Manahan, Stanley E. "ENVIRONMENTAL SCIENCE, TECHNOLOGY, AND CHEMISTRY"
Environmental Chemistry
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1 ENVIRONMENTAL SCIENCE, TECHNOLOGY, AND CHEMISTRY

1.1. WHAT IS ENVIRONMENTAL SCIENCE?

This book is about environmental chemistry. To understand that topic, it is important to have some appreciation of environmental science as a whole. **Environmental science** in its broadest sense is the science of the complex interactions that occur among the terrestrial, atmospheric, aquatic, living, and anthropological environments. It includes all the disciplines, such as chemistry, biology, ecology, sociology, and government, that affect or describe these interactions. For the purposes of this book, environmental science will be defined as *the study of the earth, air, water, and living environments, and the effects of technology thereon*. To a significant degree, environmental science has evolved from investigations of the ways by which, and places in which, living organisms carry out their life cycles. This is the discipline of **natural history**, which in recent times has evolved into **ecology**, the study of environmental factors that affect organisms and how organisms interact with these factors and with each other.[1]

For better or for worse, the environment in which all humans must live has been affected irrreversibly by technology. Therefore, technology is considered strongly in this book in terms of how it affects the environment and in the ways by which, applied intelligently by those knowledgeable of environmental science, it can serve, rather than damage, this Earth upon which all living beings depend for their welfare and existence.

The Environment

Air, water, earth, life, and technology are strongly interconnected as shown in Figure 1.1. Therefore, in a sense this figure summarizes and outlines the theme of the rest of this book.

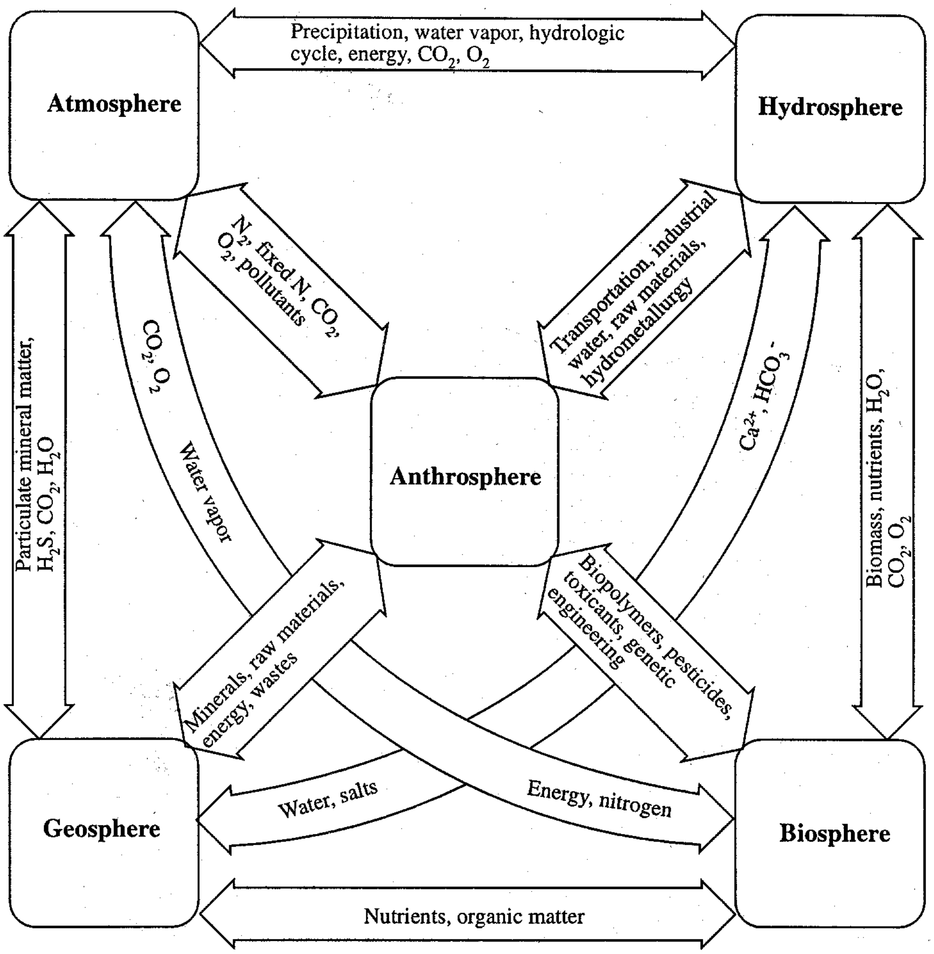


Figure 1.1. Illustration of the close relationships among the air, water, and earth environments with each other and with living systems, as well as the tie-in with technology (the anthrosphere).

Traditionally, environmental science has been divided among the study of the atmosphere, the hydrosphere, the geosphere, and the biosphere. The **atmosphere** is the thin layer of gases that cover Earth's surface. In addition to its role as a reservoir of gases, the atmosphere moderates Earth's temperature, absorbs energy and damaging ultraviolet radiation from the sun, transports energy away from equatorial regions, and serves as a pathway for vapor-phase movement of water in the hydrologic cycle. The **hydrosphere** contains Earth's water. Over 97% of Earth's water is in oceans, and most of the remaining fresh water is in the form of ice. Therefore, only a relatively small percentage of the total water on Earth is actually involved with terrestrial, atmospheric, and biological processes. Exclusive of seawater, the water that circulates through environmental processes and cycles occurs in the atmosphere, underground as groundwater, and as surface water in streams, rivers, lakes, ponds, and reservoirs. The **geosphere** consists of the solid earth, including soil, which supports most plant life. The part of the geosphere that is directly involved with environmental processes through contact with the atmosphere, the hydrosphere, and living things is the solid **lithosphere**. The lithosphere varies from 50 to 100 km in thickness. The most important part of it insofar as interactions with the other spheres of the environment are concerned is its thin outer skin composed largely of lighter silicate-based minerals and called the **crust**. All living entities on Earth compose the **biosphere**. Living organisms and the aspects of the environment pertaining directly to them are called **biotic**, and other portions of the environment are **abiotic**.

To a large extent, the strong interactions among living organisms and the various spheres of the abiotic environment are best described by cycles of matter that involve biological, chemical, and geological processes and phenomena. Such cycles are called **biogeochemical cycles**, and are discussed in more detail in Section 1.6 and elsewhere in this book.

1.2. ENVIRONMENTAL CHEMISTRY AND ENVIRONMENTAL BIOCHEMISTRY

Environmental chemistry encompasses many diverse topics. It may involve a study of Freon reactions in the stratosphere or an analysis of PCB deposits in ocean sediments. It also covers the chemistry and biochemistry of volatile and soluble organometallic compounds biosynthesized by anaerobic bacteria. Literally thousands of other examples of environmental chemical phenomena could be given. **Environmental chemistry** may be defined as *the study of the sources, reactions, transport, effects, and fates of chemical species in water, soil, air, and living environments, and the effects of technology thereon*.

Environmental chemistry is not a new discipline. Excellent work has been done in this field for the greater part of a century. Until about 1970, most of this work was done in academic departments or industrial groups other than those primarily concerned with chemistry. Much of it was performed by people whose basic education was not in chemistry. Thus, when pesticides were synthesized, biologists observed firsthand some of the less desirable consequences of their use. When detergents were formulated, sanitary engineers were startled to see sewage treatment plant aeration tanks vanish under meter-thick blankets of foam, while limnologists wondered why previously normal lakes suddenly became choked with stinking cyanobacteria. Despite these long standing environmental effects, and even more recent and serious problems, such as those from hazardous wastes, relatively few chemists have been exposed to material dealing with environmental chemistry as part of their education.

Environmental Chemistry and the Environmental Chemist

An encouraging trend is that in recent years many chemists have become deeply involved with the investigation of environmental problems. Academic chemistry departments have found that environmental chemistry courses appeal to students, and many graduate students are attracted to environmental chemistry research. Help-wanted ads have included significant numbers of openings for environmental chemists among those of the more traditional chemical subdisciplines. Industries have found that well-trained environmental chemists at least help avoid difficulties with regulatory agencies, and at best are instrumental in developing profitable pollution-control products and processes.

