Content

Soil water content can be expressed in terms of mass (θ_g) or volume (θ_v). Gravimetric (mass) water content is the ratio of water mass to soil mass, usually expressed as a percentage. Typically, the mass of dry soil material is considered as the reference state, thus:

$$\theta_g\% = [(\text{mass wet soil} - \text{mass dry soil})/\text{mass dry soil}] \times 100.$$

Volumetric water content expresses the volume (or mass, assuming a water density, ρ_w, of $1\,\text{g}\,\text{cm}^3$) of water per volume of soil, where the soil volume is comprised of the solid grains and the pore spaces between the grains. When the soil is completely saturated with water, θ_v should generally equal the porosity. The relationship between gravimetric and volumetric water contents is given by:

$$\theta_v = \theta_g \left[\frac{\rho_b}{\rho_w}\right]$$

A related term that is often used to quantify the amount of water associated with a sample of soil is "saturation", S_w, which describes the fraction of the pore volume (void space) filled with water:

$$S_w = \frac{\theta_v}{n}$$

2.5.4 Soil Temperature

Soil temperature is often a significant factor especially in agriculture and land treatment of organic wastes, since growth of biological systems is influenced by soil temperature. In addition, soil temperature influences the physical, chemical, and microbiological processes that take place in soil. These processes may control the fate and transport of contaminants in the subsurface environment. The temperature of the soil zone fluctuates throughout the year in accordance with the above-ground temperature. Conversely, the temperature below the upper few meters of the subsurface remains relatively constant throughout the year.

QUESTIONS AND PROBLEMS

1. The hydrogen ion concentration of the soil solution from a particular soil is $3 \times 10^{-6}\,\text{mol L}^{-1}$. What is the pH of the soil solution?
2. What is the soil textural class of a soil with 20% sand, 60% silt, and 20% clay?
3. A 100-g sample of a moist soil initially has a moisture content of 15% on a dry weight basis. What is the new moisture content if 10 g of water is uniformly mixed into the soil?
4. Which factors within this chapter affect the cation-exchange capacity (CEC) of a soil? Explain why.
5. Which factors can potentially affect the transport of contaminants through soil and vadose zone? Explain why.
6. How does soil moisture content affect the activity of aerobic and anaerobic soil microorganisms?
7. Compare and contrast surface soils with the vadose zone.

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Chapter 3

Physical-Chemical Characteristics of Water

M.L. Brusseau, D.B. Walker and K. Fitzsimmons

Apache Reservoir, Arizona. *Photo courtesy D. Walker.*

3.1 THE WATERY PLANET

3.1.1 Distribution

Ninety seven percent of water on the Earth is marine (saltwater), while only 3% is freshwater (Fig. 3.1). With regard to the freshwater, 79% is stored in polar ice caps and mountain glaciers, 20% is stored in aquifers or soil moisture, and 1% is surface water (primarily lakes and rivers). An estimated 110,000 km^3 of rain, snow, and ice falls annually on land surfaces, and this is what replenishes fresh water resources. Possible effects of climate change, combined with continued increases in human population and economic development are resulting in critical concern for the future sustainability of freshwater resources.

The limited supplies of surface waters and groundwater receive significant amounts of the pollutants generated by humans. Lakes across the planet have an average retention time of 100 years, meaning it takes 100 years to replace that volume of water. Rivers, on the other hand, have a much shorter retention time. The relatively long retention time in lakes exacerbates the impacts of introducing pollutants that will be present for a long time (i.e., they are "environmentally persistent"). The short retention time in rivers means that pollutants are transferred rapidly to other water bodies such as groundwater, lakes, or oceans. The retention time of groundwater is measured in hundreds if not thousands of years. In the groundwater environment, persistent pollutants may persist for extremely long periods because of constraints to transformation. The characteristics of oceans, surface water bodies, and groundwater are described in upcoming sections. Pollution of groundwater and surface water is discussed in Chapters 15 and 16, respectively.

3.1.2 The Hydrologic Cycle

Water covers much more of Earth's surface than does land. The continual movement of water across the Earth due to evaporation, condensation, or precipitation is called the hydrologic cycle (Fig. 3.2). The consistency of this cycle has taken millennia to establish, but can be greatly altered by human activities including climate change, desertification, or excessive groundwater pumping. Water, in its constantly changing and various forms, has been and continues to be an essential factor for all living things.

