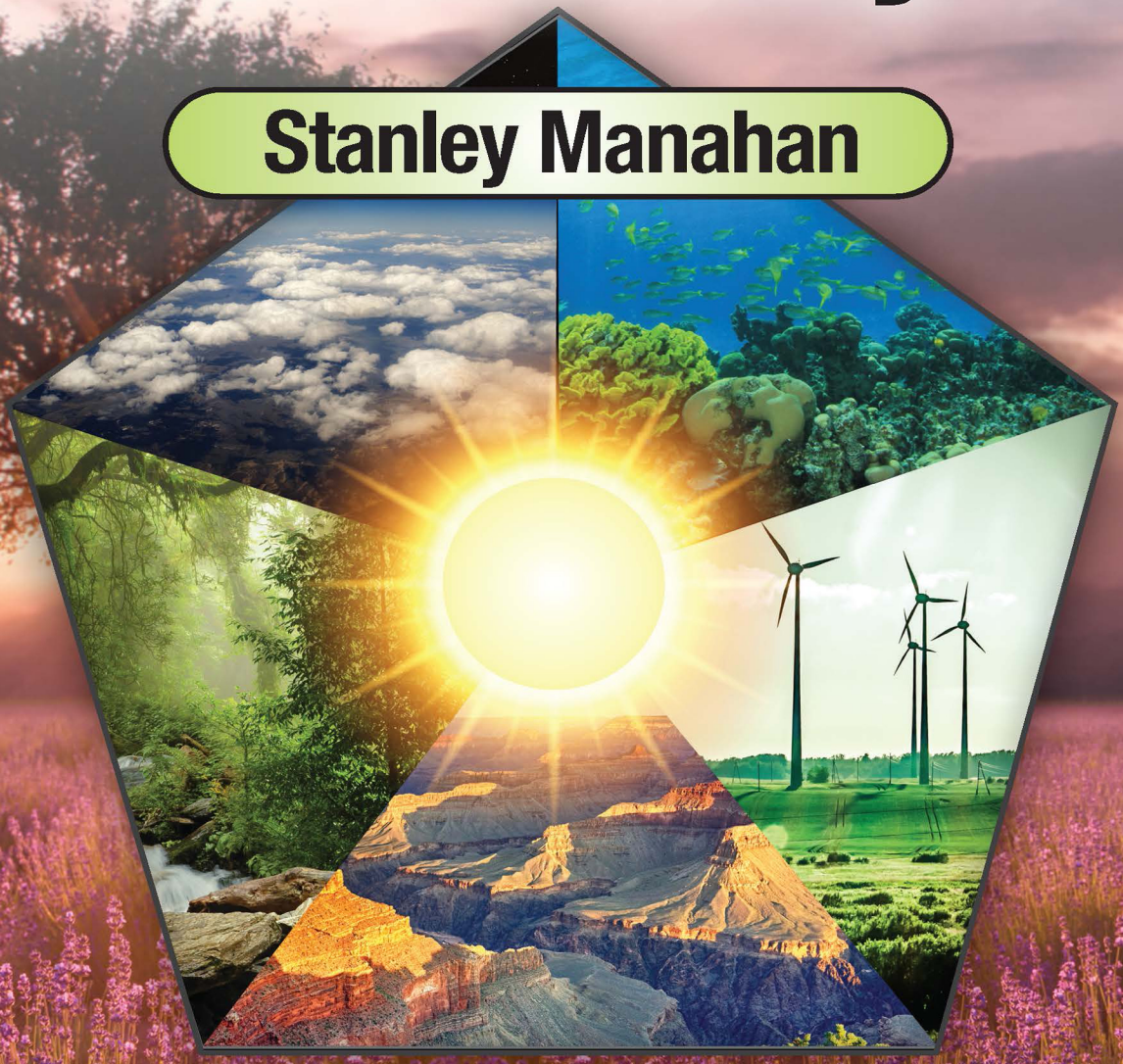
Eleventh Edition

Environmental Chemistry

Stanley Manahan



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"This book is dedicated to the memory of Professor Reynold T. Iwamoto, who served as a graduate faculty member of the University of Kansas Department of Chemistry from 1956 to 1990. Dr. Iwamoto was born in Hawaii in 1928 and died in Lawrence, Kansas in 2015. Everything that I accomplished in life I owe to this man, a wonderful mentor and dear friend."

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Preface

The year 2020 has been a particularly momentous one in which to undertake a revision of *Environmental Chemistry*. That is because the year saw two particularly earth-shattering phenomena of great consequence for Planet Earth and its human population. First, numerous events around the globe have forcefully brought home the reality of global climate change. For example, on February 20, 2020, an all-time record high temperature of 18.3°C (64.9°F) was set in Antarctica; unprecedented wildfires ravished the US west coast and Colorado; and so many hurricanes occurred in the Gulf of Mexico that it was necessary to go deep into the Greek alphabet to name them all. On November 3, Hurricane Eta hit Central America as a powerful Category 4 storm, and just two weeks later, Category 5 Hurricane Iota traversed an almost identical path, leaving the populace devastated. The second momentous event characterizing 2020 is that the human population that depends on Planet Earth for its existence and well-being has been devastated by the worst pandemic to hit in more than a century, the deadly COVID-19 coronavirus. Either individually or in combination, these phenomena have altered living conditions on the Earth, toppled governments, threatened wars, resulted in mass migrations, and generally changed the complexion of Planet Earth and its population of humans and other species.

Environmental Chemistry, Eleventh Edition, generally retains the organization and approach that have proven popular in earlier editions. This includes viewing the Earth System as consisting of five closely interacting spheres—the hydrosphere, atmosphere, geosphere, anthrosphere, and biosphere, that part of the Earth System constructed and operated by humans. The book acknowledges the importance of the Earth's natural capital, which includes materials, water resources, air resources, biological resources, and conditions generally conducive to life on the planet.

Environmental Chemistry recognizes that the Earth is entering a new epoch, leaving the Holocene epoch in which humankind has existed in relative comfort for the last approximately 10,000 years, and is well into a new epoch, the Anthropocene, in which conditions on the Earth are determined largely by human influences. Of overwhelming importance in the Anthropocene are human influences on climate, especially global warming, which is largely attributed to emissions to the atmosphere of carbon dioxide from fossil fuel combustion.

Environmental chemistry deals with chemical phenomena and conditions in the five spheres of the Earth System and how human activities influence these phenomena. The tenth and now the eleventh edition of *Environmental Chemistry* differed from the preceding edition in that it goes directly to the topic of environmental chemistry. In order to understand the environmental chemistry and phenomena that occur in each of the five environmental spheres, it is useful to have a general understanding of environmental chemistry. Therefore, Chapter 1, "Environmental Chemistry: An Essential Discipline in Coping with Challenges Facing Humankind," is a general survey of environmental chemistry as a whole. Though deemed essential to provide perspective on the remainder of the book, Chapter 1 needs to be as short and concise as possible to enable the reader to quickly move on to the remaining chapters, which pertain to the body of knowledge that comprise environmental chemistry. Therefore, Chapter 1 has been revised significantly for brevity and conciseness.

Chapters 2–7 address the environmental chemistry of the hydrosphere. Chapter 2, "The Hydrosphere and Water Chemistry," provides an overview of the hydrosphere and the nature of water that composes it. This chapter deals with some of the key aspects of aquatic chemistry, including the nature of the water molecule, which determines the physical nature of the hydrosphere, and the chemistry of water in the hydrosphere. Aspects of aquatic chemistry addressed in this chapter include acid–base reactions and equilibria, carbon dioxide in water, alkalinity, water hardness, and complexation and chelation.

Chapter 3, "Oxidation/Reduction in Aquatic Chemistry," discusses oxidation and reduction reactions in water. It emphasizes the importance of microorganisms as catalysts that mediate oxidation

and reduction in water and the concept of p*E*, analogous to pH and defined as the negative log of the activity of the electron in water. A simplified p*E*/pH diagram for iron is used to illustrate the p*E* concept and its interaction with pH. The concept of expressing energy transitions for oxidation–reduction reactions on the basis of one electron-mole of reaction is introduced, enabling the energy changes in such reactions to be expressed on a common basis.

Chapter 4, "Phase Interactions in Aquatic Chemistry," addresses the interactions that occur between species in water and those in solid and gaseous phases. The importance of sediments in determining water quality is stressed. This chapter also explains the important roles played by colloids in water.

Chapter 5, "Aquatic Microbial Biochemistry," provides details regarding the crucial role played by microorganisms in the environmental chemistry of water, including algae, bacteria, protozoa, and fungi. Also considered are microbial transformations of carbon; the microorganism-mediated biodegradation of organic matter; and the transformations of nitrogen, sulfur, and phosphorus species carried out by bacteria. This chapter concludes with a discussion of the influence bacteria have on metal species and water, including the formation of pollutant acid mine water from the bacterially mediated oxidation of iron pyrite, FeS_2.

Chapter 6, "Water Pollutants and Water Pollution," covers the nature and effects of various kinds of water pollutants. The chapter covers inorganic pollutants, organic pollutants, organometallics, and pesticides among the topics pertinent to water pollution.

The emphasis of Chapter 7, "World Water Crisis and Climate Change: Water Renovation and Recycling," is on the worldwide water crisis, which has been exacerbated by global climate change. Various water treatment processes are covered in this chapter. Also covered are means for dealing with water shortages, including schemes for the complete recycling of water.

Chapter 8, "The Atmosphere and Atmospheric Chemistry," is the first chapter that addresses the atmosphere. This chapter covers general characteristics of the atmosphere, including stratification of the atmosphere into the troposphere, the stratosphere, and higher layers. A number of general topics pertaining to the atmosphere are addressed, including movement of masses of air, transport of energy, and weather and climate. Basic photochemistry and the role of solar radiation in determining atmospheric phenomena such as photochemical smog are introduced.

Chapter 9, "Particles in the Atmosphere," deals with particulate matter suspended in the atmosphere. It includes a discussion of particles as air pollutants and the role of particulate matter in determining atmospheric chemistry. Also discussed is the influence of the anthrosphere in introducing pollutant particles into the atmosphere, which cause pollutant phenomena such as the Asian brown cloud.

"Gaseous Inorganic Air Pollutants" addressed in Chapter 10 include prominently oxides of sulfur and nitrogen, which, as primary air pollutants, may devolve into more harmful secondary air pollutants, such as acid rain and corrosive sulfate and nitrate salts. The chapter discusses the importance of nitrogen dioxide in capturing photons of sunlight, thus initiating the process of the formation of photochemical smog.

Chapter 11, "Organic Air Pollutants," discusses the wide variety of organic compounds that pollute the atmosphere, including hydrocarbons, oxygen-containing organics, organonitrogen compounds, and organosulfur compounds. Sources of organic air pollutants, from both the anthrosphere and the biosphere, especially plants, are discussed.

Chapter 12, "Photochemical Smog," deals with arguably the most annoying air pollution phenomenon, the photochemical smog that forms when reactive hydrocarbons, nitrogen oxides, and sunlight interact to produce a noxious mixture of ozone, organic oxidants, aldehydes, and particles that constitute photochemical smog. Sources of the primary pollutants that are precursors to the formation of photochemical smog are discussed, as is their control.

Chapter 13, "The Endangered Global Atmosphere," addresses climate change and its effects, which may pose the greatest danger to the Earth System and the biosphere in modern times. Carbon dioxide emission to the atmosphere as a major contributor to global climate change is discussed.

Various trends pertaining to global climate change, including temperatures, ice cover, and precipitation are discussed. The chapter also addresses means for slowing global climate change and for dealing with it as it occurs.

Chapter 14, "The Geosphere and Geochemistry," introduces the geosphere as one of the major environmental spheres. The nature and behavior of the geosphere and of the rocks and solids that compose it are discussed. The crucial role of the geosphere in providing the Earth's natural capital is covered in this chapter. Also covered are hazards from the geosphere, including devastating earthquakes and potentially climate-altering volcanic eruptions.

Chapter 15, "Soil: Earth's Lifeline," addresses the most important part of the geosphere for life on the Earth, the soil upon which humans and many other organisms depend to provide the food necessary for their existence. The chapter explains what soil is and the kinds of mineral matter that compose it. Various soil characteristics, such as the layers called soil horizons, are discussed. Also covered are the challenges involved with managing soil during an era of global climate change.

The sphere of the environment made and controlled by humans is introduced in Chapter 16, "The Anthrosphere: Industrial Ecology and Green Chemistry." This chapter defines what the anthrosphere is and how it has come to be recognized as an integral sphere of the Earth System to the extent that the Earth is entering a new epoch, the Anthropocene. The chapter discusses in some detail the interactions of the anthrosphere with the other spheres of the Earth System. Two important approaches to making the anthrosphere compatible with other environmental spheres—industrial ecology and its environmental chemistry aspect, green chemistry—are introduced and explained.

The anthrosphere is a voracious consumer of the Earth's resources and its natural capital, as discussed in Chapter 17, "Resources and Sustainable Materials." This chapter deals with resources such as metals, some of which are in short supply, and how renewable alternatives to some of these resources may be developed. The roles played by the practices of industrial ecology and green chemistry in extending limited resources are discussed.

The availability of abundant, environmentally friendly energy is of utmost importance in the achievement of sustainability as discussed at length in Chapter 18, "Sustainable Energy: The Key to Everything." Reflecting the importance of energy, this chapter is relatively long and emphasizes renewable sources of energy, including wind, water, solar, and biological energy sources.

For decades, a major problem posed by the anthrosphere has been the generation and disposal of hazardous wastes as discussed in Chapter 19, "The Nature, Sources, and Environmental Chemistry of Hazardous Wastes." Dealing with hazardous wastes sustainably is discussed in Chapter 20, "Industrial Ecology for Waste Minimization, Utilization, and Treatment."

The first of three chapters on the biosphere is Chapter 21, "The Biosphere: Environmental Biochemistry." This chapter introduces basic biochemistry. A very important aspect of the biosphere as related to environmental chemistry is the influence of toxic substances, discussed in Chapter 22, "Toxicological Chemistry." The toxic effects and toxicological chemistry of specific substances are discussed in Chapter 23, "Toxicological Chemistry of Chemical Substances."

The book concludes with an overview of chemical analysis in environmental chemistry, Chapter 24, "Chemical Analysis in Environmental and Toxicological Chemistry." This chapter also includes brief coverage of the determination of toxicants and their products in living systems.

PowerPoint presentations are available for each of the chapters to users of the book free of charge by request from CRC Press or from the author. The author welcomes input from readers and may be contacted by e-mail at manahans@missouri.edu.

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About the Author

Stanley E. Manahan is Professor Emeritus of Chemistry at the University of Missouri, Columbia, where he has been on the faculty since 1965. He earned an Bachelor of Arts (BA) degree in chemistry at Emporia State University in Kansas in 1960 and a PhD in analytical chemistry at the University of Kansas in 1965. Since 1968, his primary research and professional activities have been in environmental chemistry, with recent emphasis on hazardous waste treatment. His latest research has involved gasification of wastes and gasification of sewage sludge and crop by-product biomass for energy production. He is the author of approximately 90 research papers. Professor Manahan has taught courses on environmental chemistry, hazardous wastes, toxicological chemistry, and analytical chemistry, and has lectured on these topics throughout the United States as an American Chemical Society Local Sections tour speaker and in countries abroad, including France, Italy, Austria, Japan, Mexico, and Venezuela. Since 1970, Professor Manahan has written books in his areas of expertise, including printed works and more recently electronic versions. His longest standing and most popular book has been *Environmental Chemistry*, the first of its kind, initially published in 1972 through numerous editions, of which this work is the eleventh edition. Other topics on which the author has written books include general chemistry, applied chemistry, toxicological chemistry, toxicology, quantitative chemical analysis, sustainable chemical science, green chemistry, water chemistry, energy, environmental geology and geochemistry, global climate change, environmental and sustainability science, the anthrosphere and the Anthropocene epoch, hazardous wastes, and industrial ecology.

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1 Environmental Chemistry
An Essential Discipline in Coping with Challenges Facing Humankind

1.1 A CATASTROPHIC YEAR FOR EARTH AND HUMANKIND

As this is being written at the end of 2020, it has been an *annus horribilis* (a term popularized by Queen Elizabeth II of England in 1992), a truly horrible year for Earth, its environment, its climate, and its human residents. COVID-19 coronavirus, a deadly pathogen that, by the end of the year 2021, had killed over 1 million people worldwide, afflicted tens of millions, and disrupted the global economy, has spread throughout the planet. Out-of-control wildfires, exacerbated by global-warming-induced drought on the US West coast and later in Colorado, have spread an evil yellow haze across the nation causing the sun to appear as a dull red circle resting on the horizon just before sunset. Later, in October 2020, fire outbreaks in southern California, fueled by hurricane-force Santa Ana winds approaching 100 miles per hour in some cases, have prompted evacuation orders. Because of rapidly approaching wildfires, Colorado's Rocky Mountain National Park had to be abandoned in October 2020. Regulations requiring wearing of masks in public to prevent the spread of coronavirus sparked civil unrest in some places, fueled in part by the economic burden posed by measures taken to contain the coronavirus, resulting in rioting and destruction of infrastructure.

By mid-November of 2021, the deadly COVID-19 virus had swept the world with a steeply rising toll of deaths. The United States was leading the world in total cases and deaths, although several other smaller nations had the dubious distinction of having larger numbers of cases and deaths per 100,000 population. It is no exaggeration to assert that as 2020 was coming to a close, humankind was in a deadly race between this raging pandemic and the development and deployment of effective vaccines and treatments for it.

In 2018, some disease experts warned of a "Disease X" that could devastate humankind on Earth. The hypothetical disease that was the subject of the warning had characteristics remarkably like those of COVID-19 sweeping the world in 2020. It is estimated that there are more than 700 coronaviruses carried by bats, 50 of them closely related to severe acute respiratory syndrome (SARS) of which COVID-19 is a prime example. It is not improbable that more pandemics similar to COVID-19 are on the way. Humans need to be more intelligent in their appreciation of such onslaughts and develop rapid and effective responses to them.