Some background in environmental chemistry should be part of the training of every chemistry student. The ecologically illiterate chemist can be a very dangerous species. Chemists must be aware of the possible effects their products and processes might have upon the environment. Furthermore, any serious attempt to solve environmental problems must involve the extensive use of chemicals and chemical processes.

There are some things that environmental chemistry is not. It is not just the same old chemistry with a different cover and title. Because it deals with natural systems, it is more complicated and difficult than “pure” chemistry. Students sometimes find this hard to grasp, and some traditionalist faculty find it impossible. Accustomed to the clear-cut concepts of relatively simple, well-defined, though often unrealistic systems, they may find environmental chemistry to be poorly delineated, vague, and confusing. More often than not, it is impossible to come up with a simple answer to an environmental chemistry problem. But, building on an ever-increasing body of knowledge, the environmental chemist can make educated guesses as to how environmental systems will behave.

Chemical Analysis in Environmental Chemistry

One of environmental chemistry’s major challenges is the determination of the nature and quantity of specific pollutants in the environment. Thus, chemical analysis is a vital first step in environmental chemistry research. The difficulty of analyzing for many environmental pollutants can be awesome. Significant levels of air pollutants may consist of less than a microgram per cubic meter of air. For many water pollutants, one part per million by weight (essentially 1 milligram per liter) is a very high value. Environmentally significant levels of some pollutants may be only a few parts per trillion. Thus, it is obvious that the chemical analyses used to study some environmental systems require a very low limit of detection.

However, environmental chemistry is not the same as analytical chemistry, which is only one of the many subdisciplines that are involved in the study of the chemistry of the environment. Although a “brute-force” approach to environmental control, involving attempts to monitor each environmental niche for every possible pollutant, increases employment for chemists and raises sales of analytical instruments, it is a wasteful way to detect and solve environmental problems, degenerating into a mindless exercise in the collection of marginally useful numbers. Those responsible for environmental protection must be smarter than that. In order for chemistry to make a maximum contribution to the solution of environmental problems, the chemist must work toward an understanding of the nature, reactions, and transport of chemical species in the environment. Analytical chemistry is a fundamental and crucial part of that endeavor.

Environmental Biochemistry

The ultimate environmental concern is that of life itself. The discipline that deals specifically with the effects of environmental chemical species on life is

environmental biochemistry. A related area, **toxicological chemistry**, is *the chemistry of toxic substances with emphasis upon their interactions with biologic tissue and living organisms*.[2] Toxicological chemistry, which is discussed in detail in Chapters 22 and 23, deals with the chemical nature and reactions of toxic substances and involves their origins, uses, and chemical aspects of exposure, fates, and disposal.

1.3. WATER, AIR, EARTH, LIFE, AND TECHNOLOGY

In light of the above definitions, it is now possible to consider environmental chemistry from the viewpoint of the interactions among water, air, earth, life, and the anthrosphere outlined in Figure 1.1. These five environmental "spheres" and the interrelationships among them are summarized in this section. In addition, the chapters in which each of these topics is discussed in greater detail are designated here.

Water and the Hydrosphere

Water, with a deceptively simple chemical formula of H_2O, is a vitally important substance in all parts of the environment. Water covers about 70% of Earth's surface. It occurs in all spheres of the environment—in the oceans as a vast reservoir of saltwater, on land as surface water in lakes and rivers, underground as groundwater, in the atmosphere as water vapor, in the polar icecaps as solid ice, and in many segments of the anthrosphere such as in boilers or municipal water distribution systems. Water is an essential part of all living systems and is the medium from which life evolved and in which life exists.

Energy and matter are carried through various spheres of the environment by water. Water leaches soluble constituents from mineral matter and carries them to the ocean or leaves them as mineral deposits some distance from their sources. Water carries plant nutrients from soil into the bodies of plants by way of plant roots. Solar energy absorbed in the evaporation of ocean water is carried as latent heat and released inland. The accompanying release of latent heat provides a large fraction of the energy that is transported from equatorial regions toward Earth's poles and powers massive storms.

Water is obviously an important topic in environmental sciences. Its environmental chemistry is discussed in detail in Chapters 3-8.

Air and the Atmosphere

The atmosphere is a protective blanket which nurtures life on the Earth and protects it from the hostile environment of outer space. It is the source of carbon dioxide for plant photosynthesis and of oxygen for respiration. It provides the nitrogen that nitrogen-fixing bacteria and ammonia-manufacturing industrial plants use to produce chemically-bound nitrogen, an essential component of life molecules. As a basic part of the hydrologic cycle (Chapter 3, Figure 3.1), the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still. The atmosphere serves a vital protective function, absorbing harmful ultraviolet radiation from the sun and stabilizing Earth's temperature.

Atmospheric science deals with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and reactions. Atmospheric chemistry is covered in this book in Chapters 9–14.

Earth

The **geosphere**, or solid Earth, discussed in general in Chapter 15, is that part of the Earth upon which humans live and from which they extract most of their food, minerals, and fuels. The earth is divided into layers, including the solid, iron-rich inner core, molten outer core, mantle, and crust. Environmental science is most concerned with the **lithosphere**, which consists of the outer mantle and the **crust**. The latter is the earth's outer skin that is accessible to humans. It is extremely thin compared to the diameter of the earth, ranging from 5 to 40 km thick.

Geology is the science of the geosphere. As such, it pertains mostly to the solid mineral portions of Earth's crust. But it must also consider water, which is involved in weathering rocks and in producing mineral formations; the atmosphere and climate, which have profound effects on the geosphere and interchange matter and energy with it; and living systems, which largely exist on the geosphere and in turn have significant effects on it. Geological science uses chemistry in the form of geochemistry to explain the nature and behavior of geological materials, physics to explain their mechanical behavior, and biology to explain the mutual interactions between the geosphere and the biosphere.[3] Modern technology, for example the ability to move massive quantities of dirt and rock around, has a profound influence on the geosphere.

The most important part of the geosphere for life on earth is **soil** formed by the disintegrative weathering action of physical, geochemical, and biological processes on rock. It is the medium upon which plants grow, and virtually all terrestrial organisms depend upon it for their existence. The productivity of soil is strongly affected by environmental conditions and pollutants. Because of the importance of soil, all of Chapter 16 is devoted to it.

Life

Biology is the science of life. It is based on biologically synthesized chemical species, many of which exist as large molecules called *macromolecules*. As living beings, the ultimate concern of humans with their environment is the interaction of the environment with life. Therefore, biological science is a key component of environmental science and environmental chemistry

The role of life in environmental science is discussed in numerous parts of this book. For example, the crucial effects of microorganisms on aquatic chemistry are covered in Chapter 6, "Aquatic Microbial Biochemistry." Chapter 21, "Environmental Biochemistry," addresses biochemistry as it applies to the environment. The effects on living beings of toxic substances, many of which are environmental pollutants, are addressed in Chapter 22, "Toxicological Chemistry," and Chapter 23, "Toxicological Chemistry of Chemical Substances." Other chapters discuss aspects of the interaction of living systems with various parts of the environment.

The Anthrosphere and Technology

Technology refers to the ways in which humans do and make things with materials and energy. In the modern era, technology is to a large extent the product of engineering based on scientific principles. Science deals with the discovery, explanation, and development of theories pertaining to interrelated natural phenomena of energy, matter, time, and space. Based on the fundamental knowledge of science, engineering provides the plans and means to achieve specific practical objectives. Technology uses these plans to carry out the desired objectives.

It is essential to consider technology, engineering, and industrial activities in studying environmental science because of the enormous influence that they have on the environment. Humans will use technology to provide the food, shelter, and goods that they need for their well-being and survival. The challenge is to interweave technology with considerations of the environment and ecology such that the two are mutually advantageous rather than in opposition to each other.

Technology, properly applied, is an enormously positive influence for environmental protection. The most obvious such application is in air and water pollution control. As necessary as “end-of-pipe” measures are for the control of air and water pollution, it is much better to use technology in manufacturing processes to prevent the formation of pollutants. Technology is being used increasingly to develop highly efficient processes of energy conversion, renewable energy resource utilization, and conversion of raw materials to finished goods with minimum generation of hazardous waste by-products. In the transportation area, properly applied technology in areas such as high speed train transport can enormously increase the speed, energy efficiency, and safety of means for moving people and goods.