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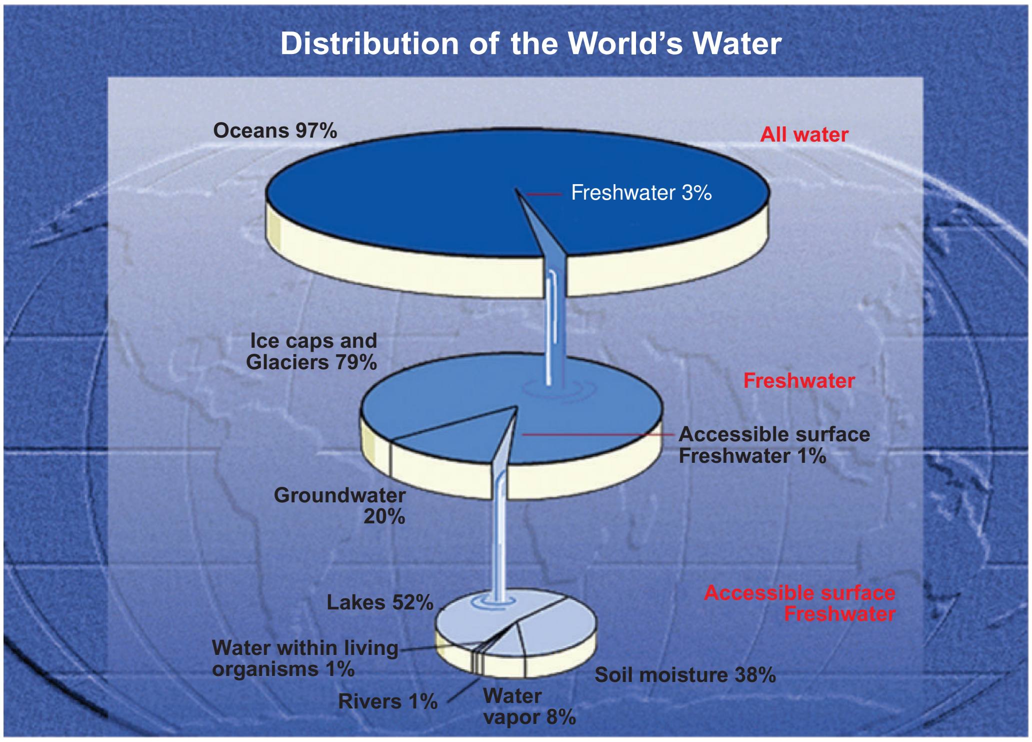

FIG. 3.1 Distribution of the world's water. *(Courtesy of Patricia Reiff and MTPE team, Rice University.)*

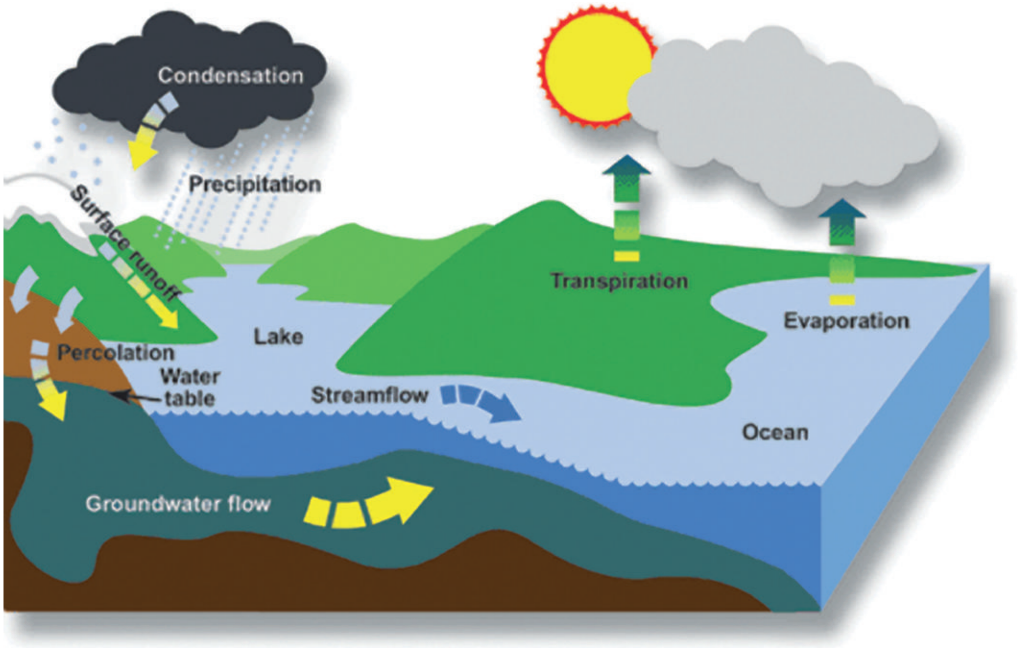

FIG. 3.2 The hydrologic cycle. *(Source: Environment Canada's Freshwater Website http://www.ec.gc.ca/water, 2004. Reproduced with the permission of the Minister of Public Works and Government Services, 2006.)*

Evaporating water moderates temperature; clouds and water vapor protect us from various forms of radiation; and precipitation spreads water to all regions of the globe, allowing life to flourish from the highest peaks to the deepest caves. Solar energy drives evaporation from open water surfaces as well as soil and plants. Air currents distribute this vaporized water around the globe. Cloud formation, condensation, and precipitation are functions of cooling. When vaporized, water cools to a certain temperature, condensation occurs, and often results in precipitation to the Earth's surface. Once back on the surface of the Earth, whether on land or water, solar energy then continues the cycle. The latent heat of water (the energy that is required or released as water changes states) serves to moderate global temperatures, maintaining them in a range suitable for humans and other living organisms.