In 2021, the reality of global warming and climate change was obvious to all thinking people. Climate change has been very apparent in higher, normally colder latitudes. In the first half of 2020, normally frigid Siberia experienced a time of very high temperatures. On June 20, the town of Verkhoyansk reached a record-breaking temperature of 38°C (100°F). Effects of excessive heat in the fragile Siberian environment included wildfires, loss of permafrost with release of methane, a powerful greenhouse gas, and an invasion of pests. In September 2020, augmented by global warming and record-high temperatures in Siberia, the ice of Arctic Ocean reached its second lowest level ever of 3.74 million square kilometers, next to 2012's record-low level. And according to some authoritative reports, Greenland's ice sheet has melted to a point of no return, such that it is too late to make any efforts to slow global warming to stop it.

On August 17, 2020, the temperature in Death Valley, California, hit 54.4°C (130°F), which some weather experts contend is the highest temperature ever recorded anywhere on the Earth (two higher temperatures reported in Death Valley in 1913 and in Tunisia in 1931 are not deemed

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to be from reliable readings). Warming climate and drought are contributing to mass movements of "climate refugees," such as a flood of Central American refugees to the United States in 2020. These movements are expected to reach epic proportions in future years, causing daunting humanitarian and political problems with major wars a real possibility. It is possible that some areas will become uninhabitable, including Saudi Arabia hit by record heat and a total lack of rainfall and parts of Bangladesh permanently flooded by raising sea levels. The year also saw a record hurricane season in the Gulf of Mexico (the farthest in history that the naming of Gulf hurricanes has had to go so far into the Greek alphabet), and at least one record-strongest typhoon ravishing parts of Southeast Asia.[1]

An interesting change in demographics is underway and expected to accelerate in the future as the human population on the Earth is likely to stop growing or even fall in decades to come with falling fertility rates, that is, the number of live births per woman.[2] Better education and career opportunities for women, access to means to limit births, and lower child mortality rates mean women will have fewer children on average. That is generally good news for the planet Earth, which already has reached a level of human population that exceeds its comfortable carrying capacity. Lower birth rates tend to go with enhanced economic development. For countries with lower income, this should mean higher living standards with better health and education for each child born. In some countries that have experienced lower fertility rates for decades, further shrinkage could be problematic. These countries must cope with caring for an older population, with fewer young people to provide care and to pay into the system.

So, it is obvious that planet Earth and those of us who live on it are in for interesting times in decades to come. To cope with the changes that will occur, humans must apply all they can of human ingenuity and science. A key science will be environmental chemistry, the topic of this book.

1.2 EARTH AND THE EARTH SYSTEM

This book is about environmental chemistry, the chemical processes, reactions, and conditions that occur in Earth's environment. So, what is the environment? The Earth's environment may be considered consisting of five closely related and interacting spheres: (1) the **hydrosphere**, consisting of water; (2) the **atmosphere**, composed mostly of air that envelopes the Earth's surface, the bulk of which lies in proximity to the surface; (3) the **geosphere**, which makes up the rock, mineral matter, and soil on or below the Earth's surface; (4) the **anthrosphere**, consisting of the many parts of the Earth that have been made, modified, and operated by humans employing their ingenuity and technology; and (5) the **biosphere**, consisting of living organisms. These five spheres shown in Figure 1.1 make up the **Earth System**.[3] It is logical to discuss environmental chemistry on the basis of the five major environmental spheres, keeping in mind that they compose a total Earth System and interact strongly with each other, including robust exchanges of matter and energy (Figure 1.1). Since this is a book about environmental chemistry, it goes directly and specifically into environmental chemistry as it applies primarily to each of the environmental spheres. But to discuss the environmental chemistry of any segment of the Earth System, account must be taken of all the other segments; thus, each is defined and briefly described at the beginning within this introductory chapter.

As noted above, a particularly important aspect of the Earth System is the continuous exchange of matter and energy among the five major environmental spheres. One of the major factors in these exchanges consists of **two great fluids** that circulate in the Earth System: (1) surface water, especially in the oceans and rivers, and (2) air in the atmosphere, both of which transport matter and energy. Air heated in equatorial regions expands and flows away from the equator carrying heat energy as sensible heat in the air molecules and latent heat in water vapor toward polar regions. The Gulf Stream, a plume of relatively warm water, heated in the Caribbean region flows northward near the surface of the Atlantic Ocean along the east coast of North America and releases heat off the coast of Europe before sinking and flowing back at greater depths. This phenomenon, called

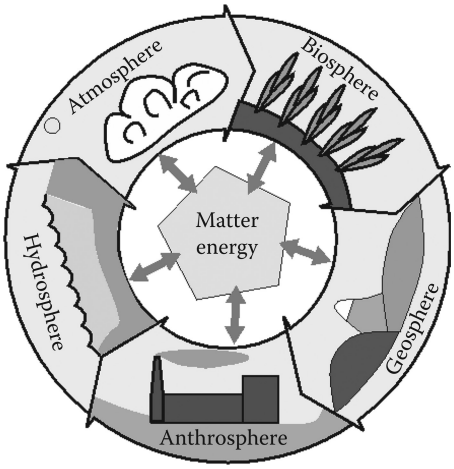

FIGURE 1.1 The Earth's environment (the Earth System) may be viewed as consisting of five spheres, which interact with robust exchanges of matter and energy among them.

the thermohaline circulation of the North Atlantic, is responsible in part for the relatively warm temperatures of Ireland, England, and Western Europe despite their more northern latitudes, and its possible demise is of concern with respect to global climate change. In addition to large quantities of water, flowing rivers carry sediments and are very much involved in the transport of waterborne pollutants.

1.3 BIOGEOCHEMICAL CYCLES IN THE EARTH SYSTEM

In addition to the two great fluids discussed above, a second pathway for the exchange of matter and energy among the environmental spheres through the Earth System is by way of **biogeochemical cycles**.[4] These are commonly expressed in terms of key elements, including essential nutrient elements. Often, as is the case with the nitrogen cycle, they contain an atmospheric component, though in some cases, such as the phosphorus cycle, the atmospheric component is not significant. Before humans' appearance on the Earth, the anthrospheric compartment did not exist, but now, as is the case of carbon dioxide emitted to the atmosphere by fossil fuel combustion, the anthrosphere is a very significant component of the Earth System. The anthrosphere is likewise a significant factor in the nitrogen cycle, in which atmospheric elemental N_2 is incorporated as chemically bound nitrogen fixed initially as ammonia (NH_3) in synthetic chemical facilities in amounts comparable to the nitrogen bound by living organisms (nitrogen-fixing bacteria).

Figure 1.2 illustrates an important example of a biogeochemical cycle, the carbon cycle. As shown in the figure, a small, but very significant fraction of the Earth's carbon is held in the atmosphere as CO_2 gas. This gas is transferred to the biosphere through the leaf surfaces of plants that photosynthetically convert it to biomass using solar energy. It also enters the hydrosphere by dissolving in surface water and enters the geosphere by precipitating as solid carbonate salts ($CaCO_3$) from water; the Earth's oceans constitute a large sink for atmospheric carbon dioxide. Carbon dioxide enters the atmosphere from the biosphere as organisms produce it as a product of their respiratory biochemical oxidation of organic matter and from the anthrosphere by the combustion of fossil fuels. Volcanoes and geothermal vents (such as those in Yellowstone National Park) emit carbon dioxide from the geosphere to the atmosphere. (Sudden emissions of large quantities of geospheric carbon dioxide underlying volcanic lakes have killed many people in Africa.) Carbon dioxide dissolved in water as HCO_3^- is converted to CO_3^{2-}, which, in the presence of dissolved Ca^{2+}, precipitates $CaCO_3$ (limestone) that ends up as solid rock in the geosphere. Carbon goes back into the hydrosphere as

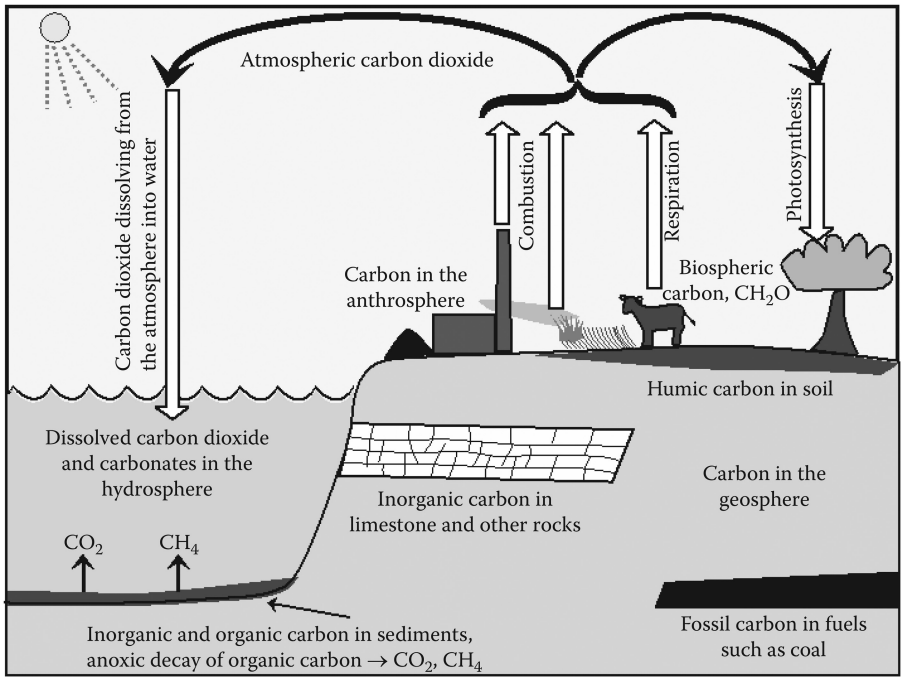

FIGURE 1.2 The carbon cycle showing the various reservoirs and conduits of carbon species in the environment. Biomass, which contains carbon, is represented by the general formula $\{CH_2O\}$. The carbon cycle is closely related to the oxygen cycle.

acidic CO_2 from the atmosphere or from the biodegradation of organic matter, reacting with solid $CaCO_3$ to produce dissolved HCO_3^-.

Several other important biogeochemical cycles involving elements that are important in living organisms may be noted here. Below are summarized cycles of four other elements that are important to living organisms.

1.3.1 Oxygen Cycle

The atmosphere, which is 21% elemental O_2 by volume, is a vast reservoir of this element. Oxygen is removed from the atmosphere as carbon dioxide by respiration process of organisms and by combustion and is returned to the atmosphere by plant photosynthesis in which oxygen is released from atmospheric CO_2 in the production of biomass. Oxygen is a component of biomass in the biosphere, and most rocks in the Earth's crust are composed of oxygen-containing compounds. Water or H_2O in the hydrosphere is predominantly oxygen.

1.3.2 Nitrogen Cycle

Nitrogen, as chemically very stable elemental N_2, composes approximately 80% of the Earth's atmosphere. Nitrogen from the atmosphere becomes chemically combined with other elements, especially H and O, by the synthesis of NH_3 in the anthrosphere, from N_2 and H_2 over a catalyst at high temperatures and very high pressures, as a by-product of combustion of fuels as gaseous NO and NO_2, and as nitrogen in biomass by some bacteria, including *Rhizobium* bacteria attached to the roots of legume plants growing under very mild conditions. Elemental N_2 and N_2O are returned to the atmosphere in the biodegradation of biomass, which also releases NH_4^+ to soil.

1.3.3 Sulfur Cycle

Chemically combined sulfur enters the atmosphere as pollutant gases such as H_2S and SO_2 gases, which are also emitted by natural sources, including volcanoes. Large quantities of H_2S are produced and released to the atmosphere by anoxic microorganisms degrading organic compounds and using sulfate, SO_4^{2-}, as an oxidizing agent. Volatile dimethyl sulfide, $(CH_3)_2S$, is released to the atmosphere by marine microorganisms. In the atmosphere, gaseous sulfur compounds are oxidized to sulfate, largely in the forms of H_2SO_4 (pollutant acid rain) and corrosive ammonium salts (NH_4HSO_4), which settle from the atmosphere or are washed out with precipitation. The geosphere is a vast reservoir of sulfur minerals, including sulfate salts ($CaSO_4$), sulfide salts (FeS), and even elemental sulfur. Sulfur is a small, though essential constituent of biomolecules.

1.3.4 Phosphorus Cycle

The phosphorus cycle does not have an atmospheric component. Phosphorus is an essential life element and ingredient of cellular DNA as well as ATP and ADP, molecules through which energy is transferred in organisms. Dissolved phosphate in the hydrosphere is required as a nutrient for aquatic organisms, although excessive phosphate may result in too much algal growth, causing an unhealthy condition called eutrophication. Phosphorus is abundant in the geosphere, especially as the mineral hydroxyapatite, $Ca_5OH(PO_4)_3$. Significant deposits of phosphorus-rich material have been formed from the feces of birds and bats (guano).

1.4 NATURAL CAPITAL OF THE EARTH SYSTEM

Every person in that very small group of humans who have been privileged to view the Earth from outer space has been struck with a sense of awe at the sight. Photographs of the Earth taken at altitudes high enough to capture its entirety reveal a marvelous sphere, largely blue in color, white where covered by clouds, with desert regions showing up in shades of brown, yellow, and red. But the Earth is far more than a beautiful globe that inspires artists and poets. In a very practical sense, it is a source of the life support systems that sustain humans and all other known forms of life. The Earth obviously provides the substances required for life including water, atmospheric oxygen, carbon dioxide from which billions of tons of biomass are made each year by photosynthesis, and ranging all the way down to the trace levels of micronutrients, such as iodine and chromium that organisms require for their metabolic processes. The Earth provides temperature conditions conducive to life and a shield against incoming ultraviolet radiation; its potentially deadly photons are absorbed by molecules in the atmosphere and their energy is dissipated as heat. The Earth also has a good capacity to deal with waste products that are discharged to the atmosphere, into water, or the geosphere.

As the industrial revolution gathered force from around 1800, unrestricted development put a rapidly increasing burden on natural capital, which continued during an era in which there was recognition of the problem. This eventually led to regulations that began to alleviate somewhat the impact on natural capital. To an extent, the regulatory approach was supplemented by pollution prevention and recycling. In an optimistic view of the future, sustainable development and green technology will further reduce the burden on natural capital even with increased economic development.

The capacity of the Earth System to provide materials, protection, and conditions conducive to life is known as its **natural capital**, which can be regarded as the sum of two major components: **natural resources** and **ecosystem services**. Early hunter–gatherer and agricultural human societies made few demands upon the Earth's natural capital. (However, they did modify it in some ways. For example, indigenous people in parts of North America regularly burned sections of forests so that grass would grow to support game animals.) As shown in Figure 1.3, as the industrial revolution

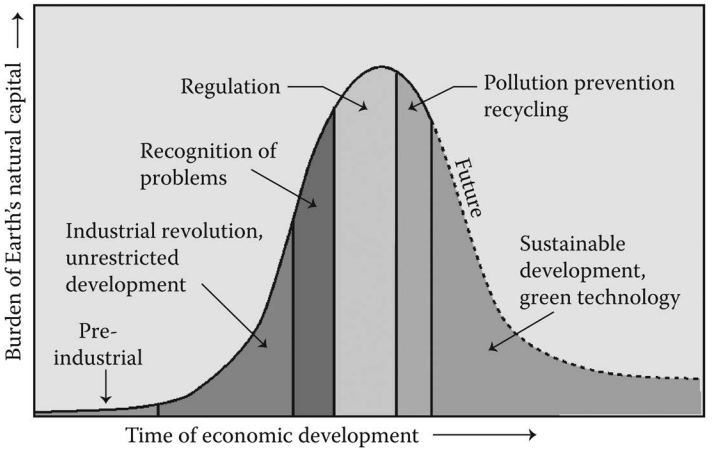

FIGURE 1.3 Stages of economic development with respect to utilization of the Earth's natural capital. The preindustrial impact of human activities was very low.

developed from around 1800, natural resources were abundant and the production of material goods was limited largely by labor and the capacity of machines to process materials. But now population is in excess, computerized machines have an enormous capacity to process materials, and the economies of once impoverished countries, including India, China, Taiwan, and South Korea, are becoming highly industrialized, with the result that the availability of natural capital is the limiting factor in production, including the availability of natural resources, the vital life support ability of ecological systems, and the capacity of the natural environment to absorb the by-products of industrial production, most notably greenhouse gas carbon dioxide.

To sustain the Earth and its natural capital for future generations, economic systems must evolve in the future such that they provide adequate and satisfying standards of living while increasing well-being, productivity, wealth, and capital and at the same time reducing waste, consumption of resources, and adverse environmental effects. The traditional capitalist economic system has proven powerful in delivering consumer goods and services using the leverage of individual and corporate incentives. Future systems must evolve in a manner that preserves these economic drivers while incorporating sustainable practices such as recycling wastes back into the raw material stream and emphasizing the provision of services rather than just material goods. In so doing, they can emulate nature's systems through the application of the principles of green chemistry and the practice of industrial ecology, which promote efficient material use and maximize recycling.