Until very recently, technological advances were made largely without heed to environmental impacts. Now, however, the greatest technological challenge is to reconcile technology with environmental consequences. The survival of humankind and of the planet that supports it now requires that the established two-way interaction between science and technology become a three-way relationship including environmental protection.

1.4. ECOLOGY AND THE BIOSPHERE

The Biosphere

The **biosphere** is the name given to that part of the environment consisting of organisms and living biological material. Virtually all of the biosphere is contained by the geosphere and hydrosphere in the very thin layer where these environmental spheres interface with the atmosphere. There are some specialized life forms at extreme depths in the ocean, but these are still relatively close to the atmospheric interface.

The biosphere strongly influences, and in turn is strongly influenced by, the other parts of the environment. It is believed that organisms were responsible for converting Earth’s original reducing atmosphere to an oxygen-rich one, a process that also resulted in the formation of massive deposits of oxidized minerals, such as iron in deposits of Fe_2O_3. Photosynthetic organisms remove CO_2 from the atmosphere, thus preventing runaway greenhouse warming of Earth's surface. Organisms strongly influence bodies of water, producing biomass required for life in the water and mediating oxidation-reduction reactions in the water. Organisms are strongly involved with weathering processes that break down rocks in the geosphere and convert rock matter to soil. Lichens, consisting of symbiotic (mutually advantageous) combinations of algae and fungi, attach strongly to rocks; they secrete chemical species that slowly dissolve the rock surface and retain surface moisture that promotes rock weathering.

The biosphere is based upon plant photosynthesis, which fixes solar energy ($h\nu$) and carbon from atmospheric CO_2 in the form of high-energy biomass, represented as $\{CH_2O\}$:

$$CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2(g) \tag{1.4.1}$$

In so doing, plants and algae function as autotrophic organisms, those that utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. The opposite process, biodegradation, breaks down biomass either in the presence of oxygen (aerobic respiration),

$$\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O \tag{1.4.2}$$

or absence of oxygen (anaerobic respiration):

$$2\{CH_2O\} \rightarrow CO_2(g) + CH_4(g) \tag{1.4.3}$$

Both aerobic and anaerobic biodegradation get rid of biomass and return carbon dioxide to the atmosphere. The latter reaction is the major source of atmospheric methane. Nondegraded remains of these processes constitute organic matter in aquatic sediments and in soils, which has an important influence on the characteristics of these solids. Carbon that was originally fixed photosynthetically forms the basis of all fossil fuels in the geosphere.

There is a strong interconnection between the biosphere and the anthrosphere. Humans depend upon the biosphere for food, fuel, and raw materials. Human influence on the biosphere continues to change it drastically. Fertilizers, pesticides, and cultivation practices have vastly increased yields of biomass, grains, and food. Destruction of habitat is resulting in the extinction of vast numbers of species, in some cases even before they are discovered. Bioengineering of organisms with recombinant DNA technology and older techniques of selection and hybridization are causing great changes in the characteristics of organisms and promise to result in even more striking alterations in the future. It is the responsibility of humankind to make such changes intelligently and to protect and nurture the biosphere.

Ecology

Ecology is the science that deals with the relationships between living organisms with their physical environment and with each other.[4] Ecology can be approached from the viewpoints of (1) the environment and the demands it places on the organisms in it or (2) organisms and how they adapt to their environmental conditions. An **ecosystem** consists of an assembly of mutually interacting organisms and their environment in which materials are interchanged in a largely cyclical manner. An ecosystem has physical, chemical, and biological components along with energy sources and pathways of energy and materials interchange. The environment in which a particular organism lives is called its **habitat**. The role of an organism in a habitat is called its **niche**.

For the study of ecology it is often convenient to divide the environment into four broad categories. The **terrestrial environment** is based on land and consists of **biomes**, such as grasslands, savannas, deserts, or one of several kinds of forests. The **freshwater environment** can be further subdivided between *standing-water habitats* (lakes, reservoirs) and *running-water habitats* (streams, rivers). The oceanic **marine environment** is characterized by saltwater and may be divided broadly into the shallow waters of the continental shelf composing the **neritic zone** and the deeper waters of the ocean that constitute the **oceanic region**. An environment in which two or more kinds of organisms exist together to their mutual benefit is termed a **symbiotic environment**.

A particularly important factor in describing ecosystems is that of **populations** consisting of numbers of a specific species occupying a specific habitat. Populations may be stable, or they may grow exponentially as a **population explosion**. A population explosion that is unchecked results in resource depletion, waste accumulation, and predation culminating in an abrupt decline called a **population crash**. **Behavior** in areas such as hierarchies, territoriality, social stress, and feeding patterns plays a strong role in determining the fates of populations.

Two major subdivisions of modern ecology are **ecosystem ecology**, which views ecosystems as large units, and **population ecology**, which attempts to explain ecosystem behavior from the properties of individual units. In practice, the two approaches are usually merged. **Descriptive ecology** describes the types and nature of organisms and their environment, emphasizing structures of ecosystems and communities, and dispersions and structures of populations. **Functional ecology** explains how things work in an ecosystem, including how populations respond to environmental alteration and how matter and energy move through ecosystems.

An understanding of ecology is essential in the management of modern industrialized societies in ways that are compatible with environmental preservation and enhancement. **Applied ecology** deals with predicting the impacts of technology and development and making recommendations such that these activities will have minimum adverse impact, or even positive impact, on ecosystems.

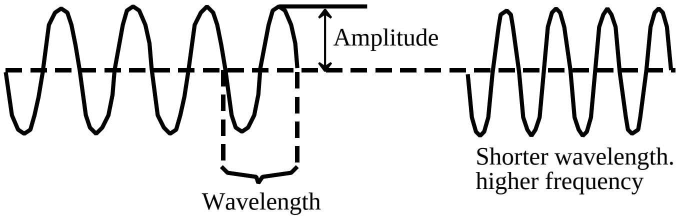
1.5. ENERGY AND CYCLES OF ENERGY

Biogeochemical cycles and virtually all other processes on Earth are driven by energy from the sun. The sun acts as a so-called blackbody radiator with an effective surface temperature of 5780 K (absolute temperature in which each unit is the same as a Celsius degree, but with zero taken at absolute zero).[5] It transmits energy to Earth as electromagnetic radiation (see below) with a maximum energy flux at about 500 nanometers, which is in the visible region of the spectrum. A 1-square-meter area perpendicular to the line of solar flux at the top of the atmosphere receives energy at a rate of 1,340 watts, sufficient, for example, to power an electric iron. This is called the **solar flux** (see Chapter 9, Figure 9.3).

Light and Electromagnetic Radiation

Electromagnetic radiation, particularly light, is of utmost importance in considering energy in environmental systems. Therefore, the following important points related to electromagnetic radiation should be noted:

- Energy can be carried through space at the speed of light (c), 3.00×10^8 meters per second (m/s) in a vacuum, by **electromagnetic radiation**, which includes visible light, ultraviolet radiation, infrared radiation, microwaves, radio waves, gamma rays, and X-rays.
- Electromagnetic radiation has a **wave character**. The waves move at the speed of light, c, and have characteristics of **wavelength** (λ), amplitude, and **frequency** (ν, Greek "nu") as illustrated below:



- The wavelength is the distance required for one complete cycle, and the frequency is the number of cycles per unit time. They are related by the following equation:

  $$\nu\lambda = c$$

  where ν is in units of cycles per second (s^{-1}, a unit called the **hertz**, Hz) and λ is in meters (m).
- In addition to behaving as a wave, electromagnetic radiation has characteristics of particles.
- The dual wave/particle nature of electromagnetic radiation is the basis of the **quantum theory** of electromagnetic radiation, which states that radiant energy may be absorbed or emitted only in discrete packets called **quanta** or **photons**. The energy, E, of each photon is given by

  $$E = h\nu$$

  where h is Planck's constant, 6.63×10^{-34} J-s (joule × second).
- From the preceding, it is seen that *the energy of a photon is higher when the frequency of the associated wave is higher* (and the wavelength shorter).