Some processes involved with the hydrologic cycle aid in purifying water of the various contaminants accumulated during its cycling. For instance, precipitation reaching the soil will react with various minerals and neutralize the acidity that was generated from atmospheric processes. Suspended sediments entrained through erosion and runoff will settle out as the water loses velocity in ponds or lakes. Other solids will be filtered out as water percolates through soil and vadose zones and ultimately to an aquifer. Many organic compounds will be degraded by bacteria in soil or sediments. Salts and other dissolved solids will be left behind as water evaporates and returns to a gaseous phase or freezes into a solid phase (ice). These processes maintained water quality of varying degrees before human impacts on the environment; however, the current scale of these impacts often tends to overwhelm the ability of natural systems to cleanse water through the hydrologic cycle. Further, we have introduced many compounds that are resistant to normal removal or degradation processes (Chapters 14–17).

3.2 UNIQUE PROPERTIES OF WATER

3.2.1 Structure and Polarity

Water is an unusual molecule in that the structure of two hydrogen atoms and one oxygen atom provides several characteristics that make it a universal solvent. First is the fact that the two hydrogen atoms, situated on one side of the oxygen atom, carry positive charges, while the oxygen atom retains a negative charge (Fig. 3.3).

This induced polarity allows water molecules to attract both positive and negative ions to the respective poles of the molecule. It also causes water molecules to attract one another. This is termed hydrogen bonding. This contributes to the viscosity of water and to the dissolution capacity of water for different materials. This unique nature of water makes it an easy conduit for the dissolution and transport for any number of pollutants. Because so many materials dissolve so completely in water, their removal from water is often difficult.

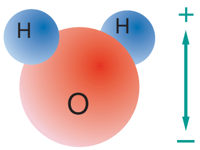

FIG. 3.3 Structure and charge distribution of water, http://faculty.uca.edu/~benw/biol1400/notes32.htm.

3.2.2 Thermal Properties

Water has unique thermal properties that enable it to exist in three different states: vapor, solid, and liquid under environmentally relevant conditions. Changes in each phase have certain terminology, depending upon state changes, as described below:

Condensation: vapor → liquid
Evaporation: liquid → vapor
Freezing: liquid → solid
Melting: solid → liquid
Sublimation: solid → vapor
Frost Formation: vapor → solid

The fact that water becomes less dense in its solid state, compared to its liquid state, is yet another unusual characteristic. Most liquids contract with decreasing temperature. This contraction also makes these liquids denser (i.e., "heavier") as temperature decreases. Water is unique because its density increases only down to approximately 4°C, at which point it starts to become less dense (Fig. 3.4). Because of this, ice floats and insulates deeper water. This is important because without this unique property, icebergs and other solid forms of water would sink to the bottom of the ocean, displacing liquid water as they did so. Also, lakes and ponds would freeze from the bottom up with the same effect. This is critical to maintaining deep bodies of liquid waters on Earth rather than a thin layer of water on top of an increasingly deep bed of solid ice.

The *specific heat* of water is the amount of energy required to raise one gram of water, one degree C, and is usually expressed as *joules per gram-degree Celsius* ($\mathrm{J\,g^{-1}\,°C^{-1}}$). Specific heat values for the different phases of water are given as follows.

Phase	$\mathrm{J\,g^{-1}\,°C^{-1}}$
Vapor	2.02
Liquid	4.18
Solid	2.06

The *latent heat of fusion* is the amount of energy required to change 1 gram of ice, at its melting point temperature, to liquid. It is considered "latent" because there is no temperature change associated with this energy transfer, only a change in phase. The heat of fusion for water is $-333\,\mathrm{J\,g^{-1}\,°C^{-1}}$.

