Water-Quality Principles
QW1022–TEL

Lesson 5, Part 1—Major Ions and Field-Measured Properties: Major Ions

Source: Girard, J.E., 2010, Principles of environmental chemistry (2d ed.): Sudbury, Mass., Jones and Bartlett Publishers, p. 25–35 (http://www.jblearning.com/). Used with permission.

U.S. Department of the Interior
U.S. Geological Survey

Nutrient Cycles

To survive, a community of plants and animals in an ecosystem requires a constant supply of both energy and **nutrients.** The energy that sustains the system is not recycled. It flows endlessly from producers to consumers, entering as light from the sun and leaving as waste heat that cannot be reused. Nutrients, however, are continually recycled and reused. When living organisms die, their tissues are broken down, and vital chemicals are returned to the soil, water, and atmosphere.

Analysis of tissues from living organisms shows that more than 95% of the mass of the tissues is made from just 6 of the Earth's 92 naturally occurring elements: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and phosphorus (P). These six elements are the building blocks for the manufacture of carbohydrates, proteins, and fats. These compounds, along with water, make up almost the entire mass of all living organisms. Plants are composed primarily of carbohydrates, whereas animals are composed primarily of proteins.

Small amounts of other elements are also required in order for plants and animals to survive and thrive. Iron (Fe), magnesium (Mg), and calcium (Ca) together make up most of the remaining 5% of the mass of living organisms. In many animals, iron is bound to hemoglobin, the protein in the blood that supplies oxygen to all parts of the body. In green plants, magnesium is bound to chlorophyll, the protein that absorbs light from the sun and that is a vital part of the process of photosynthesis. Animals with skeletons need calcium as well as phosphorus to make bones and cartilage.

Trace amounts of approximately 16 other elements are also required. Copper (Cu) and zinc (Zn), for example, are essential components of certain enzymes, specialized proteins that facilitate many vital chemical reactions within the animals' bodies.

Plants obtain the essential elements from the soil and the atmosphere. Animals obtain them from their food: plants and other animals. Consider the cycles by which supplies of oxygen, carbon, and nitrogen are constantly renewed.

The Carbon Cycle

The **carbon cycle** is illustrated in Figure 1.11. The major sources of carbon for our planet are the carbon dioxide gas in the atmosphere and the carbon dioxide dissolved in the oceans. Enormous quantities of carbon are also present in rocks, tied up in carbonates such