Energy Flow and Photosynthesis in Living Systems

Whereas materials are recycled through ecosystems, the flow of useful energy is essentially a one-way process. Incoming solar energy can be regarded as high-grade energy because it can cause useful reactions to occur, such as production of electricity in photovoltaic cells or photosynthesis in plants. As shown in Figure 1.2, solar energy captured by green plants energizes chlorophyll, which in turn powers metabolic processes that produce carbohydrates from water and carbon dioxide. These carbohydrates are repositories of stored chemical energy that can be converted to heat and work by metabolic reactions with oxygen in organisms. Ultimately, most of the energy is converted to low-grade heat, which is eventually reradiated away from Earth by infrared radiation.

Energy Utilization

During the last two centuries, the growing, enormous human impact on energy utilization has resulted in many of the environmental problems now facing humankind. This time period has seen a transition from the almost exclusive use of energy captured by photosynthesis and utilized as biomass (food to provide muscle power, wood for heat) to the use of fossil fuel petroleum, natural gas, and coal for about 90 percent, and nuclear energy for about 5 percent, of all energy employed commercially. Although fossil sources of energy have greatly exceeded the pessimistic estimates made during the “energy crisis” of the 1970s, they are limited and their pollution potential is high. Of particular importance is the fact that all fossil fuels produce carbon dioxide, a greenhouse gas. Therefore, it will be necessary to move toward the utilization of alternate renewable energy sources, including solar energy and biomass. The study of energy utilization is crucial in the environmental sciences, and it is discussed in greater detail in Chapter 18, “Industrial Ecology, Resources, and Energy.”

1.6. MATTER AND CYCLES OF MATTER

Cycles of matter (Figure 1.3), often based on elemental cycles, are of utmost importance in the environment.[6] These cycles are summarized here and are discussed further in later chapters. Global geochemical cycles can be regarded from the viewpoint of various reservoirs, such as oceans, sediments, and the atmosphere, connected by conduits through which matter moves continuously. The movement of a specific kind of matter between two particular reservoirs may be reversible or irreversible. The fluxes of movement for specific kinds of matter vary greatly as do the contents of such matter in a specified reservoir. Cycles of matter would occur even in the absence of life on Earth but are strongly influenced by life forms, particularly plants and microorganisms. Organisms participate in **biogeochemical cycles**, which describe the circulation of matter, particularly plant and animal nutrients, through ecosystems. As part of the carbon cycle, atmospheric carbon in CO_2 is fixed as biomass; as part of the nitrogen cycle, atmospheric N_2 is fixed in organic matter. The reverse of these kinds of processes is **mineralization**, in which biologically bound elements are returned to inorganic states. Biogeochemical cycles are ultimately powered by solar energy, which is fine-tuned and directed by energy expended by organisms. In a sense, the solar-energy-powered hydrologic cycle (Figure 3.1) acts as an endless conveyer belt to move materials essential for life through ecosystems.

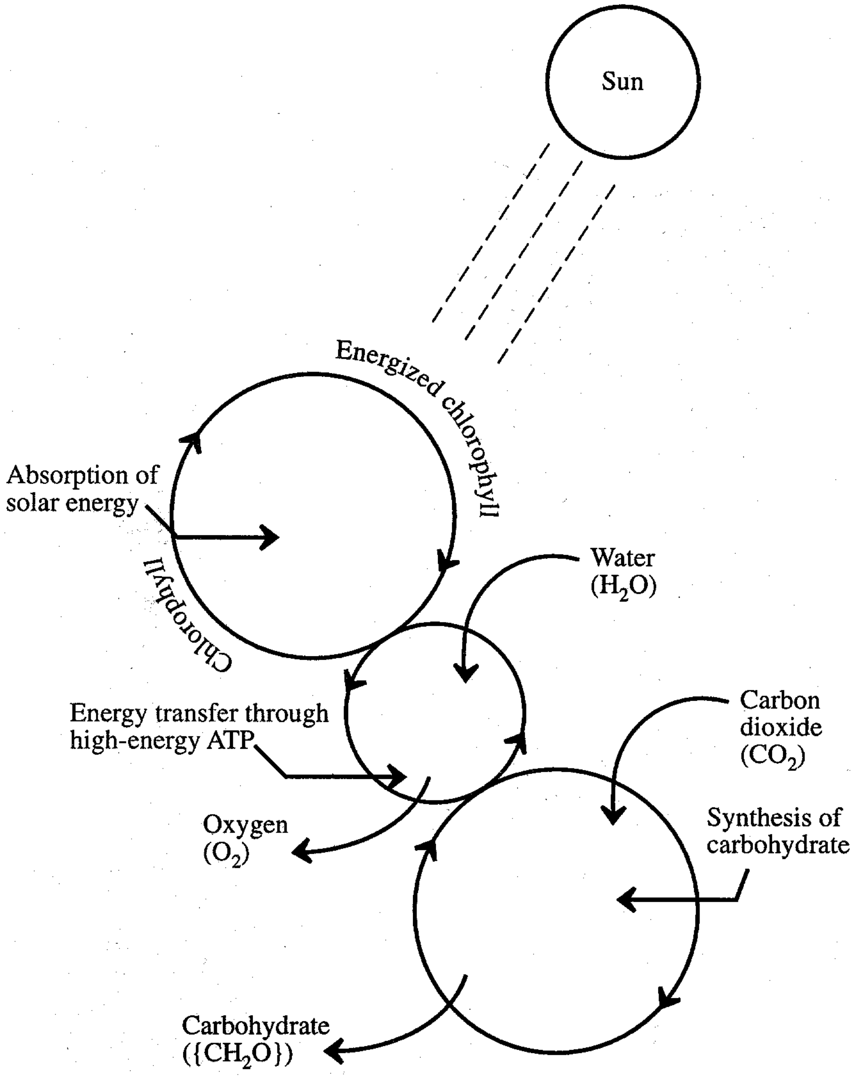


Figure 1.2. Energy conversion and transfer by photosynthesis.

Figure 1.3 shows a general cycle with all five spheres or reservoirs in which matter may be contained. Human activities now have such a strong influence on materials cycles that it is useful to refer to the “anthrosphere” along with the other environmental “spheres” as a reservoir of materials. Using Figure 1.3 as a model, it is possible to arrive at any of the known elemental cycles. Some of the numerous possibilities for materials exchange are summarized in Table 1.1.

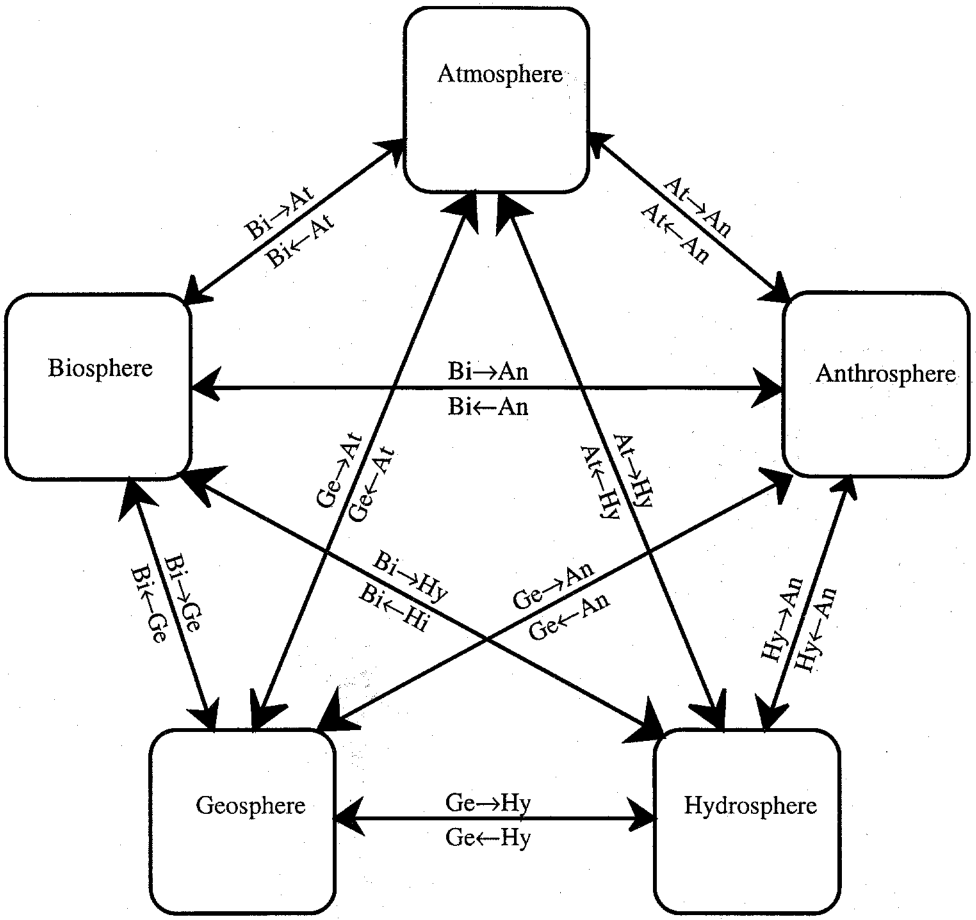


Figure 1.3. General cycle showing interchange of matter among the atmosphere, biosphere, anthrosphere, geosphere, and hydrosphere.