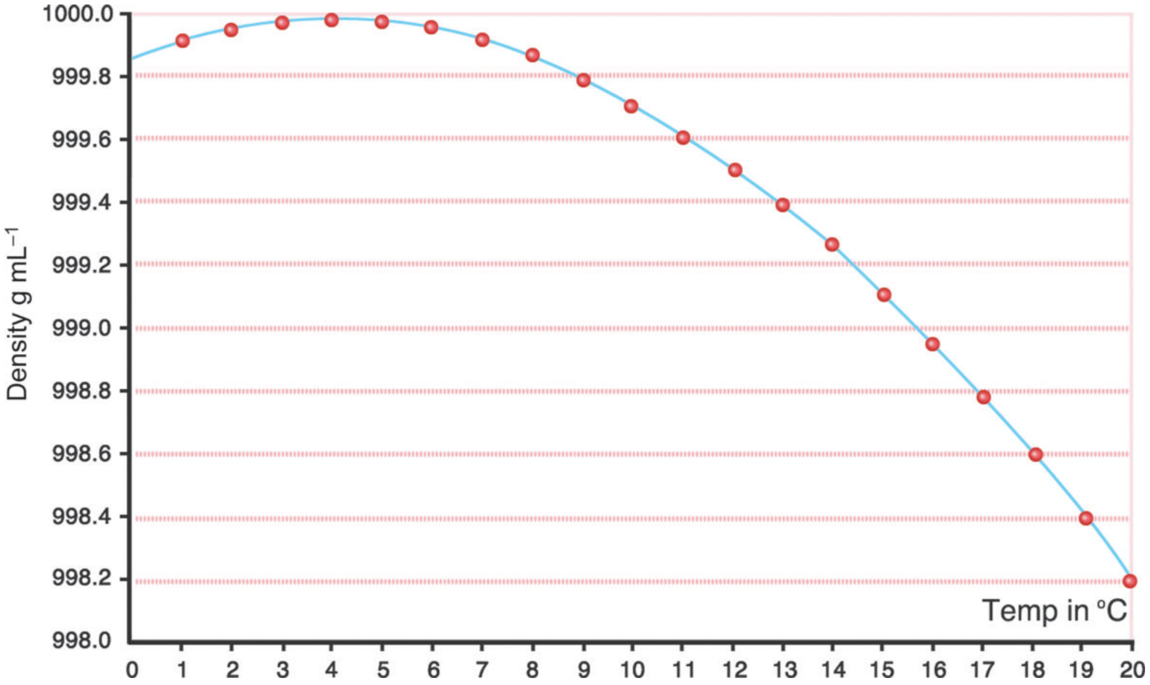

FIG. 3.4 The density of water at varying temperatures, http://www.cyberlaboratory.com/library/basicsofdensity/whatisdensity.htm.

The energy required for the phase changes of water is given in Table 3.1.

Earth is unique because it contains the necessary temperatures and pressures for all three states of water to exist. Water, under the correct combination of temperature and pressure, is capable of existing in all three states (solid, liquid, and vapor) simultaneously and in equilibrium. This is referred to as the *triple point,* where infinitesimally small increases or decreases in either pressure or temperature will cause water to be either a liquid, solid, or gas. Specifically, the triple point of water exists at a temperature and pressure of 273.16 K (0.0098°C) and 611.73 pascals (0.00603 atm), respectively. Fig. 3.5 shows that decreasing temperature and increasing pressure causes water to pass directly from a gas to a solid. At pressures higher than the triple point, increasing temperature causes solid water (ice) to transform into liquid and eventually gas (vapor). Liquid water cannot exist in pressures lower than the triple point and ice instantaneously becomes steam with increasing temperature. This process is known as sublimation.

3.3 MECHANICAL PROPERTIES

3.3.1 Interception, Evaporation, Infiltration, Runoff

Precipitation in a nonpolluted environment provides a fairly pure form of water. However, today precipitation may absorb pollutants in the environment to form acid rain (see also Chapter 17). Precipitation can also entrain fine particulates that were suspended in the air. As precipitation reaches the surface, raindrops are likely to fall upon and be

TABLE 3.1 Phase Changes of Water

Process	From	To	Energy Gained or Lost (J g^{-1} °C^{-1})
Condensation	Vapor	Liquid	2500
Deposition	Vapor	Ice	2833
Evaporation	Liquid	Vapor	–2500
Freezing	Liquid	Ice	333
Melting	Ice	Liquid	–333
Sublimation	Ice	Vapor	2833

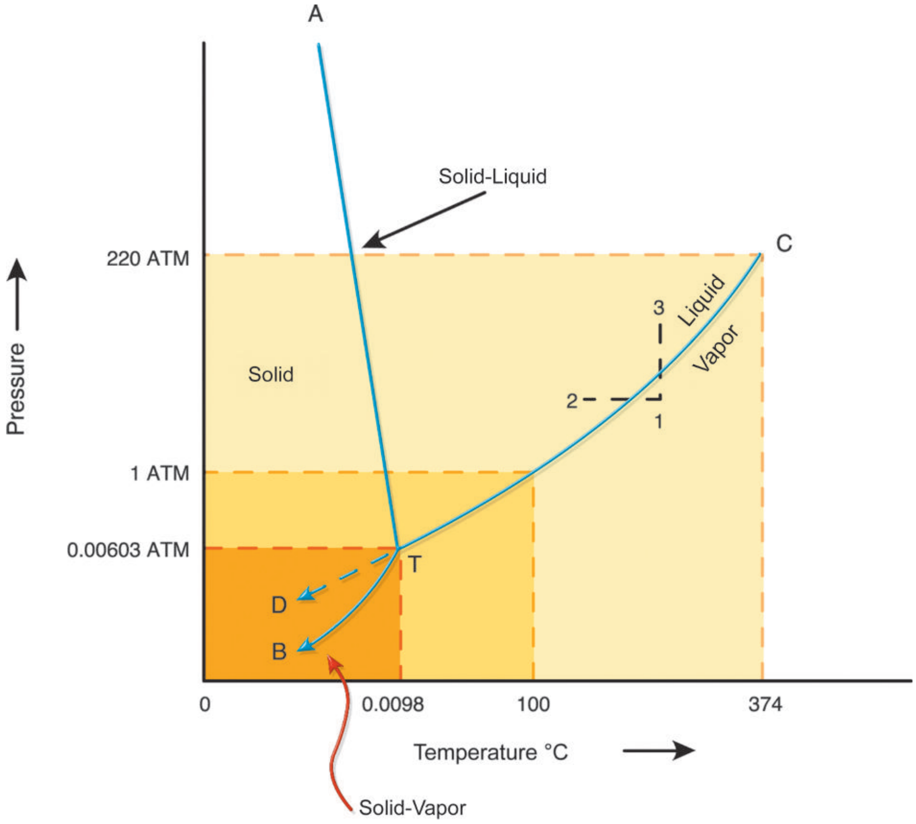

FIG. 3.5 Phase diagram of the triple point of water, http://www.sv.vt.edu/classes/MSE2094_NoteBook/96ClassProj/pics/trip_pt1.

intercepted by various types of vegetation. In many regions, much of the precipitation may fall on trees, shrubs, or grasses and never actually reach the ground. In others, the plants may slow the rate of fall of raindrops, break them into smaller drops, or channel them more gently to the surface. Interception can have multiple influences on the impact of rainfall on the land surface. First, the water may evaporate directly from the plant, never reaching the soil. Second, it may entrain materials settled on the plant surfaces. Third, by slowing the momentum and reducing the energy of falling rain, physical impacts on the soil and resulting erosion may be reduced.