1.5 WHAT IS ENVIRONMENTAL CHEMISTRY?

Environmental chemistry is the discipline that describes the origin, transport, reactions, effects, and fates of chemical species in the hydrosphere, atmosphere, geosphere, biosphere, and anthrosphere. This definition is illustrated for a typical pollutant species in Figure 1.4, which shows the following: (1) coal, which contains sulfur in the form of organically bound sulfur and pyrite, FeS_2, is mined from the geosphere. (2) The coal is burned in a power plant that is part of the anthrosphere and the sulfur is converted to sulfur dioxide, SO_2, by atmospheric chemical processes. (3) The sulfur dioxide and its reaction products are moved by wind and air currents in the atmosphere. (4) Atmospheric chemical processes convert SO_2 to sulfuric acid, H_2SO_4. (5) The sulfuric acid falls from the atmosphere as acid rain. (6) The sulfur dioxide in the atmosphere may adversely affect biospheric organisms, including asthmatic humans who inhale it; the sulfuric acid in the acid rain may be toxic to plants and to fish in the hydrosphere, and it has a corrosive effect on structures and electrical equipment in the anthrosphere. (7) The sulfuric acid ends up in a sink, either soil in the

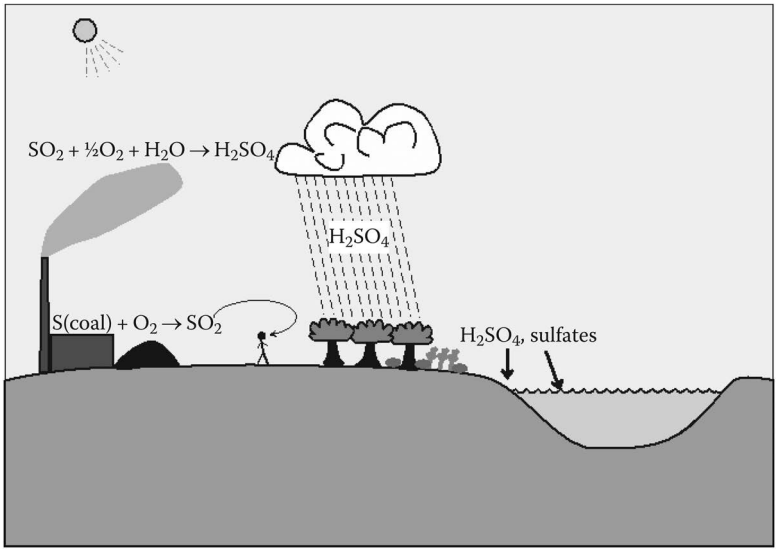

FIGURE 1.4 Illustration of the definition of environmental chemistry exemplified by the life cycle of a typical air pollutant, sulfur dioxide, produced and released to the atmosphere in coal combustion. Sulfur dioxide may affect human respiration and may be toxic to plants. Sulfur dioxide in the atmosphere may be oxidized to sulfuric acid, the main ingredient of acid rain. Acidic precipitation may adversely affect plants, materials, and water, where excessive acidity may kill fish. Eventually, the sulfuric acid or sulfate salts end up in water or in soil.

geosphere or a body of water in the hydrosphere. In these locations, H_2SO_4 may continue having toxic effects, including the leaching of phytotoxic (toxic to plants) aluminum ion from soil and rock in the geosphere and poisoning fish fingerlings in the hydrosphere.

1.5.1 Environmental Chemistry and the Spheres of the Earth System

It is convenient to consider environmental chemistry in light of the five major spheres of the Earth System defined earlier. However, none of these spheres may be considered in isolation from the other spheres. Therefore, when discussing the environmental chemistry of any specific sphere of the Earth System, it is necessary to consider interactions with each of the other spheres. The approach that is adopted here is to provide a brief introduction and overview of each of the environmental spheres to which reference may be made later in the book. For example, while discussing the environmental chemistry of the hydrosphere in later chapters, it is necessary to refer to exchanges of gases with the atmosphere, the influence of dissolved minerals and sediments from the geosphere, the effects of pollutants released from the anthrosphere, and the biochemical processes in water that are carried out by microorganisms from the biosphere. The environmental chemistry of the geosphere must consider its chemical alterations resulting from contacts with water and the influence of atmospheric oxygen on exposed minerals, as a habitat for much of the biosphere (as soil providing a medium for plants to grow), and as a repository of wastes produced in the anthrosphere. Many other such examples of environmental chemical interactions between spheres of the Earth System may be cited.

1.6 ENVIRONMENTAL CHEMISTRY OF WATER AND THE HYDROSPHERE

Earth's water is contained in the **hydrosphere**, normally regarded as surface water in the oceans, lakes, and rivers, which cover approximately 70% of Earth's surface. Water also occurs in close association with all the other spheres of the Earth System, including water vapor in the atmosphere,

subsurface groundwater in the geosphere, water contained in organisms in the biosphere, and water in the anthrosphere, such as in water distribution systems. More than 97% of Earth's water is in oceans, and most of the remaining freshwater is in the form of ice, a proportion that is lowering as Earth's ice in glaciers and polar and Greenland ice caps melts. Therefore, only a relatively small percentage of the total water on Earth participates in processes in the geosphere, the atmosphere, and the anthrosphere. Water circulates in the Earth System through the **hydrologic cycle**, a key cycle in which water is evaporated from the oceans, carried by wind as water vapor over great distances through the atmosphere, falls from the atmosphere as rain or other forms of precipitation, and eventually returns to the Earth's seas through streams and rivers that discharge into the oceans.

Although the chemical formula of water is simple, H_2O, the environmental chemistry of water is complex and varied. Much of the chemical behavior of water results from the structure of the water molecule. It is not symmetrical, because the two H atoms are on one side of the molecule, which has a partial positive charge, whereas the O atom with its much greater attraction for electrons has a partial negative charge. The result of this chemical structure is that the water molecule is **polar**, which is responsible for much of its chemical behavior, including the good solvent properties of water for ionic compounds. A second characteristic of the water molecule is its ability to form **hydrogen bonds** in which its H atoms form bridging bonds with O atoms of other water molecules or O or N atoms of other chemical compounds. In general, water is an extraordinarily good solvent, especially for ionic compounds and polar molecules.

The environmental chemistry of water is characterized by a large variety of chemical and biochemical reactions and processes, including the following: (1) **acidification** from dissolved CO_2 reacting in water; (2) **precipitation**, such as that of solid $CaCO_3$; (3) **dissolution**, dissolved CO_2 dissolves solid $CaCO_3$; (4) microorganism-catalyzed **oxidation reduction**, SO_4^{2-} reduced to odorous H_2S; (5) **photosynthesis** using solar energy to produce biomass (algae and photosynthetically produced bacteria) from dissolved CO_2; and (6) **chelation**, fulvic acid from decayed plant matter binds with dissolved Fe^{2+} to produce colored *gelbstoff*.

Other important processes in the hydrosphere include gas exchange with the atmosphere, especially O_2 and CO_2, and solute exchange between water and sediments. Colloidal suspensions of very small particles, such as bacterial cells, may exist in water and may coagulate to produce precipitates.

Water may become polluted by a variety of substances that have various adverse effects on water quality. Water pollutants include **oxygen-consuming substances** (biochemical oxygen demand), **algal nutrients** (potassium, phosphates, nitrates) that enable excessive growth of algae, **synthetic organic compounds** that may be toxic and undergo bioaccumulation in aquatic organisms, **herbicides** and **insecticides** applied to agricultural land or in landscaping, and toxic **heavy metals**, especially lead.

Some important treatment processes are applied to water in the hydrosphere. The major categories for water treatment are (1) treatment of municipal water, to remove pathogenic organisms, (2) treatment of wastewater, especially to remove organic matter that reacts biochemically to consume dissolved oxygen, (3) treatment for industrial uses, and (4) treatment for specialized applications.

1.7 ENVIRONMENTAL CHEMISTRY OF AIR AND THE ATMOSPHERE

Figure 1.5 shows the two lowest layers of the atmosphere that are closest to Earth's surface and are of the most importance for the Earth System. On a dry basis (exclusive of the 1%–3% water vapor normally in it), air is approximately 78% elemental nitrogen, N_2, 21% O_2, 0.9% argon, and 0.04% CO_2, with trace levels of some other gases including noble gases neon and helium and minuscule variable levels of NO, NO_2, and N_2O, which can be regarded as pollutants at higher levels. The lowest layer of the atmosphere extending to an altitude of approximately 11 km is the **troposphere**, which has an average global temperature of approximately 15°C at sea level, decreasing to an average temperature of approximately −56°C at its upper limit. The air pressure in the troposphere

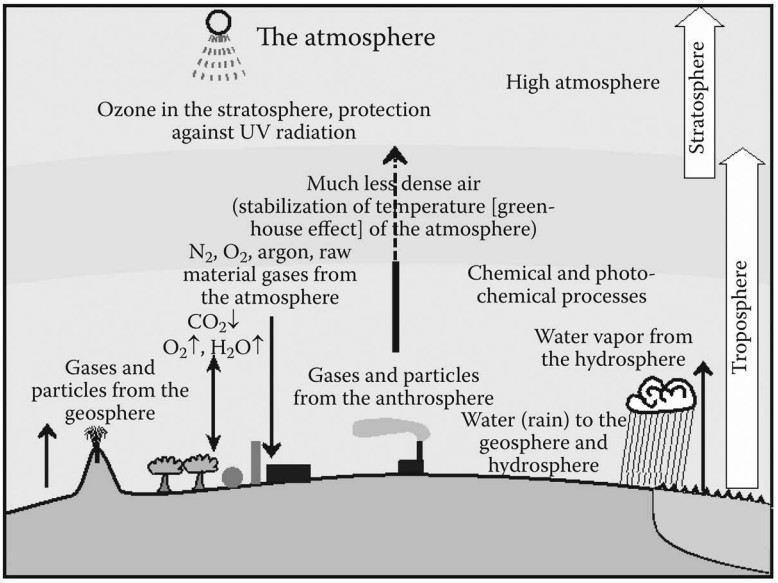

FIGURE 1.5 The atmosphere is a layer of gas above Earth's surface. Although the atmosphere extends for hundreds of kilometers in altitude, most of its mass is within just a few kilometers of Earth's surface. It serves as a source of some essential materials; protects life on Earth from deadly electromagnetic radiation; transports water as part of the hydrologic cycle; participates in the carbon, oxygen, and sulfur cycles; and is an essential part of the natural capital of the Earth System. The two lower and most important layers of the atmosphere are the troposphere and the stratosphere.

averages 1 atmosphere (atm) at sea level and only approximately 0.2 atm at the upper boundary of the troposphere. Most of the atmosphere's air is contained in the troposphere. Above the troposphere lies the **stratosphere** in which the average temperature increases with increasing altitude from approximately −56°C to approximately −2°C at the upper limit of the stratosphere around 50 km in altitude, decreasing again with altitude in the highly rarefied air of the mesosphere. The stratosphere is warmed by the absorption of ultraviolet solar radiation by ozone, O_3, in the stratosphere.

The atmosphere has some critical protective characteristics. One of these is the temperature-stabilizing **greenhouse effect** of the atmosphere, which absorbs infrared radiation by which incoming solar energy is released back to space thus keeping Earth's surface at a livable temperature. But, as noted in the introduction to this chapter, excessive amounts of CO_2 that have been released to the atmosphere by the combustion of fossil fuels are now causing an excessive greenhouse effect leading to increases in global temperatures above optimum levels and posing a profound threat to the Earth System.

A second vital protective function of the atmosphere is the role that ozone in the stratosphere plays in filtering out ultraviolet radiation from the sun. Were it not for this radiation filter, organisms could not exist on Earth's surface because of the damaging effects of ultraviolet radiation on tissue. (The ultraviolet radiation that does penetrate to Earth's surface is the major cause of skin cancer in humans.)

In addition to the protective functions mentioned above, the atmosphere is a critical part of the natural capital of the Earth System. It provides oxygen essential for human and animal life, it is the reservoir of carbon dioxide that plants and algae depend on for photosynthesis, and provides oxygen, nitrogen, and argon used for various purposes in the anthrosphere. The atmosphere has a capacity (often abused) to deal with wastes that are released to it. As one of the two great fluids of the Earth System mentioned above, circulating air in the atmosphere is a key component of the hydrologic cycle through which water circulates in the Earth System and redistributes some of the solar heat energy away from equatorial regions, leading to a more uniform distribution of global temperature.

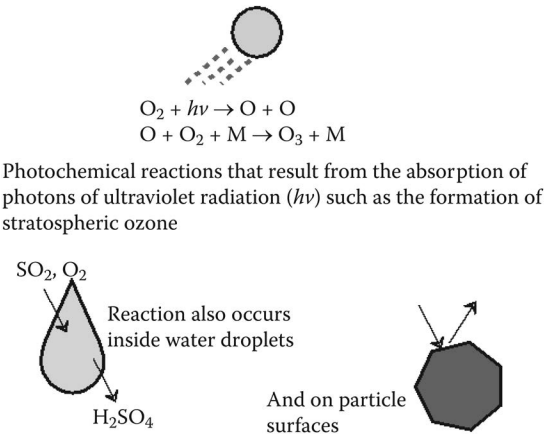

FIGURE 1.6 Many chemical reactions occur in the atmosphere. Among the most significant of these are photochemical reactions initiated by photons of ultraviolet radiation ($h\nu$) absorbed by molecules to produce reactive free radical species consisting of atoms or fragments of molecules called free radicals. The photochemical formation of stratospheric ozone is shown in this figure where "M" stands for a molecule, most commonly N_2, that absorbs excess energy from the reaction enabling the reaction product to stay intact.

Figure 1.6 illustrates some aspects of chemical reactions that occur in the atmosphere. These reactions cause many phenomena that affect the atmosphere, some beneficial and others harmful. Atmospheric chemical reactions are responsible for processes that purify contaminated air, including those in which organic air pollutants are oxidized to species that are purged from air, and pollutant inorganic gases, especially oxides of nitrogen and sulfur, are oxidized to water-soluble acids that are removed from the atmosphere with rain (but are also the constituents of pollutant acid rain). Atmospheric chemical reactions produce the stratosphere's protective ozone, but at lower altitudes in the troposphere, and, in the presence of nitrogen oxides and hydrocarbons, generate ozone, which at this level is harmful to human health as part of the atmospheric pollution phenomenon of photochemical smog. Along with reactions that take place in the gas phase of air, as illustrated in Figure 1.6, some chemical processes occur within water droplets suspended in air and on surfaces of suspended solid particles.

Of most significance in atmospheric chemistry is the role of photons of ultraviolet radiation in causing **photochemical reactions** to occur. These photons have an energy equal to the product $h\nu$ in which h is Planck's constant and ν is the frequency of radiation in units of s^{-1}, representing cycles per unit time. Electromagnetic radiation has both a particle (photon) characteristic and a wave characteristic; the higher the frequency, the shorter the wavelength and the higher the energy of the radiation. The absorption of a sufficiently energetic photon can break a chemical bond causing a cascade of atmospheric chemical reactions to occur.

Many kinds of **air pollutants** occur in the atmosphere. They may adversely affect human health and environmental quality. The most important of them are **ozone** when present in the troposphere, **particulate matter**, **carbon monoxide**, **carbon monoxide** (CO), **nitrogen oxides** (NO and NO_2, collectively denoted as NO_x), **sulfur dioxide**, **lead**, and **mercury**.

1.8 ENVIRONMENTAL CHEMISTRY OF THE GEOSPHERE

Most of the mass of the Earth System is contained in the **geosphere**, encountered by humans generally as solid rock and soil. Volcanic eruptions of lava demonstrate that much of the geosphere is not solid but consists of hot molten rock. The geosphere is composed of a solid, iron-rich inner core, molten outer core, mantle, and crust. The crust, only 5 to 40 km thick, is a thin outer skin

composed largely of lighter silicate-based minerals. With respect to interactions with the other spheres of the environment, the crust is the most important part of the geosphere. Earth's crust is that part of Earth upon which humans live and from which they extract most of their food, minerals, and fuels.

The geosphere has a very close relationship with the hydrosphere, the atmosphere, and the biosphere. The geosphere is also strongly affected by human activities in the anthrosphere.[5] On Earth's surface, the geosphere consists of rocks composed of various minerals that contain predominantly silicon and oxygen. In many areas, a thin layer of soil is present on Earth's surface. As illustrated in Figure 1.7, igneous rocks, which may be formed by the solidification of molten magma deep below Earth's surface, thrust upward by tectonic forces are broken down (weathered) by physical, chemical, and biological processes, and material from them is deposited as sedimentary rock. Heat and pressure convert sedimentary rock to metamorphic rock. Over many millions of years, the metamorphic rock may sink to depths where it is hot enough to be melted and converted to magma to start the whole cycle over again.

Geology[6] is the science of the geosphere and is very important for understanding the environmental chemistry of the geosphere. It pertains mostly to the solid mineral portions of the Earth's crust. But geology must also consider water, which is involved in weathering and eroding rocks and in producing mineral formations, and the atmosphere, which has strong effects on the geosphere and exchange matter and energy with it. Geology is also very important in respect to the biosphere. Living organisms largely exist on the geosphere and in turn have significant effects on it. Modern technology used in the anthrosphere may strongly affect the geosphere. An example is the ability to move massive quantities of dirt and rock by large machines.

Geochemistry is the science that considers chemical species, reactions, and processes of rocks and minerals in the geosphere as they relate to the hydrosphere, atmosphere, biosphere, and anthrosphere.[7] The influence of geochemistry on the anthrosphere and *vice versa* are important. As an

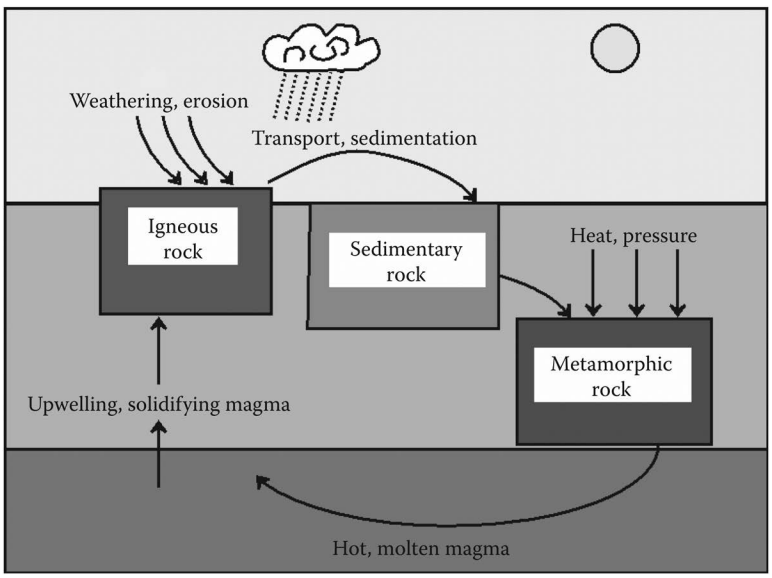

FIGURE 1.7 Simplified view of the rock cycle by which geospheric material circulates through the tectonic cycle. As liquid magma rises to the surface, it becomes cooler and forms solid igneous rock. The solid igneous rock becomes exposed to water and air. The exposed igneous rock breaks down physically and may undergo chemical changes. This is a process of weathering and it results in the formation of sedimentary rock. Heat and pressure convert sedimentary rock to metamorphic rock. Rock that sinks to lower depths may become very hot and melt to form magma again.

example of a geochemical process, consider that carbon dioxide from the atmosphere dissolves in water in the hydrosphere and then reacts with limestone in the geosphere:

$$CaCO_3(s) + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (1.1)$$

This reaction puts dissolved calcium (water **hardness**) and bicarbonate ion (water **alkalinity**) into water. The double arrow in Reaction 1.1 shows that the reaction is reversible. If water containing Ca^{2+} and HCO_3^- lose CO_2 by boiling or by consumption of CO_2 by the photosynthesis of algae, solid $CaCO_3$ (limestone) is produced.