Endogenic and Exogenic Cycles

Materials cycles may be divided broadly between **endogenic cycles**, which predominantly involve subsurface rocks of various kinds, and **exogenic cycles**, which occur largely on Earth's surface and usually have an atmospheric component.[7] These two kinds of cycles are broadly outlined in Figure 1.4. In general, sediment and soil can be viewed as being shared between the two cycles and constitute the predominant interface between them.

Most biogeochemical cycles can be described as **elemental cycles** involving **nutrient elements** such as carbon, nitrogen, oxygen, phosphorus, and sulfur. Many are exogenic cycles in which the element in question spends part of the cycle in the atmosphere—O_2 for oxygen, N_2 for nitrogen, CO_2 for carbon. Others, notably the phosphorus cycle, do not have a gaseous component and are endogenic cycles. All sedimentary cycles involve **salt solutions** or **soil solutions** (see Section 16.2) that contain dissolved substances leached from weathered minerals; these substances may be deposited as mineral formations, or they may be taken up by organisms as nutrients.

Table 1.1. Interchange of Materials among the Possible Spheres of the Environment

From / To	Atmosphere	Hydrosphere	Biosphere	Geosphere	Anthrosphere
Atmosphere	——	H_2O	O_2	H_2S, particles	SO_2, CO_2
Hydrosphere	H_2O	——	$\{CH_2O\}$	Mineral solutes	Water pollutants
Biosphere	O_2, CO_2	H_2O	——	Mineral nutrients	Fertilizers
Geosphere	H_2O	H_2O	Organic matter	——	Hazardous wastes
Anthrosphere	O_2, N_2	H_2O	Food	Minerals	——

Carbon Cycle

Carbon is circulated through the **carbon cycle** shown in Figure 1.5. This cycle shows that carbon may be present as gaseous atmospheric CO_2, constituting a relatively small but highly significant portion of global carbon. Some of the carbon is dissolved in surface water and groundwater as HCO_3^- or molecular $CO_2(aq)$. A very large amount of carbon is present in minerals, particularly calcium and magnesium carbonates such as $CaCO_3$. Photosynthesis fixes inorganic C as biological carbon, represented as $\{CH_2O\}$, which is a consituent of all life molecules. Another fraction of carbon is fixed as petroleum and natural gas, with a much larger amount as hydrocarbonaceous kerogen (the organic matter in oil shale), coal, and lignite, represented as C_xH_{2x}. Manufacturing processes are used to convert hydrocarbons to xenobiotic compounds with functional groups containing halogens, oxygen, nitrogen, phosphorus, or sulfur. Though a very small amount of total environmental carbon, these compounds are particularly significant because of their toxicological chemical effects.

An important aspect of the carbon cycle is that it is the cycle by which solar energy is transferred to biological systems and ultimately to the geosphere and anthrosphere as fossil carbon and fossil fuels. Organic, or biological, carbon, $\{CH_2O\}$, is contained in energy-rich molecules that can react biochemically with molecular oxygen, O_2, to regenerate carbon dioxide and produce energy. This can occur biochemically in an organism through aerobic respiration as shown in Equation 1.4.2, or it may occur as combustion, such as when wood or fossil fuels are burned.

Microorganisms are strongly involved in the carbon cycle, mediating crucial biochemical reactions discussed later in this section. Photosynthetic algae are the predominant carbon-fixing agents in water; as they consume CO_2 to produce biomass the

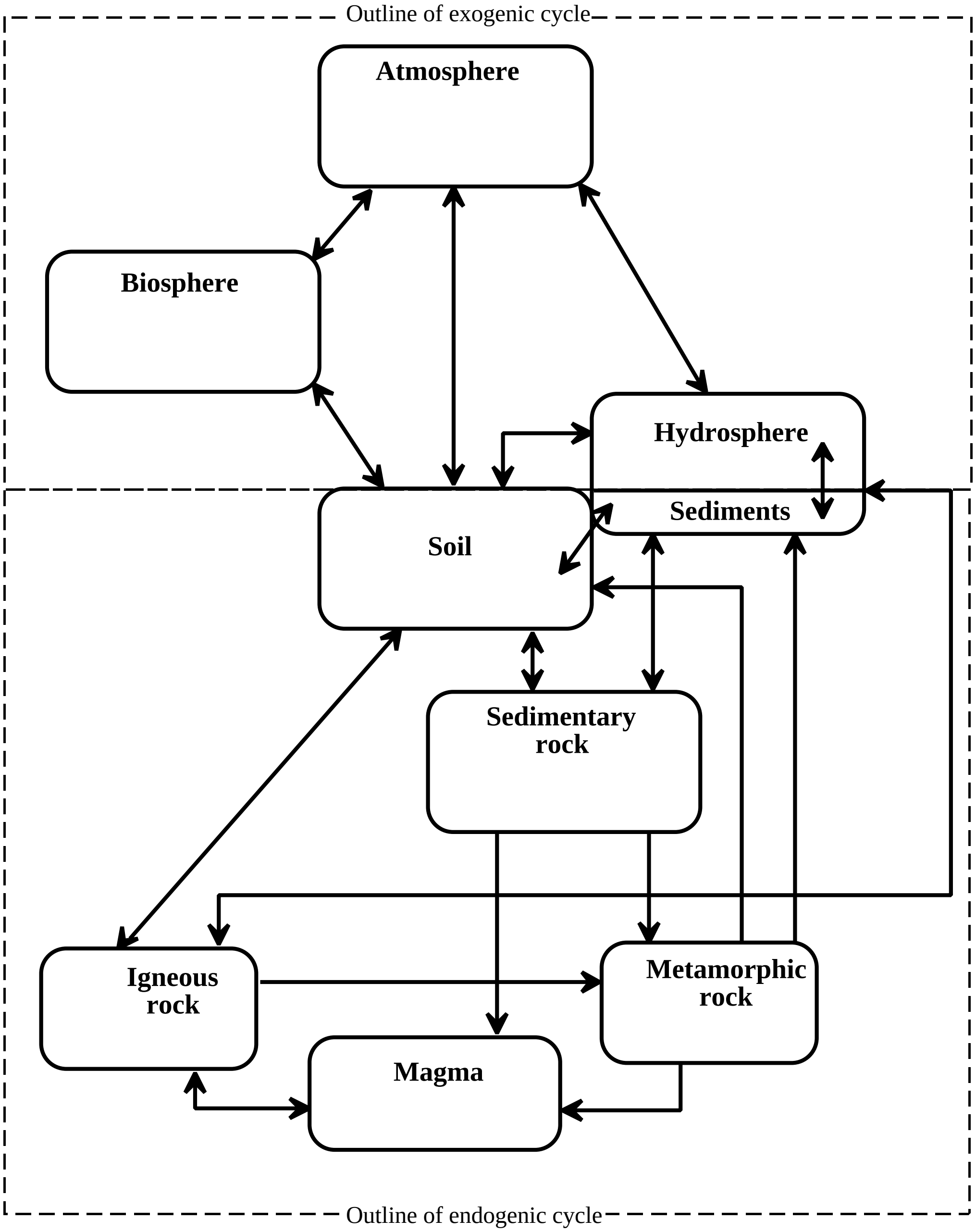


Figure 1.4. General outline of exogenic and endogenic cycles.

pH of the water is raised enabling precipitation of $CaCO_3$ and $CaCO_3 \bullet MgCO_3$. Organic carbon fixed by microorganisms is transformed by biogeochemical processes to fossil petroleum, kerogen, coal, and lignite. Microorganisms degrade organic carbon from biomass, petroleum, and xenobiotic sources, ultimately returning it to the atmosphere as CO_2. Hydrocarbons such as those in crude oil and some synthetic hydrocarbons are degraded by microorganisms. This is an important mechanism for eliminating pollutant hydrocarbons, such as those that are accidentally spilled on soil or in water. Biodegradation can also be used to treat carbon-containing compounds in hazardous wastes.