Certain anthropogenic land use practices or natural events can lead to decreases in interception and subsequent increases in sediment suspended within water. Often, sediment may have other pollutants attached to it thereby polluting the water as well. Certain mining features, if not revegetated, can result in increased erosion and subsequent contamination of streams. Natural events, such as wildfires, can also result in substantial erosion and contamination of downstream areas (see also Chapter 14).

Evaporation of water is another crucial part of the hydrologic cycle. The rate of evaporation from a body of water, or mass of soil, is a function of the relative humidity, temperature, and wind speed. An important subcomponent of evaporation is transpiration, the active transport and evaporation of water from plants. Plants transport nutrients in an aqueous solution and then dispose of the water through their leaves by evaporation. As water evaporates, it leaves a concentrated amount of compounds that were formerly dissolved in that water. This applies to nutrients left in plants, as well as to pollutants that were introduced with the water.

Water that is not contained in oceans is often referred to as "freshwater," implying that it is not saline. This is not always the case, and some inland waters can be much more saline than the world's oceans. This is especially true in arid environments or enclosed basins that have limited or no drainage. Often, salinity in inland waters reaches such high levels that it supports little, if any, life. Salinity in inland waters, and in the world's oceans, is largely a result of evaporation. As water is vaporized and once again enters the hydrologic cycle, salts accumulate on the Earth's surface, and in lieu of adequate dilution and flushing, can often make water increasingly saline (Fig. 3.6).

Precipitation that reaches the soil surface either infiltrates the ground or runs off the surface. Human uses of water also deliver enormous amounts of water onto soils or human-made structures that can either infiltrate or contribute to runoff. This is a major source of pollutants introduced into the environment. The infiltration rate of water

FIG. 3.6 This satellite image is of the Great Salt Lake in Utah. This is the largest lake in the United States west of the Mississippi River covering some 1700 square miles. It is also 3–5 times more saline than the world's oceans. It is a fishless lake with only the most saline-tolerant ("halophytic") organisms capable of surviving. The largest organisms inhabiting its waters are species of brine shrimp and brine flies, http://ut.water.usgs/gov/greatsaltlake/.

into the ground is an important measure used to determine how foundations and sewer systems are designed, how irrigation water should be applied, and how pollutants may migrate to a water supply.

How water runs off of surfaces is also a matter of interest to hydrology, fisheries, aquatic biology, and pollution science. Not only are pollutants entrained in flowing water, but erosion and flooding can also occur. Studies of runoff and surface flow focus upon the amounts of soil and pollutants that are transported and their eventual fate as they arrive into lakes or streams.

3.4 THE UNIVERSAL SOLVENT

One of the most unique properties of water is its ability to dissolve other substances. It is this ability that can lead to large-scale landscape transformations (Fig. 3.7) and the ability to carry contaminants relatively long distances. If it were not for the various substances dissolved in water, an organism's cells would quickly be deprived of essential nutrients, salts, and gasses, leading to eventual death. The dissolution of materials in water has shaped the nature of all living creatures on the planet.

FIG. 3.7 The Grand Canyon of the Colorado River was formed by the dissolution and erosion of material over eons. Historically, most of this material was deposited in the Gulf of California. With the construction of large dams along the course of the Colorado River, most of this material is now deposited in storage reservoirs, http://www.kaibab.org/tr961/lg961110.jpg.

3.4.1 Concentration Terminology

It is important to quantify the amount of material dissolved in water. Quantification requires a range of values so that we can determine high versus low concentrations for a given constituent. The values are always expressed as a ratio of quantity of solute to quantity of water (Table 3.2). The importance of very small concentrations should never be underestimated (see Information Box 3.1). This is especially true in toxicological studies where very small concentrations can lead to toxic impacts on organisms (Chapter 28).

There are two major expressions in concentration terminology.

- Mass/mass. An example would be milligrams/kilogram ($\mathrm{mg\ kg^{-1}}$), which equals milligrams of dissolved matter per kg of solution.
- Mass/volume. An example would be milligrams/liter ($\mathrm{mg\,L^{-1}}$), which equals milligrams of dissolved matter per liter of solution.

TABLE 3.2 Examples of Typical Concentrations of Solutes in Water

Percent		parts per hundred	10^2
Gram	$g\,L^{-1}$	parts per thousand	10^3
Milligram	$mg\,L^{-1}$	parts per million	10^6
Microgram	$\mu g\,L^{-1}$	parts per billion	10^9
Nanogram	$ng\,L^{-1}$	parts per trillion	10^{12}

INFORMATION BOX 3.1
Examples of Why Small Numbers are Important

- The solubility of trichloroethene in water is ~1000 mg/L or 1 g/L.
- The regulatory limit for its presence in drinking water is 5 μg/L.
  >>> the regulatory limit is 200,000 times lower than the solubility.