The geosphere is a very important source of natural capital. Some important parts of the Earth's natural capital include **fuels**, such as natural gas; **metals**, such as iron or copper; **nonmetals**, such as clay, sand, gravel; **plant nutrients**, such as phosphorus; and as a repository for wastes. Carbon dioxide from fossil fuel combustion or gasification or that occurs with some sources of natural gas is sometimes injected deep into permeable rock formations in the geosphere (carbon sequestration).

1.8.1 Soil

The most important part of the natural capital of the geosphere is **soil**. Soil is the thin layer on the surface of the geosphere surface that supports plant growth and produces food. **Soil** is composed of finely divided, highly disintegrated mineral matter and organic matter from the partial biodegradation of plant. Earth's soil is a very thin layer; if Earth were a classroom globe, the average thickness of the total soil resource would be about the same as the diameter of a human cell! This fragile layer supports the plant life that forms the base of the food web for all organisms that do not dwell in water.

Because the two most abundant elements in Earth's crust are oxygen and silicon, silicates are the most common minerals in soil. These include finely divided quartz (SiO_2), potassium feldspar (orthoclase, $KAlSi_3O_8$), and albite ($NaAlSi_3O_8$). Other elements that are relatively abundant in Earth's crust are aluminum, iron, calcium, sodium, potassium, and magnesium. These elements are contained in soil in minerals such as epidote ($4CaO{\bullet}3(AlFe)_2O_3{\bullet}6SiO_2{\bullet}H_2O$), goethite ($FeO(OH)$), magnetite ($Fe_3O_4$), calcium and magnesium carbonates ($CaCO_3$, $CaCO_3{\bullet}MgCO_3$), and oxides of manganese and titanium. Soil rocks such as potassium feldspar undergo disintegration processes (weathering) to produce finely divided colloidal particles (secondary minerals). The most abundant of these products are **clays**, which are hydrated oxides of silicon and aluminum and sometimes contain other elements. Clays hold water and can temporarily hold various cations, such as plant nutrient K^+, and exchange them for other cations such as H^+.

Some of the soil mass consists of **soil humus**, organic matter produced by the partial biodegradation of plant residues. Although often just a few percent of soil mass, this organic fraction of soil has a strong influence on the physical, chemical, and biological characteristics of soil. Among its important effects in soil, organic matter is effective in holding soil moisture, and it holds and exchanges with plant roots some of the ions that are required as plant nutrients.

Water is one of the important chemical constituents in soil and is required for plants. This water, called the **soil solution**, is taken up by plant root hairs, transferred through the plant, and evaporated from the leaves, a process called **transpiration**. The soil solution contains dissolved materials, including plant nutrients, which are carried into plants through the transpiration process. The soil solution transfers substances, such as dissolved metal cations, between roots and the soil solid. Cations commonly present in the soil solution include H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+, along with very low levels of Fe^{2+}, Mn^{2+}, and Al^{3+}. Common anions present in soil are HCO_3^-, CO_3^{2-}, HSO_4^-, SO_4^{2-}, Cl^-, F^-, NO_3^-, HPO_4^{2-}, and $H_2PO_4^-$.

Most of the plant biomass is composed of carbon, hydrogen, and oxygen, which plants extract from water and atmospheric carbon dioxide. Lower quantities of calcium, magnesium, and sulfur are required by plants, but they are usually present in sufficient abundance in soil. Some plant

nutrients of particular importance in soil are often not present naturally in soil at levels sufficiently high to support optimum plant growth. These are species of nitrogen, phosphorus, and potassium that are commonly added to soil as **plant fertilizers** in forms of chemical species that plants can absorb and utilize. The common plant fertilizers are nitrogen, commonly added to soil as salts of NH_4^+ and NO_3^-, both present in ammonium nitrate fertilizer NH_4NO_3; phosphorus as phosphate ions, HPO_4^{2-}, and $H_2PO_4^-$; and potassium as salts of K^+ added as KCl or KNO_3.

1.9 ENVIRONMENTAL CHEMISTRY OF THE ANTHROSPHERE

The **anthrosphere**, defined as that part of the environment made or modified by humans and used for their activities,[8] has a strong connection to environmental chemistry. It is closely tied to the other environmental spheres.

Like other spheres of the environment, the anthrosphere consists of a number of different parts. These may be categorized by considering where humans live; how they move; how they make or provide the things or services they need or want; how they produce food, fiber, and wood; how they obtain, distribute, and use energy; how they communicate; how they extract and process nonrenewable minerals; and how they collect, treat, and dispose of wastes. Therefore, it is possible to divide the anthrosphere into the following categories: (1) structures used for dwellings; (2) structures used for manufacturing, commerce, education, and other activities; (3) utilities, including water, fuel, and electricity distribution systems, and waste distribution systems, such as sewers; (4) structures used for transportation, including roads, railroads, airports, and waterways constructed or modified for water transport; (5) structures and other parts of the environment modified for food production, such as fields used for growing crops and water systems used to irrigate the fields; (6) machines of various kinds, including automobiles, farm machinery, and airplanes; (7) structures and devices used for communications, such as telephone lines or radio transmitter towers; and (8) structures, such as mines or oil wells, associated with extractive industries.

As shown in Figure 1.8, the anthrosphere is a big potential source of pollutants and wastes. Especially since around 1900, the anthrosphere has seen explosive growth in the chemical industry. Thousands of synthetic chemicals, including DDT insecticide, polychlorinated biphenyls (PCBs), and chlorofluorocarbon compounds (Freons), have gone into commercial production and inevitably

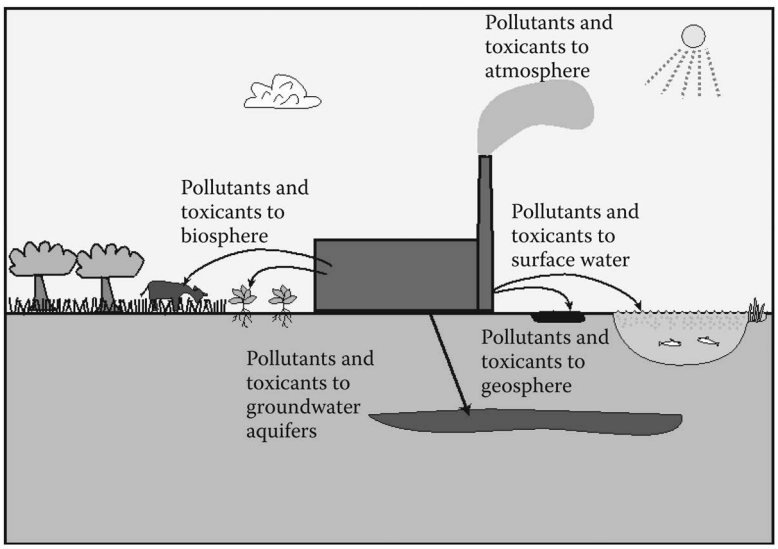

FIGURE 1.8 The anthrosphere is the major source of air and water pollutants, toxic substances that affect organisms, and wastes, including hazardous wastes, disposed to landfill and other parts of the geosphere.

have been distributed in the environment. Many of these substances are quite unlike chemical species produced by natural processes, and are very poorly biodegradable, if at all.

Sustainability of Earth and its precious natural capital requires that the anthrosphere be operated in a way that is consistent with sustainability. The sciences of industrial ecology and green chemistry are means of operating the anthrosphere in ways that ensure sustainability.

Industrial ecology views an industrial system as an artificial ecosystem, with primary sources of raw materials and energy and with many enterprises making use of what would otherwise be waste products of other members of the system. Industrial ecology is conducted in a manner that minimizes environmental impact while optimizing utilization of resources, energy, and capital.[9] When they are using the best practices of industrial ecology, commercial firms produce goods and services with maximum efficiency and with minimum environmental impact. Industrial ecology is carried out in **industrial ecosystems** analogous to natural ecosystems. The classic example of an industrial ecosystem is the one located in Kalundborg, Denmark.[10]

A companion science to industrial ecology as applied specifically to the most sustainable systems of chemical manufacturing and processing, **green chemistry** is the practice of chemical science and manufacturing within a framework of industrial ecology in a manner that is sustainable, safe, and nonpolluting and that consumes minimum amounts of materials and energy while producing little or no waste material. The practice of green chemistry plays an important role in operating the anthrosphere sustainably. Since the mid-1990s, green chemistry has emerged as a major movement in chemistry.[11]

1.10 ENVIRONMENTAL CHEMISTRY OF THE BIOSPHERE

The **biosphere** (Figure 1.9) is composed of all living organisms largely living on the surface of the geosphere on soil, or just below the soil surface. The oceans and other bodies of water support high populations of organisms. Some life forms exist at great depths on ocean floors. In general, though, the biosphere is a very thin layer at the interface of the geosphere with the atmosphere. The biosphere is involved with the geosphere, hydrosphere, and atmosphere in *biogeochemical cycles* (Section 1.3) through which materials such as nitrogen and carbon are circulated.

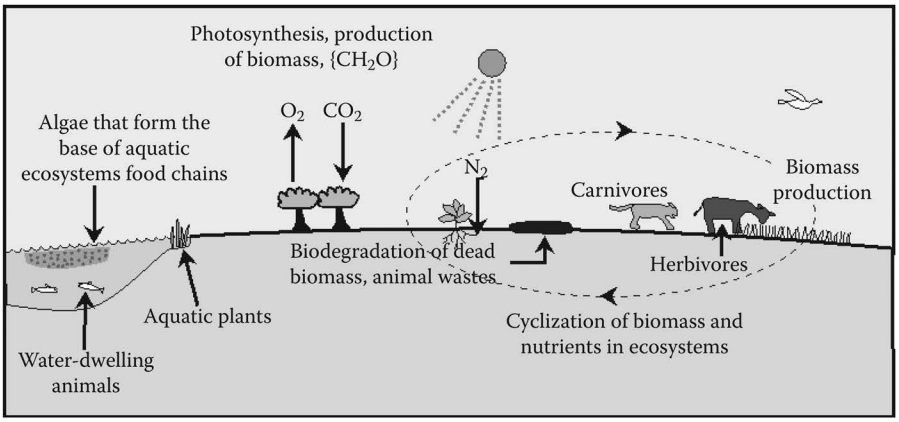

FIGURE 1.9 Organisms occur within ecosystems in the biosphere where they interact with each other and with their environment. Biological ecosystems have evolved in a manner that enables the most efficient utilization of energy and matter with complete recycling of biomass and nutrients. Ecosystems are based on photosynthetic plants and algae that produce the biomass that anchors the ecosystems. In the photosynthesis process, plants and algae remove carbon dioxide from the atmosphere and return oxygen. Some microorganisms, such as *Rhizobium* bacteria that grow on the roots of legume plants, convert elemental nitrogen from the atmosphere to biochemically bound nitrogen. Fungi and bacteria degrade dead biomass, a process that returns nutrients to the ecosystem.

Ultimately, the greatest concern with respect to chemical species in the environment is their relationships with organisms in the biosphere. Organisms in the biosphere act as sophisticated chemical reactors that carry out a very large number of chemical transformations including chemical changes to which organisms are exposed in the environment. These processes have a tremendous effect on the Earth System. The chemical processes that organisms carry out are studied under the topic of **biochemistry**. **Environmental biochemistry** deals specifically with biochemical processes that occur in the environment and that have effects on the environment.

Organisms in the biosphere produce biomass and biochemicals. By far, the greatest quantities of substances produced consist of carbohydrates generated by plant **photosynthesis**. The most common of these carbohydrates is glucose sugar, a simple sugar molecule that is the primary product of photosynthesis as shown by the following reaction:

$$6CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2 \tag{1.2}$$

In this reaction, photons of solar light represented by $h\nu$ provide the energy used for photosynthesis by plants, algae, and photosynthetic bacteria. This energy is used to break apart the very stable chemical bonds in water from the hydrosphere and carbon dioxide from the atmosphere and reassemble the carbon, hydrogen, and oxygen atoms to biomolecules. These biomolecules, which are represented in this book by the simplified chemical formula $\{CH_2O\}$, constitute the high-energy biomass in glucose and in complex molecules such as starch. Also included among biomolecules are molecules of proteins, lipids (fats and oils), nucleic acids comprising DNA, and other more specialized biomolecules.

The opposite of photosynthesis takes place when organisms break down biomolecules and chemically synthesized molecules to simpler products, often extracting energy in the process. This is shown below for the biochemical metabolism of glucose to provide energy that living organisms, including humans, use:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \tag{1.3}$$

The breakdown of organic molecules to simple inorganic species, including especially water and carbon dioxide, is the process of **biodegradation**. Biodegradation is a crucial function of organisms in the biosphere and it is an important means by which synthetic molecules transferred from the anthrosphere to the other environmental spheres are degraded to products that are usually harmless.

There are some important environmental chemical processes in which organisms in the biosphere act upon inorganic materials other than water and carbon dioxide. As an example, some transformations of nitrogen compounds carried out by microorganisms are discussed here. Of particular importance is **nitrogen fixation,** the ability of some microorganisms, including some kinds of bacteria that grow in water and on the roots of plants, to convert elemental nitrogen from the atmosphere to chemically bound nitrogen that can be used by plants to synthesize proteins as shown in the following reaction where $\{CH_2O\}$ represents biomass:

$$3\{CH_2O\} + 2N_2 + 3H_2O + 4H^+ \rightarrow 3CO_2 + 4NH_4^+ \tag{1.4}$$

This green, environment-friendly process occurs under mild conditions in organisms whereas industrial nitrification demands catalysts, extremely high pressures, and high temperatures.

Nitrification, the bacterial conversion of NH_4^+ to NO_3^-, is an important process in nature because it provides nitrogen in the nitrate form that algae and other plants can best utilize:

$$2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O \tag{1.5}$$

Bacterially mediated **denitrification**

$$4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \tag{1.6}$$

is the process by which nitrate is reduced by bacteria to gaseous nitrogen and returned to the atmosphere.

Biochemical processes in the biosphere may produce some toxic substances and air and water pollutants. An example is the production of toxic, odorous hydrogen sulfide gas by the microbial reduction of sulfate shown below.

The microbial transitions of inorganic sulfur species are important processes in the hydrosphere. An example is the bacterial reduction of sulfate to odorous, toxic H_2S with biomass ($\{CH_2O\}$) serving as the reducing agent:

$$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \tag{1.7}$$

Bacteria acting upon iron pyrite, FeS_2, produce pollutant **acid mine water** containing H_2SO_4 and acidic hydrated $Fe(H_2O)_6^{3+}$.

The biosphere provides a vast source of biomaterials including carbohydrates that can be employed for fuel or wood (largely cellulose) used as a structural material. In addition to carbohydrates, other classes of biomaterials are produced by organisms. Among the most significant of these are the **lipid oils**, which are esters of long-chain fatty acids bound with glycerol, an alcohol with three -OH groups. In addition to their food value, lipids can be used as chemical feedstocks and for the synthesis of synthetic fuels including biodiesel fuel made from soybean oil.

Some plants, including evergreens, pines, and citrus, produce hydrocarbons directly in the form of **terpenes**, hydrocarbon molecules containing at least one C=C double bond. The most useful terpene is isoprene, $H_2C{=}C(CH_3)CH{=}CH_2$, which is extracted from the rubber tree, *Hevea brasiliensis*, and is the raw material used to make natural rubber. Some terpenes emitted to the atmosphere by trees, including α-pinene, are very reactive in the atmosphere and participate in photochemical smog formation.

1.11 TOXICOLOGICAL CHEMISTRY AND BIOCHEMISTRY

A significant concern regarding the biosphere and its relationship to environmental chemistry is the effect of toxic substances on organisms. **Toxicology** is the science of **poisons** or **toxicants**, substances that damage or destroy living tissue or that cause biochemical processes to malfunction. **Toxicological chemistry** (Figure 1.10) relates the chemical nature of substances to their toxic effects on organisms.[12] A very important aspect of toxicological chemistry is how organisms metabolize toxicants. Some, such as carbon monoxide, which binds directly to blood hemoglobin, are not metabolized at all whereas others, like polycyclic aromatic hydrocarbons benzo(a)pyrene, undergo metabolic transformations that convert them to toxic forms.

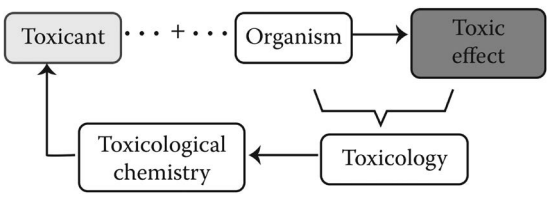

FIGURE 1.10 A major consideration with respect to the biosphere is the effect of toxic substances on organisms. Toxicology is the science dealing with various aspects of the effects of poisonous substances on organisms. Toxicological chemistry relates the chemical nature and biochemical behavior of toxic substances and precursors of toxicants to their toxic effects.

The modes and routes of exposure to toxic substances are very important in determining toxic effects. Exposure to toxicants may be either acute (short-term) or chronic (over a period of time), and exposure may be either local or systemic, with transport to other parts of the body.

1.12 AS WE ENTER THE ANTHROPOCENE

This chapter provides an overview of the Earth System and the environmental chemistry that occurs within it. Environmental chemistry has a strong role to play in preserving our planet in these challenging times in which the Earth is undergoing significant, perhaps drastic and potentially catastrophic, change, especially with respect to climate. The Earth has entered the new age of the **Anthropocene**, an evolving epoch in the Earth's lifetime.[13] The existence of the Anthropocene was first suggested in 2000 by Paul Crutzen (who shared the 1995 Nobel Prize for his work on stratospheric ozone depletion caused by chlorofluorocarbons) and his colleague Eugene Stoermer. The argument was made convincingly that the relatively hospitable Holocene epoch in which modern humans had been living since the end of the last Ice Age approximately 10,000 years ago has ended and that the Earth is entering a new epoch, the Anthropocene, in which conditions are determined largely by what humans do with their growing capacity to change global conditions, a change that poses an enormous challenge for humankind.