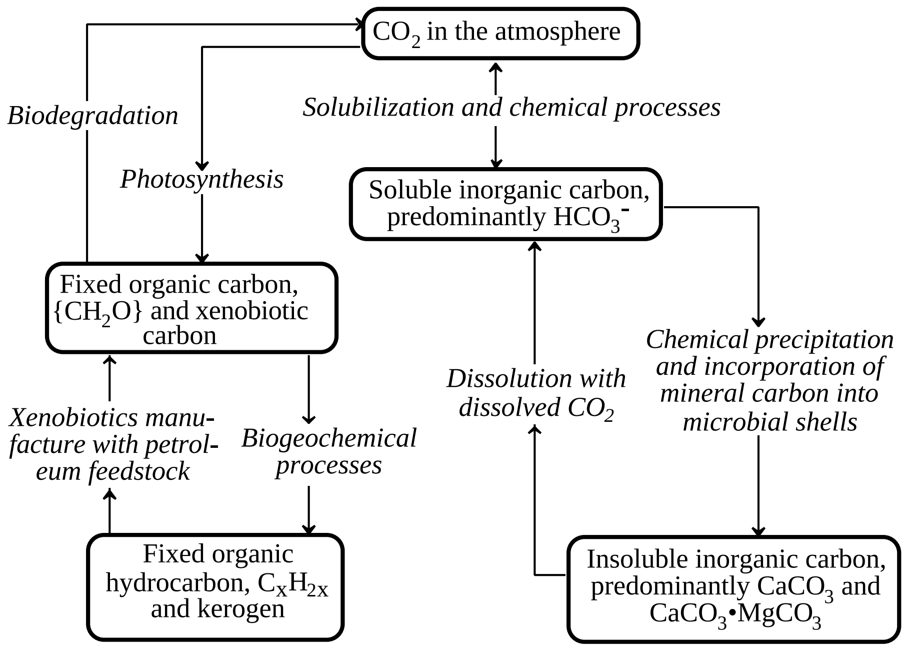


Figure 1.5. The carbon cycle. Mineral carbon is held in a reservoir of limestone, $CaCO_3$, from which it may be leached into a mineral solution as dissolved hydrogen carbonate ion, HCO_3^-, formed when dissolved $CO_2(aq)$ reacts with $CaCO_3$. In the atmosphere carbon is present as carbon dioxide, CO_2. Atmospheric carbon dioxide is fixed as organic matter by photosynthesis, and organic carbon is released as CO_2 by microbial decay of organic matter.

The Nitrogen Cycle

As shown in Figure 1.6, nitrogen occurs prominently in all the spheres of the environment. The atmosphere is 78% elemental nitrogen, N_2, by volume and comprises an inexhaustible reservoir of this essential element. Nitrogen, though constituting much less of biomass than carbon or oxygen, is an essential constituent of proteins. The N_2 molecule is very stable so that breaking it down into atoms that can be incorporated with inorganic and organic chemical forms of nitrogen is the limiting step in the nitrogen cycle. This does occur by highly energetic processes in lightning discharges that produce nitrogen oxides. Elemental nitrogen is also incorporated into chemically bound forms, or **fixed** by biochemical processes mediated by microorganisms. The biological nitrogen is mineralized to the inorganic form during the decay of biomass. Large quantities of nitrogen are fixed synthetically under high temperature and high pressure conditions according to the following overall reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (1.6.1)$$

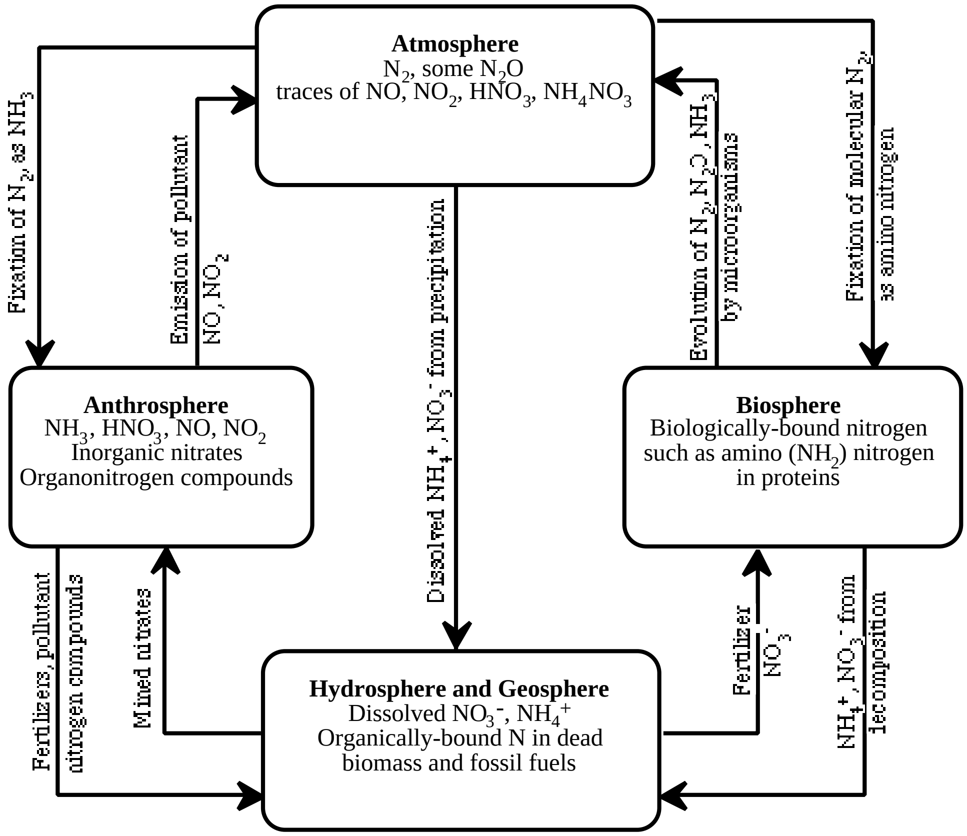


Figure 1.6. The nitrogen cycle.

The production of gaseous N_2 and N_2O by microorganisms and the evolution of these gases to the atmosphere completes the nitrogen cycle through a process called **denitrification**. The nitrogen cycle is discussed from the viewpoint of microbial processes in Section 6.11.

The Oxygen Cycle

The **oxygen cycle** is discussed in Chapter 9 and is illustrated in Figure 9.11. It involves the interchange of oxygen between the elemental form of gaseous O_2, contained in a huge reservoir in the atmosphere, and chemically bound O in CO_2, H_2O, and organic matter. It is strongly tied with other elemental cycles, particularly the carbon cycle. Elemental oxygen becomes chemically bound by various energy-yielding processes, particularly combustion and metabolic processes in organisms. It is released in photosynthesis. This element readily combines with and oxidizes other species such as carbon in aerobic respiration (Equation 1.4.2), or carbon and hydrogen in the combustion of fossil fuels such as methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1.6.2}$$

Elemental oxygen also oxidizes inorganic substances such as iron(II) in minerals:

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \qquad (1.6.3)$$

A particularly important aspect of the oxygen cycle is stratospheric ozone, O_3. As discussed in Chapter 9, Section 9.9, a relatively small concentration of ozone in the stratosphere, more than 10 kilometers high in the atmosphere, filters out ultraviolet radiation in the wavelength range of 220-330 nm, thus protecting life on Earth from the highly damaging effects of this radiation.

The oxygen cycle is completed by the return of elemental O_2 to the atmosphere. The only significant way in which this is done is through photosynthesis mediated by plants. The overall reaction for photosynthesis is given in Equation 1.4.1.