Another common concentration unit used is "parts per million" (ppm), representing the quantity of matter present out of a million. For dilute aqueous solutions, $mg\,L^{-1}$ and ppm will be the same number because the density of the solution will be close to 1. The following relationship can be used to convert units for cases where densities of the liquid or solution are significantly different than 1: specific gravity of solution × ppm = $mg\,L^{-1}$. Specific gravity is the ratio of the density of a substance to the density of a reference substance (typically water). Note that this same relationship holds true when using other concentrations such as parts per billion (ppb) and $\mu g\,L^{-1}$ or parts per trillion and $ng\,L^{-1}$.

Example Calculation 3.1

Using Concentration

Knowing the concentrations of constituents in water has many utilitarian uses. For example, an environmental scientist may need to determine the total mass of a contaminant present in a surface water reservoir to conduct a risk assessment and to develop a remediation strategy.

- Suppose the water contained 35 ppm of sulfate.
- The reservoir has a total storage volume of 1 million m^3.
- The reservoir is half full.
- How many kilograms of sulfate are contained in the reservoir?

To calculate this we determine the following:

- Volume of water = 1,000,000 m^3 × 0.5 × 1000 L/m^3 = 500,000,000 L.
- Sulfate concentration = 35 ppm = 35 mg/L.
- Mass of sulfate in the water = 35 mg/L × 500,000,000 L × 1 g/1000 mg × 1 kg/1000 g = 17,500 kg.

3.4.2 Oxygen and Other Gases in Water

Just like terrestrial counterparts, aquatic organisms (other than anaerobic microbes) need dissolved oxygen and other gases in order to survive. Additionally, the world's oceans "absorb" an estimated ¼ to ⅓ of carbon dioxide emitted by human activity. If it were not for the ocean's ability to absorb carbon dioxide, an important greenhouse gas, global warming would proceed at an unprecedented rate. The amount of gas that an aqueous solution can hold is dependent upon several variables, the most important of which is atmospheric pressure. Simply stated, increasing atmospheric pressure causes a greater amount of gas to go into solution at a given temperature (Fig. 3.8). Generally, increasing water temperature will result in an increased solubility of gas.

There is a direct, linear relationship between the partial pressure and the concentration of gas in solution. For example, if the partial pressure is increased by ¼, the concentration of gas in solution is increased by ¼ and so on. This is because the number of collisions of gas molecules with the solvent molecules (water in this case) is directly proportional to increases or decreases in partial pressure. Since the concentration:pressure ratio remains the same, we can predict the concentration of gas in water under differing partial pressures. This relationship can be written as:

$$\frac{\text{Concentration1}}{\text{Pressure1}} = \frac{\text{Concentration2}}{\text{Pressure2}}$$

For example, 1 L of water under 1 atmosphere of pressure will contain 0.0404 grams of oxygen. What will the concentration of oxygen be if the partial pressure is increased to 15 atmospheres?

$C1 = 0.0404\ g\ O_2/L$ liter solution
$P1 = 1\ atm,\ P2 = 15\ atm$
$C2 = ?$

$$\frac{0.0404 gO_2}{1\,atm} = \frac{C_2}{15\,atm}$$

$C2 = (15\ atm)\ (0.0404\ g\,O_2$ per $1\ L/1\ atm)$
$C2 = 0.606\ g\ O_2$

In any body of water, there are sources and sinks of dissolved oxygen. Sources include atmospheric reaeration through turbulence, ripples and waves, and dams and waterfalls. Another potential source of dissolved oxygen is

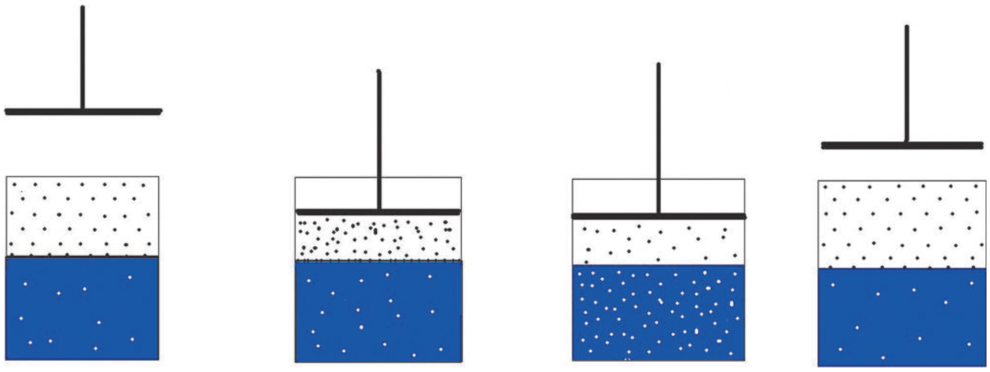

FIG. 3.8 The solubility of oxygen in water under different atmospheric pressures.

photosynthesis primarily by algae or submersed aquatic vegetation. During photosynthesis, plants convert CO_2 into oxygen in the process outlined as follows.

$$6CO_2 + 12H_2O + \text{Light energy} \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O \quad (3.1)$$

All natural waters also have sinks of dissolved oxygen, which include:

Sediment Oxygen Demand (SOD): Due to decomposition of organic material deposited on bottom sediments.