On its present trajectory, the Anthropocene epoch will have to be a brief one if a habitable Earth is to be sustained. Population pressures, depletion of the Earth's natural capital, global climate change, and other pressures on the planet dictate that an alternative to the Anthropocene must evolve if humankind is to survive in any reasonable state of well-being. What is required is that a radical change in direction must be made in the rapidly developing Anthropocene that is causing grievous harm to the Earth System, and especially its fragile biosphere, to a new epoch designed by humans for maximum sustainability and called the **Sustainocene**.[14] The term *Sustainocene* is commonly attributed to statements made in a public lecture entitled "From Anthropocene to Sustainocene. Challenges and Opportunities" presented by Bryan Furnass at the Australian National University on March 21, 2012. In transitioning to the Sustainocene, it is important to realize that human impact on the planet is a product of population, affluence, and consumptive technology. Recognition must be given to the fact that not all technology is bad and that there are technologies that not only place a relatively lighter burden on the Earth System but even have a positive influence for the benefit of the Earth. In achieving the Sustainocene, it is important to employ the science of environmental chemistry to understand and manage the Earth System. In providing the goods and services that humans need, the science of industrial ecology must be employed, and as it pertains specifically to chemistry, large-scale adoption of the practice of green chemistry will be essential.

1.13 SPECIAL CHALLENGES TO ENVIRONMENTAL CHEMISTRY AS GLOBAL CLIMATE CHANGE BECOMES REALITY

In the United States, many improvements have been made in environmental quality since the passage of important legislation including the Clean Air Act of 1970, the National Environmental Policy Act of 1970, the Clean Water Act of 1972, and the 1973 Endangered Species Act. Other nations, although not all, have made great improvements as well. But as global climate change becomes an uncomfortable reality, many of these improvements are undergoing an undoing and reversal. For example, hotter weather and more intense sunshine in areas threatened by photochemically induced air pollution means faster reactions in the atmosphere leading to formation of secondary air pollutants. Less rainfall in arid regions translates to shortages of water with challenges of keeping it pure. There is evidence that climate change is leading to mass extinctions of species along with invasions of undesirable species including, as examples, aggressive African bees and deadly "murder hornets." The spread of pathogens promoted by the conditions of global climate change,

including newly emerged deadly virus, such as COVID-19, threatens the lives of a large fraction of the Earth's population.

The climate crisis poses an existential threat to the Earth, its environment, and the human species. The big question before us is whether or not humankind can muster the will to deal constructively with this new reality, or if we are all going to "go off a cliff" together. If they will do it, people around the world can in fact muster the brain-power, and the resources to slow and perhaps stop or even reverse climate change as well as adapt to it in constructive ways. It will require a massive international effort, innovative ways to provide funding for it, and adoption of technologies that some may find intrusive or objectionable. But, the effort must be made. The alternative of a sick planet wracked with extremes of temperatures, drought, wildfires, storms, rising sea levels, food shortages, and other disastrous conditions is unthinkable. In that respect, chemistry, and specifically environmental chemistry, must play an essential role, which is the reason to study this essential discipline.

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Questions and Problems

In answering all questions, it is assumed that the reader has access to the Internet from which general information, statistics, constants, and mathematical formulas required to solve problems may be obtained. These questions are designed to promote inquiry and thought rather than just finding material in the text. So, in some cases, there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, it may be considered to be "right."

1. Much of what is known about the Earth's past history is based on paleo-environmental studies. Doing some research on the Internet suggests what is meant by these studies. How can past climatic conditions, temperature, and atmospheric carbon dioxide levels be inferred going back hundreds of thousands of years based on ice cores and even millions of years based on fossils?
2. The idea of climate change caused by human activities appears to be relatively recent. However, it was proposed quite some time ago in a paper entitled "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground." When was this paper published and who was the author? What were his credentials and credibility?
3. The definition of environmental chemistry shown in Figure 1.4 could very well be illustrated with nitrogen oxides, NO and NO_2, emitted to the atmosphere. What would be the sources of these gaseous nitrogen oxides? Which secondary air pollutant would they form interacting with volatile hydrocarbons in the sunlight? Could acid rain result from these oxides and, if so, what would be the formula of the acid?
4. Many reputable scientists now believe that the Holocene is ending and a new era has begun. What is the Holocene? What is the new era that may well be replacing it and how does it relate to material in this chapter? What are some of the environmental implications of this change?
5. In the late 1800s, there was concern that within the nitrogen biogeochemical cycle, not enough of the atmosphere's inexhaustible store of nitrogen was being "fixed" to chemical forms that could be utilized by plants and that food shortages and even mass starvation would result from a shortage of fixed nitrogen. What happened to change this situation? In what respect did this development save many lives and how did it also make possible the loss of millions of people in warfare after around 1900?
6. In what respect is the term *solid earth* a misnomer? What are some specific events in the last decade that cast some doubt on "solid earth?" How did one of these events specifically affect the anthrosphere and perhaps change the course of future energy developments?

7. In what important, fundamental respect does the phosphorus cycle differ from the carbon, oxygen, and nitrogen cycles?
8. Most people are aware that atmospheric carbon dioxide contributes to global warming and climate change. In what respect, however, is the atmosphere's carbon dioxide part of the Earth's natural capital, that is, where would we be without it? What crucial natural phenomenon causes a slight, but perceptible change in atmospheric carbon dioxide levels over the course of a year?
9. Figure 1.4 illustrates the definition of environmental chemistry in terms of a common pollutant. What command and control regulations have been implemented in limiting this source of pollution? What "end-of-pipe" measures have been used? Suggest how the practices of green chemistry might serve as alternatives to these measures.
10. As it applies to environmental processes and pollution, the term *sink* is sometimes used. With some search on the Internet, explain what is meant by a sink as it applies to environmental pollution. In what sense is the Earth's ability to act as a sink part of its natural capital? Explain.
11. In dealing with pollution and the potential for pollution, three approaches are pollution prevention, end-of-pipe measures, and remediation. What do these terms mean in terms of pollution control? Which is the most desirable, and which is the least? Explain.
12. With respect to increased production of corn to provide fuel ethanol, increased demand for fertilizer in the form of chemically combined nitrogen means that more ammonia is synthesized using atmospheric nitrogen and affecting the nitrogen cycle. With respect to which resource of the Earth's capital is the synthetic production of nitrogen fertilizer as it is now done a problem, and in respect to which resource is it **not** a problem? Explain.

2 The Hydrosphere and Water Chemistry

2.1 WATER: AN ESSENTIAL PART OF EARTH'S NATURAL CAPITAL

Figure 2.1 represents the hydrosphere, one of the major spheres of the Earth System in which the Earth's crucial store of water is found, and the **hydrologic cycle**, one of the great cycles of the Earth System through which water in the hydrosphere circulates. Along with (and connected to) the great challenges of global climate change and overpopulation, the distribution, quality, and quantity of water are among the greatest concerns facing humankind today. Indeed, the "water problem" has always challenged humankind and the biosphere as a whole. Even in temperate climates, fluctuations in precipitation have caused problems, and reductions of water availability associated with shifts in climate have caused once thriving civilizations to decline. Devastating droughts and destructive floods are frequent occurrences in many areas of the world in modern times. Ambitious programs of dam and dike construction have reduced flood damage, but they have had many undesirable side effects in some areas, such as inundation of farmland by reservoirs and damaging floods caused by failure of unsafe dams (as happened in Michigan in May, 2020, resulting in catastrophic flooding). Waterborne diseases such as cholera, typhoid, and dysentery killed millions of people in the past and still cause great misery in less developed countries.

Water covers approximately 70% of the Earth's surface. More than 97% of the Earth's water is in oceans, and most of the remaining freshwater is in the form of ice and snow in the polar ice caps, the ice pack that covers Greenland, and glaciers and snow pack in mountain regions, although the amount of water held in ice packs is diminishing as the Earth's climate warms. Less than 1% of the total water on the Earth is available to participate in processes in the geosphere, the atmosphere, and the biosphere.

The study of water is called **hydrology**. **Limnology** deals with the physical, chemical, and biological characteristics of freshwater.[1] **Oceanography** is the science of the ocean, unique because of its high salt content. **Groundwater** is contained in porous layers of minerals below ground level. **Surface water** occurs primarily in streams, lakes, and reservoirs. **Wetlands** are flooded areas in which the water is shallow enough to enable the growth of bottom-rooted plants. **Estuaries** are arms of the ocean into which streams flow, which have unique chemical and biological properties because of the mixing of freshwater and saltwater and which are the breeding grounds of much marine life.

Aquatic chemistry, the subject of this chapter, must consider water throughout the hydrosphere, as well as the phenomena that determine the distribution and circulation of chemical species in natural waters. Its study requires some understanding of the sources, transport, characteristics, and composition of water. The chemical reactions that occur in water and the chemical species found in it are very much affected by the environment in which the water is found. The physical condition of a body of water in the hydrosphere strongly influences the chemical and biological processes that occur in water. The chemistry of water exposed to the atmosphere is quite different from that of water at the bottom of a lake. Microorganisms play an essential role in determining the chemical composition of water, an important connection between the hydrosphere and the biosphere. Thus, in discussing water chemistry, it is necessary to consider the many general factors that influence this chemistry and the influence of the other environmental spheres on the hydrosphere.

An example of the influence of the physical condition of a body of water is exhibited by the thermal stratification of a lake or reservoir as shown in Figure 2.2. During the summer months, such a body of water may become divided between a surface layer (**epilimnion**) heated and made less dense by solar radiation, which, because of its lower density, rests over a cooler, more dense,

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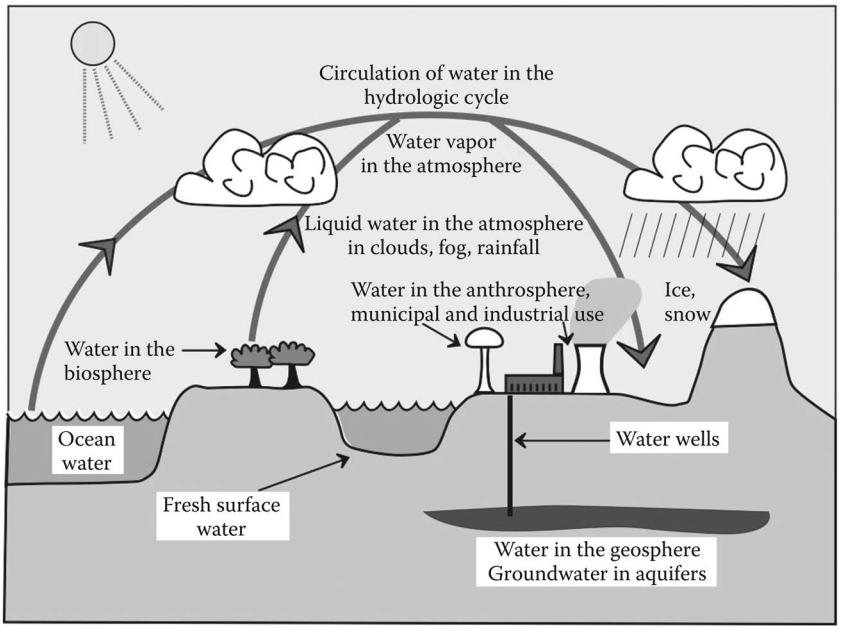


FIGURE 2.1 Water circulates through the Earth System in the hydrologic cycle. In this cycle, the hydrosphere interacts with the atmosphere, geosphere, biosphere, and anthrosphere. These interactions have strong effects on the environmental chemistry of water.

bottom layer (**hypolimnion**). Because of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is oxic (aerobic). In the hypolimnion, bacterial action on biodegradable organic material may cause the water to become anoxic (anaerobic), lacking dissolved oxygen. As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion. With cooling in the fall, the thermal stratification is reversed, resulting in mixing that may cause a number of physical, chemical, and biological changes, including increased biological activity from mixing of nutrients.

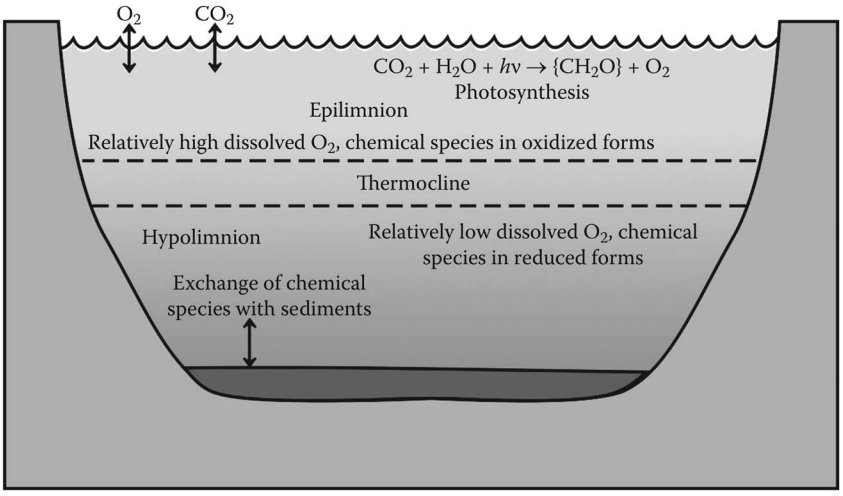


FIGURE 2.2 Stratification of a lake.

Water and the hydrosphere are crucial in the processes involved with **chemical fate and transport** of substances including pollutants in the environment. These include the physical processes of volatilization, dissolution, precipitation, and uptake and release by sediments. The chemical processes involved with chemical fate and transport in water are chemical reactions that result in dissolution or precipitation, hydrolysis, complexation of metal ions, oxidation–reduction, and photochemical reactions. These processes are very much influenced by biochemical phenomena, such as bioaccumulation and magnification in food chains and biodegradation.

2.2 SOURCES AND USES OF WATER

The most important issue in dealing with water is simply getting it, a problem largely attributed to the uneven distribution of water around the globe. Some areas of the globe are desperately short of water. Although the United States is better off with respect to water availability than many other areas of the world, it does have some serious issues with respect to water availability. In the continental United States, an average of approximately 1.48×10^{13} liters of water falls as precipitation each day, which translates to 76 cm/year. Of that amount, approximately 1.02×10^{13} L/day, or 53 cm/year, is lost by evaporation and transpiration. Thus, the water theoretically available for use is approximately 4.6×10^{12} L/day, or only 23 cm/year. At present, the United States uses 1.6×10^{12} L/day, or 8 cm of the average annual precipitation. This amounts to an almost ten-fold increase from a usage of 1.66×10^{11} L/day in 1900. Even more striking is the per-capita increase from approximately 40 L/day in 1900 to more than ten times that amount now. The two largest consumers of water are irrigation and industrial use (especially cooling water for electrical power generation), each with approximately 40% of the total. Most of the rest of the water used is for municipal water supply.

A major problem with water supply is its nonuniform distribution with location and time. Figure 2.3 illustrates the problem of uneven distribution of water. Although it is for the continental United States, it typifies the challenge of water availability around the globe. The fact that precipitation falls unevenly in the continental United States, both in terms of location and time, causes difficulties because people in areas with low precipitation often consume more water than people in regions with more rainfall. Rapid population growth in the more arid southwestern states of the United States during recent decades has further aggravated the problem. Water shortages have become more acute in this region, which contains 6 of the nation's 11 largest cities (Los Angeles,

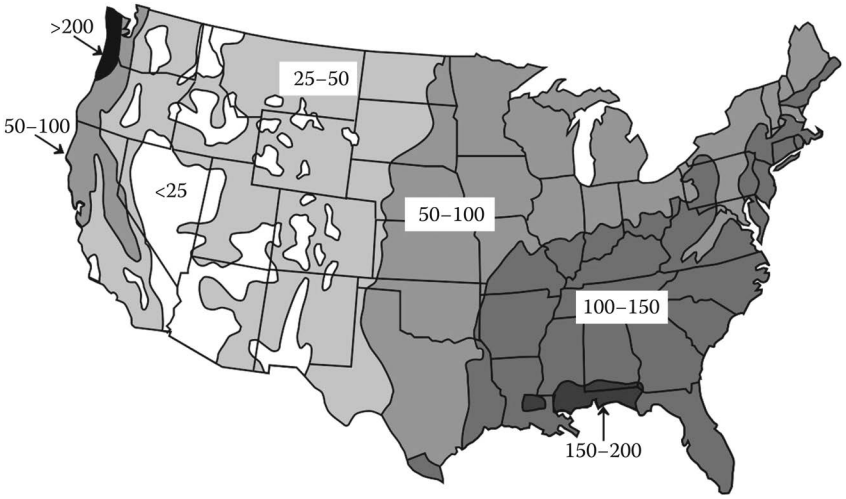


FIGURE 2.3 Distribution of precipitation in the continental United States, showing average annual rainfall in centimeters.

Houston, Dallas, San Diego, Phoenix, and San Antonio). Other problem areas include Florida, where overdevelopment of coastal areas threatens Lake Okeechobee; the Northeast, plagued by deteriorating water systems; and the High Plains, ranging from the Texas panhandle to Nebraska, where irrigation demands on the Ogallala aquifer are dropping the water table steadily with no hope of recharge. These problems are minor, however, in comparison to those in some parts of Africa where water shortages are contributing to real famine conditions.

As noted above, the use of water in the continental United States increased more than 10-fold in the decades after 1900. Starting around 1980, however, the increase in water use in the United States slowed significantly. This trend, which is illustrated in Figure 2.4, has been attributed to the success of efforts to conserve water, especially in the industrial (including power generation) and agricultural sectors. Conservation and recycling have accounted for much of the decreased use in the industrial sector. Irrigation water has been used much more efficiently by replacing spray irrigators, which lose large quantities of water to the action of wind and to evaporation, with irrigation systems that apply water directly to soil. Trickle irrigation systems that apply just the amount of water needed directly to plant roots are especially efficient. Remarkably, in the 15-year period from 2005 to 2020, water use in the United States actually *decreased*, owing to the measures described above and in part to the fact that simply less water was available in areas of high demand (a trend likely to continue as global warming and drought conditions that go with it in some regions continue to develop).