The Phosphorus Cycle

The phosphorus cycle, Figure 1.7, is crucial because phosphorus is usually the limiting nutrient in ecosystems. There are no common stable gaseous forms of phosphorus, so the phosphorus cycle is endogenic. In the geosphere, phosphorus is held largely in poorly soluble minerals, such as hydroxyapatite a calcium salt, deposits of which constitute the major reservoir of environmental phosphate. Soluble phosphorus from phosphate minerals and other sources such as fertilizers is taken up by plants and incorporated into nucleic acids which make up the genetic material of

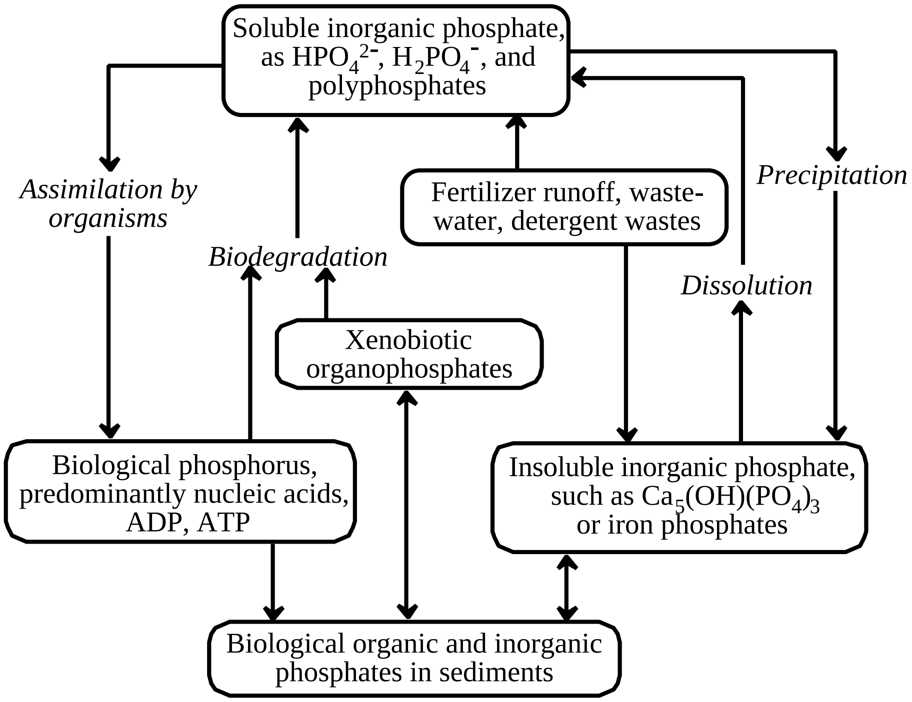


Figure 1.7. The phosphorus cycle.

organisms. Mineralization of biomass by microbial decay returns phosphorus to the salt solution from which it may precipitate as mineral matter.

The anthrosphere is an important reservoir of phosphorus in the environment. Large quantities of phosphates are extracted from phosphate minerals for fertilizer, industrial chemicals, and food additives. Phosphorus is a constituent of some extremely toxic compounds, especially organophosphate insecticides and military poison nerve gases.

The Sulfur Cycle

The sulfur cycle, which is illustrated in Figure 1.8, is relatively complex in that it involves several gaseous species, poorly soluble minerals, and several species in solution. It is tied with the oxygen cycle in that sulfur combines with oxygen to form gaseous sulfur dioxide, SO_2, an atmospheric pollutant, and soluble sulfate ion, SO_4^{2-}.

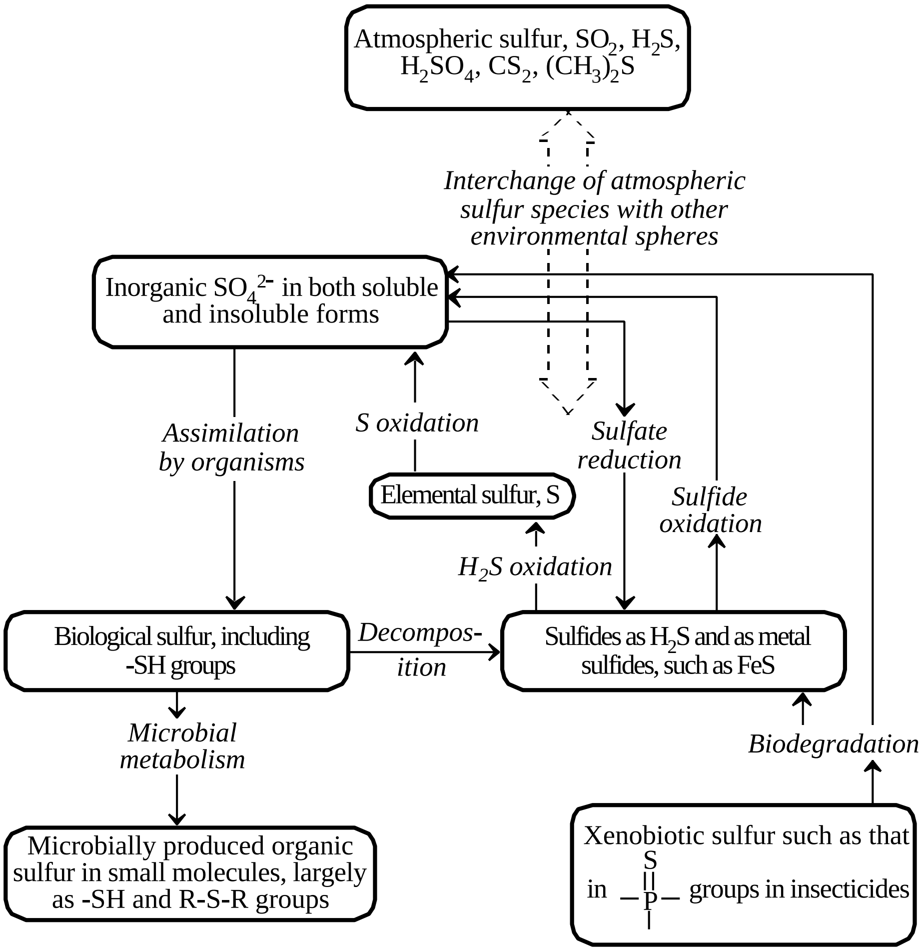


Figure 1.8. The sulfur cycle.

Among the significant species involved in the sulfur cycle are gaseous hydrogen sulfide, H_2S; mineral sulfides, such as PbS, sulfuric acid, H_2SO_4, the main constituent of acid rain; and biologically bound sulfur in sulfur-containing proteins.

Insofar as pollution is concerned, the most significant part of the sulfur cycle is the presence of pollutant SO_2 gas and H_2SO_4 in the atmosphere. The former is a somewhat toxic gaseous air pollutant evolved in the combustion of sulfur-containing fossil fuels. Sulfur dioxide is discussed further as an air pollutant in Chapter 11, and its toxicological chemistry is covered in Chapter 22. The major detrimental effect of sulfur dioxide in the atmosphere is its tendency to oxidize in the atmosphere to produce sulfuric acid. This species is responsible for acidic precipitation, “acid rain,” discussed as a major atmospheric pollutant in Chapter 14.

1.7. HUMAN IMPACT AND POLLUTION

The demands of increasing population coupled with the desire of most people for a higher material standard of living are resulting in worldwide pollution on a massive scale. Environmental pollution can be divided among the categories of water, air, and land pollution. All three of these areas are linked. For example, some gases emitted to the atmosphere can be converted to strong acids by atmospheric chemical processes, fall to the earth as acid rain, and pollute water with acidity. Improperly discarded hazardous wastes can leach into groundwater that is eventually released as polluted water into streams.

Some Definitions Pertaining to Pollution

In some cases pollution is a clear-cut phenomenon, whereas in others it lies largely in the eyes of the beholder. Toxic organochlorine solvent residues leached into water supplies from a hazardous waste chemical dump are pollutants in anybody’s view. However, loud rock music amplified to a high decibel level by the sometimes questionable miracle of modern electronics is pleasant to some people, and a very definite form of noise pollution to others. Frequently, time and place determine what may be called a pollutant. The phosphate that the sewage treatment plant operator has to remove from wastewater is chemically the same as the phosphate that the farmer a few miles away has to buy at high prices for fertilizer. Most pollutants are, in fact, resources gone to waste; as resources become more scarce and expensive, economic pressure will almost automatically force solutions to many pollution problems.