Biological Oxygen Demand (BOD): The oxygen required for aerobic biodegradation (respiration) of contaminants by microorganisms.

Chemical Oxygen Demand (COD): The oxygen required for degradation or oxidation of *all* labile contaminants. Note that BOD is a subset of COD.

Respiration is the metabolic process by which organic carbon is oxidized to carbon dioxide and water with a net release of energy (see also Chapter 5). Aerobic respiration requires, and therefore consumes, oxygen.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \quad (3.2)$$

This is, essentially, the opposite of photosynthesis. In the absence of light, the CO_2 collected by plants via photosynthesis during the day is released back into the water at night, resulting in a net loss of dissolved oxygen. Depending upon the amount of nutrients, algae, and available light, this often results in large daily fluctuations in dissolved oxygen levels known as Diel patterns (Fig. 3.9).

The implications of dissolved oxygen sinks and sources on aquatic organisms and overall water quality are crucial in determining whether or not a river, lake, or stream is impaired and to what degree. If dissolved oxygen sinks are greater than sources for extended periods of time, it is safe to assume some degree of contamination has occurred.

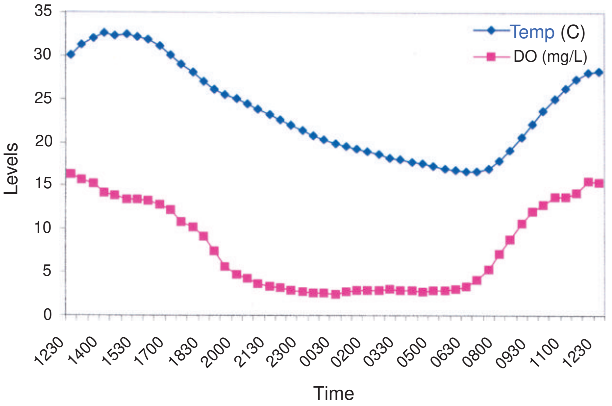

FIG. 3.9 Diel pattern of temperature and dissolved oxygen in Rio de Flag, an effluent-dominated stream in Flagstaff, Arizona. Data was collected every 30 minutes over a 24-hour period on December 08, 2003.

Examples of anthropogenic wastes that can cause dissolved oxygen impairment of receiving waters are sewage (raw and treated, human and nonhuman), agricultural runoff, slaughterhouses, and pulp mills.

3.4.3 Carbon Dioxide in Water

Carbon dioxide only accounts for approximately 0.033% of the gases in Earth's atmosphere, yet is abundant in surface water. The biggest reason for the abundance of carbon dioxide in water is due to its relatively high solubility—about 30 times that of oxygen. At room temperature, carbon dioxide has a solubility in water of 1.45 g/L. In the atmosphere, carbon dioxide is released when fossil fuels are burned for human uses, and as a result of large worldwide increases in the use of fossil fuels during the last century or so, the amount of carbon dioxide in the atmosphere has steadily increased.

Carbon dioxide dissociates and exists in several forms in water. First, carbon dioxide can simply dissolve into water going from a gas to an aqueous form. A very small portion of carbon dioxide (less than 1%) dissolved in water is hydrated to form carbonic acid (H_2CO_3). Equilibrium is then established between the dissolved carbon dioxide and carbonic acid.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{3.3}$$

Carbonic acid, a very weak acid, is then dissociated in two steps.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3{}^- \tag{3.4}$$

$$HCO_3{}^- \leftrightarrow H^+ + CO_3{}^{2-} \tag{3.5}$$

As carbon dioxide is dissolved in water, equilibrium is eventually established with the bicarbonate $(HCO_3{}^-)$ and carbonate $(CO_3{}^{2-})$ ions. Carbonate, being a largely insoluble anion, then reacts with cations in the water, causing these cations to precipitate out of solution. As a result, Ca^{2+} and Mg^{2+} often precipitate as carbonates. Calcium carbonate ($CaCO_3$), otherwise known as limestone, has been generated in large deposits as a result of this process. As limestone is once again dissolved, carbon dioxide is released back into the atmosphere. In addition, several aquatic organisms, such as corals and shelled creatures such as clams, oysters, and scallops, are capable of converting the carbon dioxide in water into calcium carbonate.

Diel fluctuations in oxygen and pH levels can occur during the day in waters where photosynthesis is taking place (see Fig. 3.10). Algae and plants convert carbon dioxide into carbohydrates to be used in metabolic processes. In very productive waters, this process can leave bicarbonate or carbonate in excess, leading to increased pH levels. In the absence of adequate light for photosynthesis, respiration predominates, resulting in carbon dioxide once again being restored to the water resulting in decreased pH levels.