Infrastructure is a vitally important factor in the sustainable utilization of water and there are many examples of deficient water supply because of inadequacy or failures in water infrastructure. As an example, in May 2020, a concrete drop structure collapsed on Montana's St. Mary irrigation canal threatening water supplied to an area of eastern Montana twice the size of Maryland. The canal, one of the earliest Federal water projects, was constructed in the early 1900s to carry water from Montana's Glacier Park to an area of eastern Montana that is highly dependent on the water it provides. Despite a lack of funding, in July work had begun on an

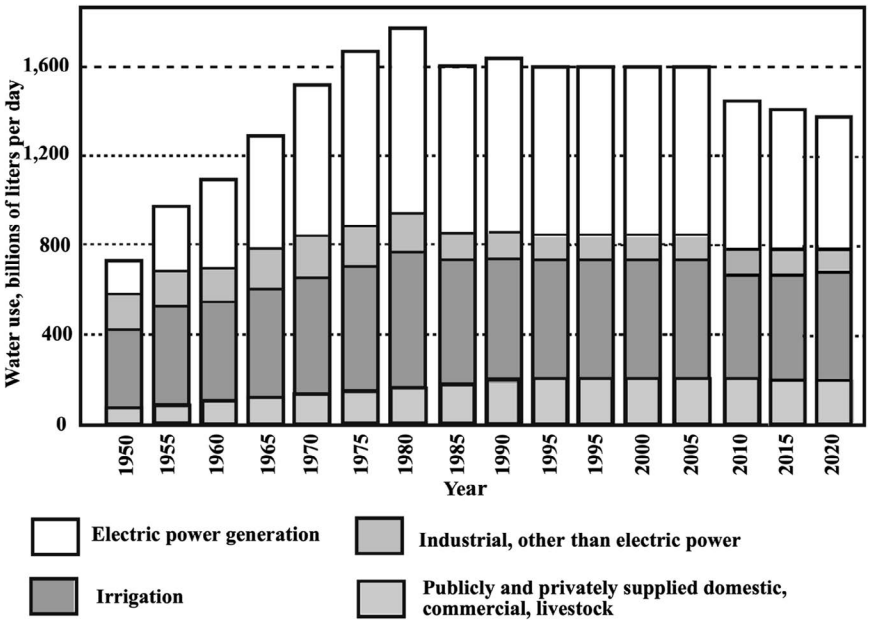


FIGURE 2.4 Trends in water use in the United States showing a steady increase until 1980 followed by level demand in the following decades and a significant decrease from 2005 to 2020 attributed largely to reductions in use for electric power generation as renewable solar and wind energy provide greater shares of energy production. (Data from U.S. Geological Survey, http://water.usgs.gov/watuse/wutrends.html.)

$8 million emergency repair, although about $200 million is needed for a badly needed refurbishing of the entire canal complex.

Dams, dikes, levees, and reservoirs are parts of the infrastructure involved in handling water and in controlling floods. Their failure can cause significant, even catastrophic, problems. In a recent example, following torrential rains, on May 19, 2020, failures of the Edenville and Sanford dams in Michigan caused catastrophic flooding along the Tittabawassee River. Parts of downtown Midland, Michigan, were flooded and the large Dow Chemical Company chemical plant in Midland was threatened along with a downstream Superfund site under remediation by Dow, although both escaped major damage.

2.2.1 The Groundwater Crisis

Groundwater is water contained below ground in porous aquifers (Figure 2.5). Most groundwater infiltrates from the surface where it has fallen as precipitation. A key measure of groundwater availability is the level of the **water table**, which is defined by the depth of the surface of water that stands in a well drilled into the aquifer. Groundwater is a major source of municipal water supplies, and in some rural areas, it is the only source of water. On average, approximately 190 billion L/day of groundwater is used for irrigation in the United States.

Now, groundwater resources are being depleted at an alarming rate in many areas of the United States and around the world. As the result of two periods of intense drought, 2006–2010 and 2011–2019, the problem of depleted groundwater had become especially acute in California. This state supplies more than half of the fresh fruit and vegetables consumed in the United States, and agriculture accounts for approximately 80% of the water used by humans in California. The problem has become especially severe in California's Central Valley, which cuts across the middle of the state from well north of San Francisco almost to Los Angeles. The trend has been to drill deeper wells to replenish groundwater sources, and in many areas, maximum well depth has been reached to

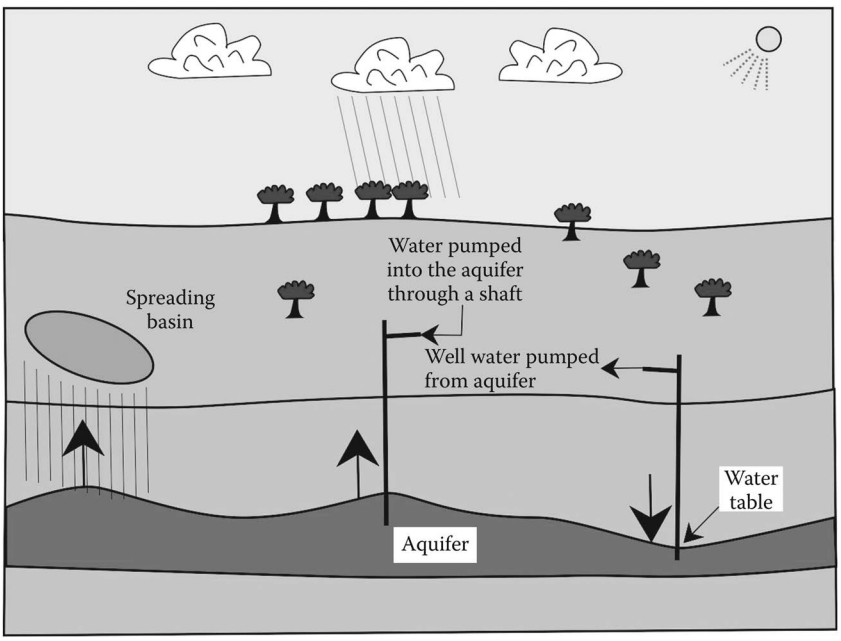


FIGURE 2.5 Groundwater is contained in underground aquifers beneath the Earth's surface. The water table can be lowered by pumping water from an aquifer and raised by pumping water into an aquifer or from natural infiltration of water in a spreading basin on the surface.

the point that no more groundwater is available, or saline water is reached. So much water has been sucked from some underground aquifers that there is perceptible surface subsidence and even damage to surface structures. The problem of saltwater intrusion can be especially troublesome in coastal areas where saltwater intrudes from oceanic sources. In addition to a lowered water table and lower water quality, exploitation of groundwater sources can lead to depletion of surface water in rivers and lakes, and land subsidence as mineral matter composing the aquifer becomes compacted. Groundwater depletion usually accompanies the phenomenon of desertification in which once productive land reverts to desert.

2.3 H_2O: SIMPLE FORMULA, REMARKABLE MOLECULE

The chemical formula of water, H_2O, is the best known of all chemical compounds. This simple formula represents a substance that is unique and complex in its behavior. These special properties are attributed to the molecular structure of the H_2O molecule represented in Figure 2.6. There are four pairs of electrons in the outer electron shell of the O atom in the H_2O molecule, two of which compose the bonds between the H and O atoms and two of which are lone pairs. The distribution of these pairs as far apart as possible around an imaginary sphere representing the outer electron shell of the O atoms results in the two H–O bonds being located at an angle rather than at a straight line. The side of the molecule with the two H atoms has a partial positive charge and the side with the two nonbonding pairs has a partial negative charge; thus, the water molecule is **polar**. This polarity and the ability of the H atoms on one molecule to form hydrogen bonds in which a hydrogen atom acts as a bridge between two O atoms on separate H_2O molecules determine the remarkable chemical and physical diversity of water.

Especially because of their hydrogen bonding capability, water molecules are strongly attracted to each other. Water's unique properties resulting from its polar character and ability to form hydrogen bonds make it essential to life and determine its behavior in the hydrosphere and in interactions with other environmental spheres, including its many uses in the anthrosphere. The more important characteristics of water pertinent to its environmental behavior, uses, and interactions with all the environmental spheres are summarized in Table 2.1.

Water is an excellent solvent for many materials; thus, it is the basic transport medium for nutrients and waste products in life processes. The extremely high dielectric constant of water relative to other liquids has a profound effect upon its solvent properties in that most ionic materials are dissociated in water.

Because of the attraction of water molecules for each other, water has the highest **heat capacity** of any liquid or solid, 4.186 J × g^{-1} × deg^{-1} (1 cal × g^{-1} × deg^{-1}). This means that a relatively large

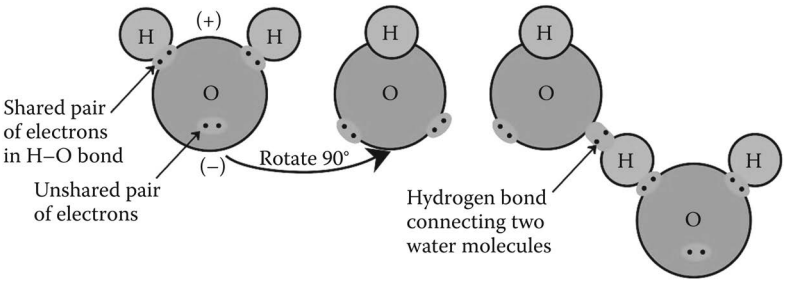


FIGURE 2.6 Because of the arrangement of the two bonding pairs and the two nonbonding pairs of electrons as far as possible from each other around the sphere of the oxygen atom in the water molecule, the molecule is polar. The nonbonding pairs of electrons can form hydrogen bonds with hydrogen atoms in other water molecules. This hydrogen bonding and the polar nature of the water molecule are responsible for the unique solvent properties, heat/temperature behavior, and other characteristics of water.

TABLE 2.1
Important Properties of Water

Property	Effects
Excellent solvent	Transport of nutrients and waste products enabling biological processes to occur in an aqueous medium
Highest dielectric constant of any common liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer-wavelength ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats and vertical circulation is restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	The temperature of water in a body of water is stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

amount of heat is required to change appreciably the temperature of a mass of water; hence, a body of water can have a stabilizing effect on the temperature of nearby geographic regions. In addition, this property prevents sudden large changes of temperature in large bodies of water and thereby protects aquatic organisms from the shock of abrupt temperature variations. The extremely high **heat of vaporization** of water, 2446 $J \times g^{-1}$ at 25°C, likewise stabilizes the temperature of bodies of water and the surrounding geographic regions. It also influences the transfer of heat and water vapor between bodies of water and the atmosphere. A very large amount of energy must be put into a mass of ice to break the hydrogen bonds holding the molecules in place in the solid as it melts and an equally large amount of heat energy is released when liquid water freezes. Thus, water has a very high **latent heat of fusion** equal to 334 $J \times g^{-1}$.

The ability of water to absorb, release, and store heat is crucial to its role in the environment and its practical uses. Water's high heat capacity stabilizes temperatures of organisms and geographical areas. Steam produced in a boiler can be transferred through insulated pipes to remote locations and condensed to release heat. The heat released when atmospheric water condenses warms the surrounding air and is the driving force behind tropical storms. Europe owes its relatively mild weather despite its northern latitudes to heat carried by water across the North Atlantic Ocean from the Gulf of Mexico.

2.4 LIFE IN WATER

As discussed in more detail in Chapter 5, "Aquatic Microbial Biochemistry," the environmental chemistry of water is largely determined by the biochemical activity of aquatic organisms, especially microorganisms, which produce the organic matter that forms the basis of food chains in the hydrosphere, biodegrade organic matter, and act as catalysts to mediate oxidation/reduction transitions of chemical species in water. In addition, the effect of chemical species and pollutants in water on higher organisms, especially fish, is a very important consideration as well.

The living organisms (**biota**) in an aquatic ecosystem may be classified as either autotrophic or heterotrophic. **Autotrophic** organisms utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Algae and photosynthetic cyanobacteria are the most important autotrophic aquatic organisms because they are **producers** that utilize solar energy to generate biomass from CO_2 and other simple inorganic species.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass. **Decomposers** (or **reducers**) are a subclass of the heterotrophic organisms consisting chiefly of bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms.

The ability of a body of water to produce living material is known as its **productivity**. Productivity results from a combination of physical and chemical factors. High productivity requires an adequate supply of carbon (CO_2), nitrogen (nitrate), phosphorus (orthophosphate), and trace elements such as iron. Water of low productivity is generally desirable for water supply or for swimming. Relatively high productivity is required for the support of fish and to serve as the basis of the food chain in an aquatic ecosystem. Excessive productivity results in decay of the biomass produced, consumption of dissolved oxygen, and odor production, a condition called **eutrophication**.

Life-forms higher than algae and bacteria—fish, for example—comprise a comparatively small fraction of the biomass in most aquatic systems. The influence of these higher life-forms on aquatic chemistry is minimal. However, aquatic life is strongly influenced by the physical and chemical properties of the body of water in which it lives. *Temperature*, *transparency*, and *turbulence* are the three main physical properties affecting aquatic life. Very low water temperatures result in very slow biological processes, whereas excessively high temperatures can be fatal to organisms. The transparency of water is particularly important in determining the growth of algae. Turbulence is an important factor in mixing processes and transporting nutrients and waste products in water. Some small organisms (**plankton**) depend on water currents and turbulence for their own mobility.

Dissolved oxygen (**DO**) frequently is the key substance in determining the extent and kinds of life in a body of water. Oxygen deficiency is fatal to many aquatic animals such as fish. The presence of oxygen can be equally fatal to many kinds of anoxic bacteria. **Biochemical oxygen demand** (**BOD**), discussed as a water pollutant in Chapter 6, refers to the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically.

Carbon dioxide is produced by respiratory processes in water and sediments and can also enter water from the atmosphere. Carbon dioxide is required for the photosynthetic production of biomass by algae and in some cases is a limiting factor. High levels of carbon dioxide produced by the degradation of organic matter in water can cause excessive biomass production and eutrophication.

The salinity of water also determines the kinds of life-forms present. Irrigation waters may pick up harmful levels of salt. Marine life obviously requires or tolerates saltwater, whereas many freshwater organisms are intolerant of salt.

2.5 CHEMISTRY OF WATER

To understand water pollution, it is first necessary to have an appreciation of chemical phenomena that occur in water. The remaining sections of this chapter discuss aquatic acid–base and complexation phenomena. Oxidation–reduction reactions and equilibria are discussed in Chapter 3, and details of solubility calculations and interactions between liquid water and other phases are given in Chapter 4. The main categories of aquatic chemical phenomena are illustrated in Figure 2.7.

Aquatic environmental chemical phenomena involve processes familiar to chemists, including acid–base, solubility, oxidation–reduction, and complexation reactions. Although most aquatic chemical phenomena are discussed here from the thermodynamic (equilibrium) viewpoint, it is important to keep in mind that reaction rates (kinetics) are very important in aquatic chemistry. Biological processes play a key role in aquatic chemistry. For example, algae undergoing photosynthesis can raise the pH of water by removing aqueous CO_2, thereby converting an HCO_3^- to a CO_3^{2-}; this ion in turn reacts with Ca^{2+} in water to precipitate $CaCO_3$.

Compared to the carefully controlled conditions of the laboratory, it is much more difficult to describe chemical phenomena in natural water systems. Such systems are very complex and a

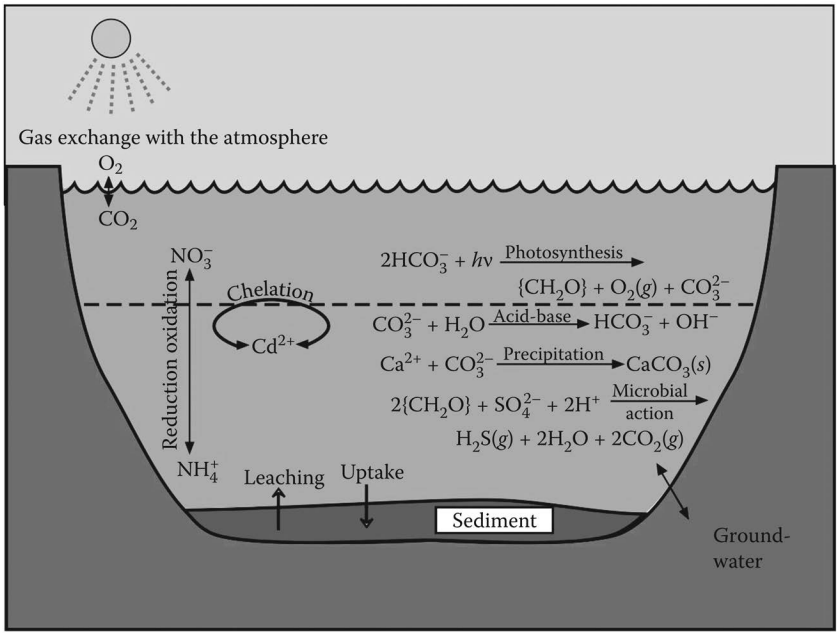


FIGURE 2.7 Major aquatic chemical processes.

description of their chemistry must take many variables into consideration. In addition to water, these systems contain mineral phases, gas phases, and organisms. As open, dynamic systems, they have variable inputs and outputs of energy and mass. Therefore, except under unusual circumstances, a true equilibrium condition is not obtained, although an approximately steady-state aquatic system frequently exists. Most metals found in natural waters do not exist as simple hydrated cations in the water, and oxyanions often are found as polynuclear species, rather than as simple monomers. The nature of chemical species in water containing bacteria or algae is strongly influenced by the action of these organisms. Thus, an exact description of the chemistry of a natural water system based on acid–base, solubility, and complexation equilibrium constants, redox potential, pH, and other chemical parameters is not possible. Therefore, the systems must be described by simplified **models**, often based around equilibrium chemical concepts. Though not exact or entirely realistic, such models can yield useful generalizations and insights pertaining to the nature of aquatic chemical processes, and provide guidelines for the description and measurement of natural water systems. Though greatly simplified, such models are very helpful in visualizing the conditions that determine chemical species and their reactions in natural waters and wastewaters.