A reasonable definition of a **pollutant** is a substance present in greater than natural concentration as a result of human activity that has a net detrimental effect upon its environment or upon something of value in that environment. **Contaminants**, which are not classified as pollutants unless they have some detrimental effect, cause deviations from the normal composition of an environment.

Every pollutant originates from a **source**. The source is particularly important because it is generally the logical place to eliminate pollution. After a pollutant is released from a source, it may act upon a receptor. The **receptor** is anything that is affected by the pollutant. Humans whose eyes smart from oxidants in the atmosphere are receptors. Trout fingerlings that may die after exposure to dieldrin in water are also receptors. Eventually, if the pollutant is long-lived, it may be deposited in a **sink**, a long-time repository of the pollutant. Here it will remain for a long time, though not necessarily permanently. Thus, a limestone wall may be a sink for atmospheric sulfuric acid through the reaction,

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad (1.7.1)$$

which fixes the sulfate as part of the wall composition.

Pollution of Various Spheres of the Environment

Pollution of surface water and groundwater are discussed in some detail in Chapter 7, Particulate air pollutants are covered in Chapter 10, gaseous inorganic air pollutants in Chapter 11, and organic air pollutants and associated photochemical smog in Chapters 12 and 13. Some air pollutants, particularly those that may result in irreversible global warming or destruction of the protective stratospheric ozone layer, are of such a magnitude that they have the potential to threaten life on earth. These are discussed in Chapter 14, “The Endangered Global Atmosphere.” The most serious kind of pollutant that is likely to contaminate the geosphere, particularly soil, consists of hazardous wastes. A simple definition of a **hazardous waste** is that it is a potentially dangerous substance that has been discarded, abandoned, neglected, released, or designated as a waste material, or is one that may interact with other substances to pose a threat. Hazardous wastes are addressed specifically in Chapters 19 and 20.

1.8. TECHNOLOGY: THE PROBLEMS IT POSES AND THE SOLUTIONS IT OFFERS

Modern technology has provided the means for massive alteration of the environment and pollution of the environment. However, technology intelligently applied with a strong environmental awareness also provides the means for dealing with problems of environmental pollution and degradation.

Some of the major ways in which modern technology has contributed to environmental alteration and pollution are the following:

- Agricultural practices that have resulted in intensive cultivation of land, drainage of wetlands, irrigation of arid lands, and application of herbicides and insecticides
- Manufacturing of huge quantities of industrial products that consumes vast amounts of raw materials and produces large quantities of air pollutants, water pollutants, and hazardous waste by-products
- Extraction and production of minerals and other raw materials with accompanying environmental disruption and pollution
- Energy production and utilization with environmental effects that include disruption of soil by strip mining, pollution of water by release of salt-

water from petroleum production, and emission of air pollutants such as acid-rain-forming sulfur dioxide

- Modern transportation practices, particularly reliance on the automobile, that cause scarring of land surfaces from road construction, emission of air pollutants, and greatly increased demands for fossil fuel resources

Despite all of the problems that it raises, technology based on a firm foundation of environmental science can be very effectively applied to the solution of environmental problems. One important example of this is the redesign of basic manufacturing processes to minimize raw material consumption, energy use, and waste production. Consider a generalized manufacturing process shown in Figure 1.9. With proper design the environmental acceptability of such a process can be greatly enhanced. In some cases raw materials and energy sources can be chosen in ways that minimize environmental impact. If the process involves manufacture of a chemical, it may be possible to completely alter the reactions used so that the entire operation is more environmentally friendly. Raw materials and water may be recycled to the maximum extent possible. Best available technologies may be employed to minimize air, water, and solid waste emissions.

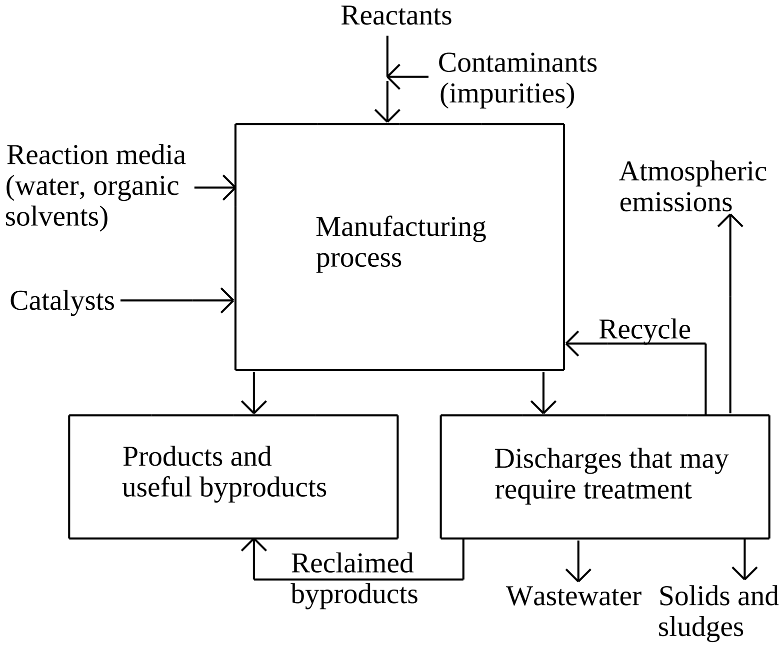


Figure 1.9. A manufacturing process viewed from the standpoint of minimization of environmental impact.

There are numerous ways in which technology can be applied to minimize environmental impact. Among these are the following:

- Use of state-of-the-art computerized control to achieve maximum energy efficiency, maximum utilization of raw materials, and minimum production of pollutant by-products

- Use of materials that minimize pollution problems, for example heat-resistant materials that enable use of high temperatures for efficient thermal processes
- Application of processes and materials that enable maximum materials recycling and minimum waste product production, for example, advanced membrane processes for wastewater treatment to enable water recycling
- Application of advanced biotechnologies such as in the biological treatment of wastes
- Use of best available catalysts for efficient synthesis
- Use of lasers for precision machining and processing to minimize waste production

The applications of modern technology to environmental improvement are addressed in several chapters of this book. Chapter 8, "Water Treatment," discusses technologically-based treatment of water. The technology of air pollution control is discussed in various sections of Chapters 10-13. Hazardous waste treatment is addressed specifically in Chapter 20.

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QUESTIONS AND PROBLEMS

1. Under what circumstances does a contaminant become a pollutant?

2. Examine Figure 1.1 and abbreviate each “sphere” with its first two letters of At, Hy, An, Bi, Ge. Then place each of the following with the appropriate arrow, indicating the direction of its movement with a notation such as At → Hy: (a) Iron ore used for steel making, (b) waste heat from coal-fired electricity generation, (c) hay, (d) cotton, (e) water from the ocean as it enters the hydrologic cycle, (f) snow, (g) argon used as an inert gas shield for welding.

3. Explain how Figure 1.1 illustrates the definition of environmental chemistry given at the beginning of Section 1.2.

4. Explain how toxicological chemistry differs from environmental biochemistry.

5. Distinguish among geosphere, lithosphere, and crust of the Earth. Which science deals with these parts of the environment?

6. Define ecology and relate this science to Figure 1.1.

7. Although energy is not destroyed, why is it true that the flow of useful energy through an environmental system is essentially a one-way process?

8. Describe some ways in which use of energy has “resulted in many of the environmental problems now facing humankind.”

9. Compare nuclear energy to fossil fuel energy sources and defend or refute the statement, “Nuclear energy, with modern, safe, and efficient reactors, is gaining increasing attention as a reliable, environmentally friendly energy source.”

10. What is shown by the reaction below?

$$2\{CH_2O\} \rightarrow CO_2(g) + CH_4(g)$$

How is this process related to aerobic respiration?

11. Define cycles of matter and explain how the definition given relates to the definition of environmental chemistry.
12. What are the main features of the carbon cycle?
13. Describe the role of organisms in the nitrogen cycle.
14. Describe how the oxygen cycle is closely related to the carbon cycle.
15. In what important respect does the phosphorus cycle differ from cycles of other similar elements such as nitrogen and sulfur?