Calcium carbonate, while insoluble at neutral to basic pH levels, readily dissolves in acidic conditions. In the initial step, carbonate acts as a base resulting in calcium ions and carbonic acid. In the next step, carbonic acid is dissociated releasing carbon dioxide as a gas.

$$CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + H_2CO_3 \tag{3.6}$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2 \tag{3.7}$$

Rain is often slightly acidic due to the presence of atmospheric carbon dioxide. Recently, due to the burning of fossil fuels, other gases can also be dissolved in rain resulting in "acid rain." Atmospheric pollutants responsible for acid rain include sulfur dioxide (SO^2) and nitrous oxides (NO_x). More than 2/3 of these pollutants come from burning fossil fuels for electrical power generation, and prevailing winds can result in acid rain being deposited far from its original source. Acid rain has far-reaching environmental consequences including acidification of lakes and streams, making them uninhabitable by aquatic life; extensive damage to forests, plants, and soil; damage to building materials and automotive finishes; and human health concerns.

Natural conditions often exist that can result in the dissolution of limestone:

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3{}^- \tag{3.8}$$

The remaining reaction is a three-step process:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3{}^{2-} \tag{3.9}$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{3.10}$$

$$H_2CO_3 + CO_3{}^{2-} \leftrightarrow 2HCO_3{}^- \tag{3.11}$$

This reaction can result in the formation of caves when naturally acidic rainwater reacts with a subterranean layer of limestone, dissolving the calcium carbonate and forming

FIG. 3.10 Profuse growth of attached algae ("periphyton") growing in the Rio de Flag stream at the time the data reported in Fig. 3.9 were recorded. Photosynthesis and respiration by these algae likely contributed to the large swings in dissolved oxygen levels within the water over the 24-hour period. *(Photo courtesy D. Walker.)*

FIG. 3.11 Cave formation in the Big Room, Carlsbad Caverns National Park, New Mexico, http://www.nps.gov/cave/home.htm.

openings. As slightly acidic water reaches the cave ceiling, the water evaporates and carbon dioxide escapes. It is this reaction that is responsible for the many elaborate formations in cave ecosystems (Fig. 3.11).

Total alkalinity is the total concentration of bases, usually carbonate and bicarbonate, in water and is expressed as mg/L of calcium carbonate. Analytically, total alkalinity is expressed as the amount of sulfuric acid needed to bring a solution to a pH of 4.2. At this pH, the alkalinity in the solution is "used up," and any further addition of an acid results in drastic decreases in pH levels. Total alkalinity, by definition, is the ability of a water body to neutralize acids. In other words, it is the "buffering capacity" of a water body, and it is influenced by the minerals in local soils. In areas of the northeastern United States, where parent material contributes little to the total alkalinity in the water, the cumulative effects of acid rain have been most devastating and have reduced levels of aquatic life in many streams. Mining activity and pulp mills can also add to reductions in total alkalinity and subsequent decreases in pH. Stopgap measures in watersheds, lakes, or streams where alkalinity has been depleted include such drastic actions as dropping lime from helicopters to increase the buffering capacity for aquatic life.

3.5 LIGHT IN AQUATIC ENVIRONMENTS

Just as in terrestrial systems, light at the water's surface marks the beginning of photosynthesis or "primary production." Light is the driving force behind almost all metabolic processes in aquatic ecosystems. Light carries heat energy to be used in many chemical and biological processes, and can simultaneously regulate and/or damage aquatic biota. Pollutants, especially suspended and dissolved substances, can have profound effects on both the amount of light available for photosynthesis and the heat energy needed for these processes.

3.5.1 Light at and Below the Water Surface

Several processes can affect both the intensity and quality of light reaching the Earth's surface. One such process is simple scattering of light by particles in the atmosphere, including water vapor. Refraction of light occurs when the speed of light changes going from one medium, such as air, into another, such as water. Light can also be reflected off of a water surface due to several factors such as the incident angle of light, wave height and frequency, or the presence of ice. Another factor affecting light intensity is absorption due to the decrease in light energy by its transformation into heat. Both atmospheric gases and water can cause absorption.

Absorption (i.e., "quenching") of light entering a body of water can be quantified using a *vertical absorption coefficient* expressed as:

$$k = \frac{\ln I_0 - \ln lz}{z}$$

where:

I_o is the natural log of the initial amount of light entering the water
I_z is the natural log of light remaining at any given depth
z is the thickness of the water in meters

The vertical absorption coefficient is somewhat analogous to the coefficient of extinction, except that the latter uses the base10 logarithm. The vertical coefficient of absorption is therefore 2.3 times the coefficient of extinction. Another important variable when considering the fate of light in water is *the total coefficient of absorption*, which is the sum of all factors leading to the intensity (or "extinction") of light at any given depth. The total coefficient of absorption can be expressed as:

$$I_z = I_{o-}{}^{-kw} + I_{o-}{}^{-kp} + I_{o-}{}^{-kc}$$

where:

kw = the coefficient of absorption in pure water
kp = suspended particulate matter
kc = dissolved substances

Note that kp or kc can only be determined after filtration or centrifugation. The total coefficient of absorption is different for each body of water and is dependent upon the amount of dissolved or suspended material in the water. Dissolved substances are normally humic or fulvic acids, tannins, lignins, or anything that constitutes colored, dissolved, organic matter absorbing light strongly at relatively short wavelengths (e.g., blues and ultraviolet radiation < 500 nm). Suspended material includes fine clays,