2.6 GASES IN WATER

Dissolved gases—O_2 for fish and CO_2 for photosynthetic algae—are crucial to the welfare of living species in water. Some gases in water can also cause problems, such as the death of fish from bubbles of nitrogen formed in the blood caused by exposure to water supersaturated with N_2. Volcanic carbon dioxide evolved from supersaturated dissolved CO_2 in the waters of Lake Nyos in the African country of Cameroon asphyxiated 1,700 people in 1986. The only other dangerous "exploding lakes" known in the world are Lake Monoun in Cameroon and Lake Kivu located between the Democratic Republic of Congo and Rwanda. Vertical pipes inserted from the surface to near the bottom of Lake Nyos enable the carbon dioxide-saturated deep water in the lake to come to the surface where the gas in it is dissipated slowly.

The solubilities of gases in water are calculated with **Henry's law**, which states that *the solubility of a gas in a liquid is proportional to the partial pressure of that gas in contact with the liquid.* These calculations are discussed in some detail in Chapter 4.

2.6.1 Oxygen in Water

Without an appreciable level of dissolved oxygen, many kinds of aquatic organisms cannot exist in water. Dissolved oxygen is consumed by the degradation of organic matter in water. Many fish kills are caused not by the direct toxicity of pollutants but by a deficiency of oxygen because of its consumption in the biodegradation of pollutants.

Most elemental oxygen comes from the atmosphere, which is 20.95% oxygen by volume of dry air. Therefore, the ability of a body of water to re-oxygenate itself by contact with the atmosphere is an important characteristic. Oxygen is produced by the photosynthetic action of algae, but this process is really not an efficient means of oxygenating water because some of the oxygen formed by photosynthesis during the daylight hours is lost at night when the algae consume oxygen as part of their metabolic processes. When the algae die, the degradation of their biomass also consumes oxygen.

The solubility of oxygen in water depends on water temperature, the partial pressure of oxygen in the atmosphere, and the salt content of the water. It is important to distinguish between oxygen *solubility*, the maximum dissolved O_2 concentration at equilibrium, and dissolved oxygen *concentration*, which is generally not the equilibrium concentration and is limited by the rate at which oxygen dissolves. The calculation of oxygen solubility as a function of partial pressure is discussed in Section 4.3, where it is shown that the concentration of oxygen in water at 25°C in equilibrium with air at atmospheric pressure is only 8.32 mg/L. Thus, water in equilibrium with air cannot contain a high level of dissolved oxygen compared to many other solute species. If oxygen-consuming processes are occurring in the water, the dissolved oxygen level may rapidly approach zero unless some efficient mechanism for the reaeration of water is operative, such as turbulent flow in a shallow stream or air pumped into the aeration tank of an activated sludge secondary waste treatment facility (see Chapter 7). The problem becomes largely one of kinetics, in which there is a limit to the rate at which oxygen is transferred across the air–water interface. This rate depends on turbulence, air bubble size, temperature, and other factors.

If organic matter of biological origin is represented by the formula $\{CH_2O\}$, the consumption of oxygen in water by the degradation of organic matter may be expressed by the following biochemical reaction:

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O \tag{2.1}$$

The mass of organic material required to consume the 8.3 mg of O_2 in 1 L of water in equilibrium with the atmosphere at 25°C is given by a simple stoichiometric calculation based on Equation 2.1, which yields a value of 7.8 mg of $\{CH_2O\}$. Thus, the microorganism-mediated degradation of only 7 or 8 mg of organic material can completely consume the O_2 in 1 L of water initially saturated with air at 25°C. The depletion of oxygen to levels below those that sustain oxic organisms requires the degradation of even less organic matter at higher temperatures (where the solubility of oxygen is less) or in water not initially saturated with atmospheric oxygen. Furthermore, there are no common aquatic chemical reactions that replenish dissolved oxygen; except for oxygen provided by photosynthesis, it must come from the atmosphere.

The temperature effect on the solubility of gases in water is especially important in the case of oxygen. The solubility of oxygen in water in equilibrium with atmospheric air decreases from 14.74 mg/L at 0°C to 7.03 mg/L at 35°C. At higher temperatures, the decreased solubility of oxygen, combined with the increased respiration rate of aquatic organisms, frequently causes a condition in which a higher demand for oxygen accompanied by lower solubility of the gas in water results in severe oxygen depletion.

2.7 WATER ACIDITY AND CARBON DIOXIDE IN WATER

Acid–base phenomena in water involve loss and acceptance of H^+. Many species act as **acids** in water by releasing H^+, others act as **bases** by accepting H^+, and the water molecule itself does both. An important species in the acid–base chemistry of water is bicarbonate ion, HCO_3^-, which may act as either an acid or a base:

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{2.2}$$

$$HCO_3^- + H^+ \leftrightarrow CO_2(aq) + H_2O \tag{2.3}$$

Acidity as applied to natural water and wastewater is the capacity of the water to neutralize OH^-; it is analogous to alkalinity, the capacity to neutralize H^+, which is discussed in Section 2.8. Although virtually all water has some alkalinity, acidic water is not frequently encountered, except in cases of severe pollution, such as acid mine water. Acidity generally results from the presence of weak acids, particularly CO, but sometimes includes others such as $H_2PO_4^-$, H_2S, proteins, and fatty acids. Acidic metal ions, particularly Fe^{3+}, may also contribute to acidity.

Strong acids are the most important contributors to water-pollutant acidity. The term **free mineral acid** is applied to strong acids, such as H_2SO_4 and HCl in water. Acid mine water is a common water pollutant that contains an appreciable concentration of free mineral acid. Whereas total acidity is determined by titration with base to the phenolphthalein endpoint (pH 8.2), free mineral acid is determined by titration with base to the methyl orange endpoint (pH 4.3).

As shown by the hydrolysis of hydrated Al^{3+} below, the acidic character of some hydrated metal ions may contribute to acidity. Some industrial wastes, such as spent steel pickling liquor, contain acidic metal ions and often some excess strong acid.

$$Al(H_2O)_6^{3+} \leftrightarrow Al(H_2O)_5OH^{2+} + H^+ \tag{2.4}$$

2.7.1 Carbon Dioxide in Water

The most important weak acid in water is carbon dioxide or CO_2. Because of the presence of carbon dioxide in air and its production from microbial decay of organic matter, dissolved CO_2 is present in virtually all natural waters and wastewaters. Rainfall from even an absolutely unpolluted atmosphere is slightly acidic because of the presence of dissolved CO_2. Dissolution in seawater is an important mechanism for the removal of carbon dioxide from the atmosphere, the "greenhouse" gas that makes the greatest contribution to climate warming. Proposals have been made to pump CO_2 from combustion into places in the ocean where seawater is sinking to sequester it from the atmosphere for thousands of years, although a major concern is acidification of seawater.[2]

Carbon dioxide and its ionization products, bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}), have an extremely important influence on the chemistry of water. Many minerals are deposited as salts of the carbonate ion. Algae in water utilize dissolved CO_2 in the synthesis of biomass. The equilibrium of dissolved CO_2 with gaseous carbon dioxide in the atmosphere

$$CO_2\,(\text{water}) \leftrightarrow CO_2\,(\text{atmosphere}) \tag{2.5}$$

and equilibrium of CO_3^{2-} between aquatic solution and solid carbonate minerals

$$MCO_3(\text{slightly soluble carbonate salt}) \leftrightarrow M^{2+} + CO_3^{2-} \tag{2.6}$$

have a strong buffering effect on the pH of water.

Carbon dioxide is only slightly above 0.040% by volume of normal dry air. As a consequence of the low level of atmospheric CO_2, water totally lacking in alkalinity (capacity to neutralize H^+, see Section 2.8) in equilibrium with the atmosphere contains only a very low level of carbon dioxide. However, the formation of HCO_3^- and CO_3^{2-} greatly increases the solubility of carbon dioxide. High concentrations of free carbon dioxide in water may adversely affect respiration and gas exchange of aquatic animals. It may even cause death and should not exceed levels of 25 mg/L in water.

A large share of the carbon dioxide found in water is a product of the breakdown of organic matter by bacteria. Even algae, which utilize CO_2 in photosynthesis, produce it through their metabolic processes in the absence of light. As water seeps through layers of decaying organic matter while infiltrating the ground, it may dissolve a great deal of CO_2 produced by the respiration of organisms in the soil. Later, as water goes through limestone formations, it dissolves calcium carbonate because of the presence of the dissolved CO_2:

$$CaCO_3(s) + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{2.7}$$

This process is the one by which limestone caves are formed. The implications of the above reaction for aquatic chemistry are discussed in greater detail in Section 2.9.

The concentration of gaseous CO_2 in the atmosphere varies with location and season; it is now increasing by approximately 2 parts per million (ppm) by volume per year. For purposes of calculation here, the concentration of atmospheric CO_2 will be taken as 415 ppm (0.04% as of January 1, 2014, and increasing by 0.0002% or 2 ppm per year) in dry air. At 25°C, water in equilibrium with unpolluted air containing 415 ppm (estimated mean global level in 2020) carbon dioxide has a $CO_2(aq)$ concentration of 1.358×10^{-5} M (see Henry's law for calculation of gas solubility in Section 4.3), and this value will be used for subsequent calculations.

Although CO_2 in water is often represented as H_2CO_3, the equilibrium constant for the reaction

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \tag{2.8}$$

is only around 2×10^{-3} at 25°C, so just a small fraction of the dissolved carbon dioxide is actually present as H_2CO_3. In this text, nonionized carbon dioxide in water will be designated simply as CO_2, which, in subsequent discussions, will stand for the total of dissolved molecular CO_2 and undissociated H_2CO_3.

The $CO_2 - HCO_3^- - CO_3^{2-}$ system in water may be described by the equations

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^- \tag{2.9}$$

$$K'_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35 \tag{2.10}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{2.11}$$

$$K'_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33 \tag{2.12}$$

where $pKa = -\log Ka$. The predominant species formed by CO_2 dissolved in water depends on pH. This is best shown by a distribution of species diagram with pH as a master variable as illustrated in Figure 2.8. Such a diagram shows the major species present in solution as a function of pH.

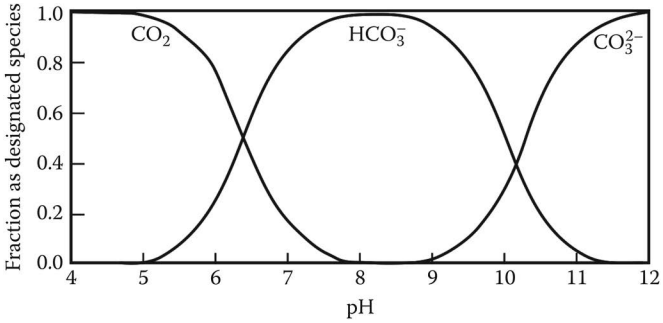


FIGURE 2.8 Distribution of species diagram for the $CO_2 - HCO_3^- - CO_3^{2-}$ system in water.

For CO_2 in aqueous solution, the diagram is a series of plots of the fractions present as CO_2, HCO_3^-, and CO_3^{2-} as a function of pH. These fractions, designated as α_a, are given by the following expressions:

$$^{\alpha}CO_2 = \frac{[CO_2]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]} \tag{2.13}$$

$$^{\alpha}HCO_3^- = \frac{[HCO_3^-]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]} \tag{2.14}$$

$$^{\alpha}CO_3^{2-} = \frac{[CO_3^{2-}]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]} \tag{2.15}$$

Substitution of the expressions for K_{a1} and K_{a1} into the α expressions gives the fractions of species as a function of acid dissociation constants and hydrogen ion concentration:

$$^{\alpha}CO_2 = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{2.16}$$

$$^{\alpha}HCO_3^- = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{2.17}$$

$$^{\alpha}CO_3^{2-} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{2.18}$$

Calculations from these expressions show the following:

- For pH significantly below pK_{a1}, $^{\alpha}CO_2$ is essentially 1
- When $pH = pK_{a1}$, $^{\alpha}CO_2 = {}^{\alpha}HCO_3^-$
- When $pH = \frac{1}{2}(pK_{a1} + pK_{a2})$, $^{\alpha}HCO_3^-$ is at its maximum of 0.98
- When $pH = pK_{a2}$, $^{\alpha}HCO_3^- = {}^{\alpha}CO_3^{2-}$
- For pH significantly above pK_{a2}, $^{\alpha}CO_3^{2-}$ is essentially 1

The distribution of species diagram in Figure 2.8 shows that hydrogen carbonate (bicarbonate) ion (HCO_3^-) is the predominant species in the pH range found in most waters, with CO_2 predominating in more acidic waters.

As mentioned above, the value of $[CO_2(aq)]$ in water at 25°C in equilibrium with air that is 415 ppm CO_2 is 1.358×10^{-5} M. The carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^-:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{2.19}$$

The concentrations of H^+ and HCO_3^- are calculated from K_{a1}:

$$K_{a1} \quad \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{[H^+]^2}{1.358 \times 10^{-5}} = 4.45 \times 10^{-7} \tag{2.20}$$

$$[H^+] = [HCO_3^-] = (1.358 \times 10^{-5} \times 4.45 \times 10^{-7})^{1/2} = 2.46 \times 10^{-6}$$

$$pH = 5.61$$

This calculation explains why pure water that has equilibrated with the unpolluted atmosphere is slightly acidic with a pH somewhat less than 7.

2.8 ALKALINITY

The capacity of water to accept H^+ (protons) is called **alkalinity**. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing, and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algal growth and other aquatic life, so that it can be used as a measure of water fertility. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \tag{2.21}$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \tag{2.22}$$

$$OH^- + H^+ \leftrightarrow H_2O \tag{2.23}$$

Other, usually minor, contributors to alkalinity are ammonia and the conjugate bases of phosphoric, silicic, boric, and organic acids.

At pH values below 7, $[H^+]$ in water detracts significantly from alkalinity, and its concentration must be subtracted in computing the total alkalinity. Therefore, the following equation is the complete equation for alkalinity in a medium where the only contributors to it are HCO_3^-, CO_3^{2-}, and OH^-:

$$[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{2.24}$$

Alkalinity is generally expressed as *phenolphthalein alkalinity*, corresponding to titration with acid to the pH at which HCO_3^- is the predominant carbonate species (pH 8.3), or *total alkalinity*,

corresponding to titration with acid to the methyl orange endpoint (pH 4.3), where both bicarbonate and carbonate species have been converted to CO_2.

It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H^+. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor. This may be illustrated by comparing a solution of 1.00×10^{-3} M NaOH with a solution of 0.100 M $NaHCO_3$. The sodium hydroxide solution is very basic, pH 11, but a liter of it will neutralize only 1.00×10^{-3} mol of acid. The pH of the $NaHCO_3$ solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mol of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

In engineering terms, alkalinity is frequently expressed in units of milligrams per liter of $CaCO_3$, based on the following acid-neutralizing reaction:

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O \tag{2.25}$$

The equivalent mass of calcium carbonate is one-half of its formula mass. Expressing alkalinity in terms of milligrams per liter of $CaCO_3$ can, however, lead to confusion, and the preferable notation for the chemist is equivalents per liter, the number of moles of H^+ neutralized by the alkalinity in a liter of solution.

2.8.1 Contributors to Alkalinity at Different pH Values

Natural water typically has an alkalinity ("[alk]") of 1.00×10^{-3} equivalents per liter (eq/L), meaning that the alkaline solutes in 1 L of water will neutralize 1.00×10^{-3} mol of acid. The contributions made by different species to alkalinity depend on pH. This is shown here by calculation of the relative contributions to alkalinity of HCO_3^-, CO_3^{2-}, and OH^- at pH 7 and pH 10. First, for water at pH 7, $[OH^-]$ is too low to make any significant contribution to the alkalinity. Furthermore, as shown in Figure 2.8, at pH 7, $HCO_3^- \gg CO_3^{2-}$. Therefore, the alkalinity is attributed to HCO_3^- and $HCO_3^- = 1.00 \times 10^{-3}$ M. Substitution into the expression for K_{a1} shows that at pH 7 and $HCO_3^- = 1.00 \times 10^{-3}$ M, the value of $[CO_2(aq)]$ is 2.25×10^{-4} M, higher than the value that arises from water in equilibrium with atmospheric air, but readily reached owing to the presence of carbon dioxide from bacterial decay in water and sediments.

Consider next the case of water with the same alkalinity, 1.00×10^{-3} eq/L that has a pH of 10. At this higher pH, both OH^- and CO_3^{2-} are present at significant concentrations compared to HCO_3^-, and the following may be calculated:

$$[\text{alk}] = HCO_3^- + 2CO_3^{2-} + [OH^-] = 1.00 \times 10^{-3} \tag{2.26}$$

The concentration of CO_3^{2-} is multiplied by 2 because each CO_3^{2-} can neutralize $2H^+$. The other two equations that must be solved to get the concentrations of HCO_3^-, CO_3^{2-}, and OH^- are

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-10}} = 1.00 \times 10^{-4} \tag{2.27}$$

and

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} \tag{2.28}$$

Solving these three equations gives $HCO_3^- = 4.64 \times 10^{-4}$ M and $CO_3^{2-} = 2.18 \times 10^{-4}$ M; thus, the contributions to the alkalinity of this solution are the following:

$$\begin{aligned} &4.64 \times 10^{-4} \text{ eq/L from } HCO_3^- \\ &4.36 \times 10^{-4} \text{ eq/L from } CO_3^{2-} \\ 2 \times 2.18 \times 10^{-4} = &\frac{1.00 \times 10^{-4} \text{ eq/L from } OH^-}{\text{alk} = 1.00 \times 10^{-3} \text{ eq/L}} \end{aligned}$$

2.8.2 Dissolved Inorganic Carbon and Alkalinity

The values given above can be used to show that at the same alkalinity value, 1.00×10^{-3} eq/L, the concentration of total dissolved inorganic carbon [C]

$$[C] = [CO_2] + HCO_3^- + CO_3^{2-} \tag{2.29}$$

varies with pH. At pH 7,

$$[C]\text{pH } 7 = 2.25 \times 10^{-4} + 1.00 \times 10^{-3} + 0 = 1.22 \times 10^{-3} \text{ mol/L} \tag{2.30}$$

whereas at pH 10.00,

$$[C]\text{pH } 10 = 0 + 4.64 \times 10^{-4} + 2.18 \times 10^{-4} = 6.82 \times 10^{-4} \text{ mol/L} \tag{2.31}$$

The calculation above shows that the dissolved inorganic carbon concentration at pH 10 is only approximately half that at pH 7. This is because at pH 10, major contributions to alkalinity are made by CO_3^{2-}, each of which has twice the alkalinity of each HCO_3^-, and by OH^-, which does not contain any carbon. The lower inorganic carbon concentration at pH 10 shows that an initially relatively low pH aquatic system (pH 7) can donate dissolved inorganic carbon for use in photosynthesis with a change in pH but none in alkalinity. This pH-dependent difference in dissolved inorganic carbon concentration represents a significant potential source of carbon for algae growing in water that fix carbon by the overall reactions

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2 \tag{2.32}$$

and

$$HCO_3^- + H_2O + h\nu \rightarrow \{CH_2O\} + OH^- + O_2 \tag{2.33}$$

As dissolved inorganic carbon is used up to synthesize biomass, $\{CH_2O\}$, the water becomes more basic. The amount of inorganic carbon that can be consumed before the water becomes too basic to allow algal reproduction is proportional to the alkalinity. In going from pH 7 to pH 10, the amount of inorganic carbon consumed from 1 L of water having an alkalinity of 1.00×10^{-3} eq/L is

$$[C]\text{pH } 7 \times 1 \text{ L} - [C]\text{pH } 10 \times 1 \text{ L} = 1.22 \times 10^{-3} \text{ mol} - 6.82 \times 10^{-4} \text{ mol} = 5.4 \times 10^{-4} \text{ mol} \tag{2.34}$$

This translates to an increase of 5.4×10^{-4} mol/L of biomass. Since the formula mass of $\{CH_2O\}$ is 30, the weight of biomass produced amounts to 16 mg/L. Assuming no input of additional CO_2, at higher alkalinity, more biomass is produced for the same change in pH, whereas at lower alkalinity, less is produced. Because of this effect, biologists use alkalinity as a measure of water fertility.

2.8.3 Influence of Alkalinity on CO_2 Solubility

The increased solubility of carbon dioxide in water with an elevated alkalinity can be illustrated by comparing its solubility in pure water (alkalinity 0) to its solubility in water initially containing 1.00×10^{-3} M NaOH (alkalinity 1.00×10^{-3} eq/L). The number of moles of CO_2 that will dissolve in a liter of pure water from the atmosphere containing 415 ppm carbon dioxide is

$$\text{Solubility} = [CO_2(aq)] + [HCO_3^-] \tag{2.35}$$

Substituting values calculated in Section 2.7 gives
Solubility = $1.358 \times 10^{-5} + 2.46 \times 10^{-6} = 1.604 \times 10^{-5}$ M.

The solubility of CO_2 in water, initially 1.00×10^{-3} M in NaOH, is approximately 100-fold higher because of uptake of CO_2 by the reaction

$$CO_2(aq) + OH^- \rightarrow HCO_3^- \tag{2.36}$$

so that

$$\text{Solubility} = [CO_2(aq)] + [HCO_3^-] = 1.358 \times 10^{-5} + 1.00 \times 10^{-3} = 1.01 \times 10^{-3}\ \text{M} \tag{2.37}$$

2.9 CALCIUM AND OTHER METALS IN WATER

The kinds and concentrations of metal ions in water are determined largely by the rocks that the water contacts. Metal ions in water, commonly denoted by M^{n+}, exist in numerous forms. A bare metal ion, Ca^{2+} for example, cannot exist as a separate entity in water. In order to secure the highest stability of their outer electron shells, metal ions in water are bonded or *coordinated* to other species. These may be water molecules or other stronger bases (electron-donor partners) that might be present. Therefore, metal ions in water solution are present in forms such as the **hydrated metal cation** $M(H_2O)_x^{n+}$. Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid–base:

$$Fe(H_2O)_6^{3+} \leftrightarrow FeOH(H_2O)_5^{2+} + H^+ \tag{2.38}$$

precipitation:

$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(OH)_3(s) + 3H_2O + 3H^+ \tag{2.39}$$

and oxidation–reduction reactions:

$$Fe(H_2O)_6^{2+} \leftrightarrow Fe(OH)_3(s) + 3H_2O + e^- + 3H^+ \tag{2.40}$$

These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as $Fe_2OH_2^{4+}$, the concentration of simple hydrated $Fe(H_2O)_6^{3+}$ ion in water is vanishingly small; the same holds true for many other hydrated metal ions dissolved in water.

2.9.1 Hydrated Metal Ions as Acids

Hydrated metal ions, particularly those with a charge of +3 or more, tend to lose H^+ from the water molecules bound to them in aqueous solution and fit the definition of Brönsted acids, according to

which acids are H^+ donors and bases are H^+ acceptors. The acidity of a metal ion increases with charge and decreases with increasing radius. As shown by the reaction

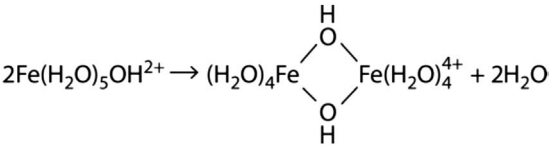
$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(H_2O)_5OH^{2+} + H^+ \tag{2.41}$$

hydrated iron(III) ion is an acid, a relatively strong one with a K_{a1} of 8.9×10^{-4}, so that solutions of iron(III) tend to have low pH values. Hydrated trivalent metal ions, such as iron(III), are generally at loss of at least one hydrogen ion at neutral pH values or above. For tetravalent metal ions, the completely protonated forms, $M(H_2O)_x^{4+}$, are rare even at very low pH values. Commonly, O^{2-} is coordinated to tetravalent metal ions; an example is the vanadium(IV) species, VO^{2+}. Generally, divalent metal ions do not lose a hydrogen ion at pH values below 6, whereas monovalent metal ions such as Na^+ do not act as acids at all and exist in water solution as simple hydrated ions.

The tendency of hydrated metal ions to behave as acids may have a profound effect on the aquatic environment. A good example is *acid mine water* (see Chapter 5), which derives part of its acidic character from the acidic nature of hydrated iron(III):

$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(OH)_3(s) + 3H^+ + 3H_2O \tag{2.42}$$

Hydroxide or OH^- bonded to a metal ion, may function as a bridging group to join two or more metals together as shown by the following dehydration–dimerization process:



(2.43)

Among the metals other than iron(III) forming polymeric species with OH^- as a bridging group are Al(III), Be(II), Bi(III), Ce(IV), Co(III), Cu(II), Ga(III), Mo(V), Pb(II), Sc(II), Sn(IV), and U(VI). Additional hydrogen ions may be lost from water molecules bonded to the dimers, furnishing OH^- groups for further bonding and leading to the formation of polymeric hydrolytic species. If the process continues, colloidal hydroxy polymers are formed and, finally, precipitates are produced. This process is thought to be the general one by which hydrated iron(III) oxide $Fe_2O_3 \cdot x(H_2O)$ (also called iron(III) hydroxide, $Fe(OH)_3$) is precipitated from solutions containing iron(III).

2.9.2 Calcium in Water

Of the cations found in most freshwater systems, calcium generally has the highest concentration. The chemistry of calcium, although complicated enough, is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in waters. Among the primary contributing minerals are gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), dolomite ($CaMg(CO_3)_2$), and calcite and aragonite, which are different mineral forms of $CaCO_3$.

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water. *Temporary hardness* is attributed to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + CO_2(g) + H_2O \tag{2.44}$$

Increased temperature may force this reaction to the right by evolving CO_2 gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals:

$$CaCO_3(s) + CO_2(g) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{2.45}$$

When this reaction is reversed and CO_2 is lost from the water, calcium carbonate deposits are formed (Reaction 2.44). The concentration of CO_2 in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by equilibration with the atmosphere is not sufficient to account for the levels of calcium dissolved in natural waters, especially groundwaters. Rather, the respiration of microorganisms degrading organic matter in water, sediments, and soil

$$\{CH_2O\} + O_2 \leftrightarrow CO_2 + H_2O \tag{2.46}$$

accounts for the very high levels of CO_2 and HCO_3^- observed in water and is very important in aquatic chemical processes and geochemical transformations.

2.9.3 Dissolved Carbon Dioxide and Calcium Carbonate Minerals

The equilibrium between dissolved carbon dioxide and calcium carbonate minerals is important in determining several natural water chemistry parameters, such as alkalinity, pH, and dissolved calcium concentration (Figure 2.9). For freshwater, the typical figures quoted for the concentrations of both HCO_3^- and Ca^{2+} are 1.00×10^{-3} M. It may be shown that these are reasonable values when the water is in equilibrium with limestone or $CaCO_3$ and with atmospheric CO_2. The concentration of CO_2 in water in equilibrium with air has already been calculated as 1.358×10^5 M. The other constants needed to calculate HCO_3^- and $[Ca^{2+}]$ are the acid dissociation constant for CO_2 shown in

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35, \tag{2.47}$$

the acid dissociation constant of HCO_3^-

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33, \tag{2.48}$$

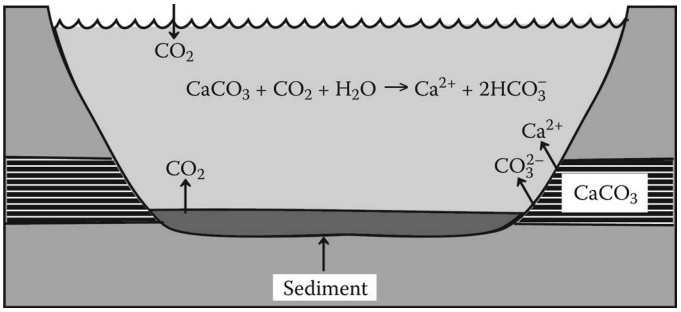


FIGURE 2.9 Carbon dioxide–calcium carbonate equilibria.

and the solubility product of calcium carbonate (calcite)

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.47 \times 10^{-9} \tag{2.49}$$

The reaction between calcium carbonate and dissolved CO_2 is

$$CaCO_3(s) + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{2.50}$$

for which the equilibrium expression is the following:

$$K' = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]} = \frac{K_{sp}K_{a1}}{K_{a2}} = 4.24 \times 10^{-5} \tag{2.51}$$

The stoichiometry of Reaction 2.50 gives a bicarbonate ion concentration that is twice that of calcium. Substitution of the value of CO_2 concentration into the expression for K' yields values of 5.24×10^{-4} M for $[Ca^{2+}]$ and 1.05×10^{-3} for $[HCO_3^-]$. Substitution into the expression for K_{sp} yields 8.53×10^{-6} M for $[CO_3^{2-}]$. When known concentrations are substituted into the product $K_{a1}K_{a2}$

$$K_{a1}K_{a2} = \frac{[H^+]^2[CO_3^{2-}]}{[CO_2]} = 2.09 \times 10^{-17} \tag{2.52}$$

a value of 5.77×10^{-9} M is obtained for $[H^+]$ (pH 8.24). The alkalinity is essentially equal to $[HCO_3^-]$, which is much higher than $[CO_3^{2-}]$ or $[OH^-]$.

To summarize, for water in equilibrium with solid calcium carbonate and atmospheric CO_2, the following concentrations are calculated:

$$[CO_2] = 1.358 \times 10^{-5}\,M \quad [Ca^{2+}] = 5.24 \times 10^{-4}\,M$$
$$[HCO_3^-] = 1.05 \times 10^{-3}\,M \quad [H^+] = 5.77 \times 10^{-9}\,M$$
$$[CO_3^{2-}] = 8.53 \times 10^{-6}\,M \quad pH = 8.24$$

Factors such as nonequilibrium conditions, high CO_2 concentrations in bottom regions, and increased pH owing to algal uptake of CO_2 cause deviations from these values. Nevertheless, they are close to the values found in a large number of natural water bodies.

2.10 COMPLEXATION AND CHELATION

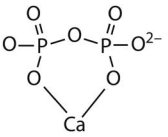
The properties of metals dissolved in water depend largely on the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example, $Fe(H_2O)_6^{3+}$ and hydroxy species such as $FeOH(H_2O)_5^{2+}$ discussed in the preceding section, metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**. For example, a cyanide ion can bond to dissolved iron(II):

$$Fe(H_2O)_6^{3+} + CN^- \leftrightarrow FeCN(H_2O)_5^{2+} + H_2O \tag{2.53}$$

Additional cyanide ions may bond to the iron to form $Fe(CN)_2$, $Fe(CN)_3^-$, $Fe(CN)_4^{2-}$, $Fe(CN)_5^{3-}$, and $Fe(CN)_6^{4-}$, where the water molecules still bound to the iron(II) are omitted for simplicity.

This phenomenon is called **complexation**; the species that binds with the metal ion, CN^- in the example above, is called a **ligand**, and the product in which the ligand is bound with the metal ion is a **complex**, **complex ion**, or **coordination compound**. A special case of complexation in which a ligand bonds in two or more places to a metal ion is called **chelation**. In addition to being present as metal complexes, metals may occur in water as **organometallic** compounds containing carbon-to-metal bonds. The solubilities, transport properties, and biological effects of such species are often vastly different from those of the metal ions themselves. Subsequent sections of this chapter consider metal species with an emphasis on metal complexation, especially chelation, in which particularly strong metal complexes are formed.

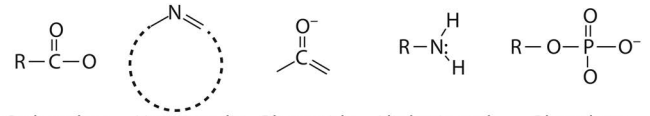
In the example above, the cyanide ion is a **unidentate ligand**, which means that it possesses only one site that bonds to a metal ion. Of considerably more importance than those with unidentate ligands are complexes with **chelating agents**. A chelating agent has more than one atom that may be bonded to a central metal ion at one time to form a ring structure. Thus, pyrophosphate ion $P_2O_7^{4-}$ bonds to two sites on a calcium ion to form a chelate:



In general, since a chelating agent may bond to a metal ion in more than one place simultaneously (Figure 2.10), chelates are more stable than complexes with unidentate ligands. Stability tends to increase with the number of chelating sites available on the ligand. Structures of metal chelates take a number of different forms, all characterized by rings in various configurations. The structure of a tetrahedrally coordinated chelate of nitrilotriacetate (NTA) ion is shown in Figure 2.10.

The ligands found in natural waters and wastewaters contain a variety of functional groups that can donate the electrons required to bond the ligand to a metal ion. Among the most common of these groups are as follows:

These ligands complex most metal ions found in unpolluted waters and biological systems (Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, VO^{2+}). They also bind to contaminant metal ions, such as Co^{2+}, Ni^{2+}, Sr^{2+}, Cd^{2+}, and Ba^{2+}.



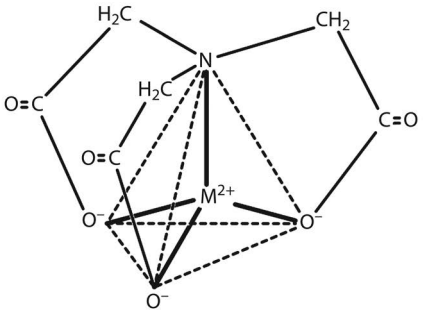


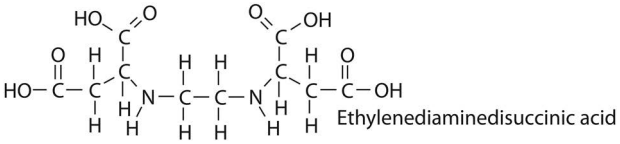
FIGURE 2.10 Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

Complexation may have a number of effects, including reactions of both ligands and metals. Among the ligand reactions are oxidation–reduction, decarboxylation, hydrolysis, and biodegradation. Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution. Complexation may strongly influence metals' adsorption, distribution, transport, and fate as well as biochemical effects including bioavailability, toxicity, and plant uptake.[3]

Complex compounds of metals such as iron (in hemoglobin) and magnesium (in chlorophyll) are vital to life processes. Naturally occurring chelating agents, such as humic substances and amino acids, are found in water and soil. The high concentration of chloride ion in seawater results in the formation of some chloro complexes. Synthetic chelating agents, such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium NTA, and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, and food preparation. These compounds may enter aquatic systems through waste discharges. An even stronger chelating agent than EDTA is diethylenetriaminepentaacetic acid (DTPA), which has three N atoms (amino groups) that are on a six-carbon atom chain to which are attached a total of five carboxymethyl groups. DTPA is capable of forming up to eight bonds with a metal ion. This compound, which has a number of uses, sometimes shows up as a water pollutant.

2.10.1 Occurrence and Importance of Chelating Agents in Water

Chelating agents are common potential water pollutants. These substances can occur in sewage effluent and industrial wastewater, such as metal plating wastewater. In addition to pollutant sources, there are natural sources of chelating agents. One such chelating agent is ethylenediaminedisuccinic acid,



a metabolite of the soil actinomycete, *Amycolatopsis orientalis*. Unlike a number of common synthetic chelating agents, such as EDTA, ethylenediaminedisuccinic acid is biodegradable and has been used as an extractant for phytoremediation (uptake of waste substances by plants from soil).[4]

The most important pollutant chelating agents are aminopolycarboxylates, of which the most common examples are NTA (Figure 2.10) and EDTA (structure illustrated at the beginning of Section 2.13). Both EDTA and NTA have been encountered as water pollutants.[5] Because of their strong bonding to metal ions, the aminopolycarboxylate chelating agents are almost always encountered in the bound form, which has a strong effect on their chemistry and environmental fate and transport. To the extent that EDTA is present in wastewater, it prevents some metals from binding to and settling out with biomass sludge in biological wastewater treatment processes. Therefore, EDTA chelates compose most of the copper, nickel, and zinc in wastewater effluents (most of these metals in excess of strong chelating agents present are incorporated into the sludge).

Chelation by EDTA has been shown to greatly increase the migration rates of radioactive ^{60}Co from pits and trenches used by the Oak Ridge National Laboratory in Oak Ridge, Tennessee, for disposal of intermediate-level radioactive waste. EDTA was used as a cleaning and solubilizing agent for the decontamination of hot cells, equipment, and reactor components. Analysis of water from sample wells in the disposal pits showed EDTA concentrations of 3.4×10^{-7} M. The presence of EDTA 12–15 years after its burial attests to its low rate of biodegradation. In addition to cobalt,