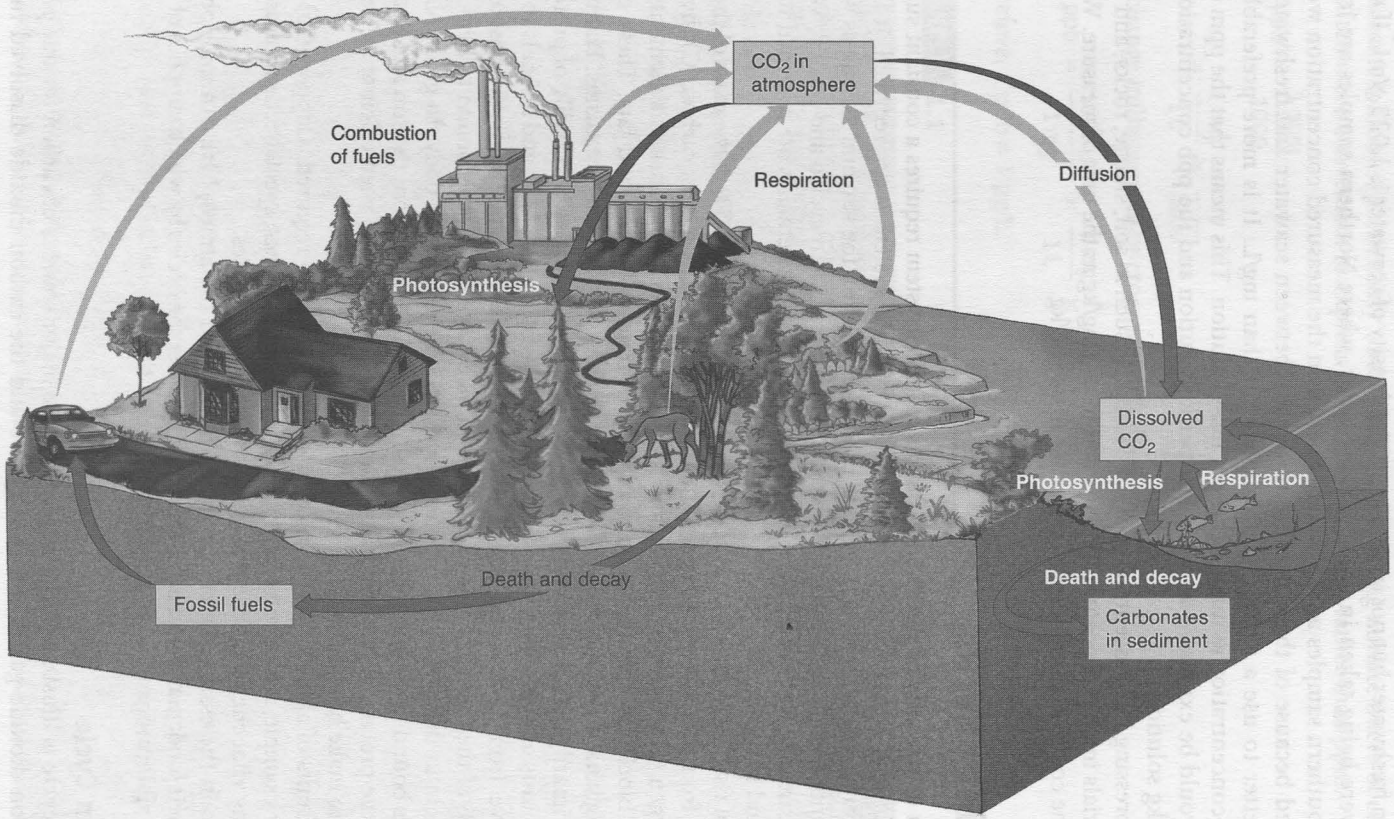

Figure 1.11 The carbon cycle: Atmospheric carbon dioxide is consumed by green plants in photosynthesis. Respiration in animals and plants and combustion of fossil fuels return carbon dioxide to the atmosphere. Carbon also cycles through water; dissolved carbon dioxide reacts with minerals and water to form carbonates, which are deposited in sediments.

as limestone, but this source recycles so slowly that it is not available to plants and animals for their daily needs.

Atmospheric carbon dioxide, although it makes up only 0.036% (360 ppm) of the atmosphere by volume, is the starting material on which all living organisms depend. In the process of photosynthesis, carbon dioxide is taken into the leaves of green plants, where it combines with water to form sugar (glucose) and oxygen, as shown in this equation:

$$\text{Solar energy} + \underset{\text{carbon dioxide}}{6\,CO_2} + \underset{\text{water}}{6\,H_2O} \xrightarrow{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6\,O_2}$$

Plants on land obtain the needed water from the soil; aquatic plants obtain it from their surroundings. The water is absorbed through the plant's roots and is then transported to the leaves. Part of the sugar that is formed is stored in the leaves, and part is converted into the complex carbohydrates and other large molecules that make up plant tissues. The oxygen is released to the atmosphere.

Photosynthesis is a very complex process that is still not fully understood. It involves many chemical reactions in which the green pigment chlorophyll plays an important role. We consider only the overall result of photosynthesis, as summarized by the previous equation.

When an animal such as a deer or rabbit eats a green plant, the carbohydrates in the plant are digested and broken into simple sugars, including glucose. Glucose is absorbed into the bloodstream and carried to the cells of the animal's body, where in the process of **respiration**, it reacts with oxygen in the blood. Carbon dioxide and water are formed, and energy is released.

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

Part of the energy released in respiration is used to power the many activities that go on in living cells, and part is lost as heat.

Notice that the overall reaction for respiration is the same as the overall reaction for photosynthesis written backward. However, although cellular respiration is essentially the reverse of photosynthesis, the complex intermediate steps that are involved in the two processes are very different.

Plants engage in both photosynthesis and respiration. During the day, photosynthesis is the dominant process. At night, when there is no sunlight, respiration is dominant. Decomposers also play a part in the carbon cycle. They feed on the dead remains of plants and animals and via respiration release carbon dioxide and water to the atmosphere.

Approximately 300-million years ago, huge quantities of dead and decaying plant and animal remains became buried deeply under sediments before they could be completely broken down. Over time, the remains were compressed, and chemical reactions gradually transformed them into the fossil fuels: coal, oil, and natural gas. When these fuels are burned to release the chemical energy stored within their molecules' bonds, oxygen from the atmosphere is used to convert their carbon into carbon dioxide.

$$C + O_2 \rightarrow CO_2 + \text{energy}$$

The combustion of the fossil fuels that powers our industrialized society therefore forms an integral part of the carbon cycle. Humans also intervene in the carbon cycle when they cut down more trees than they replace, thereby decreasing the amount of carbon dioxide that otherwise would be taken from the atmosphere and converted to nutrients. The climatic implications of these two activities, both of which tend to increase carbon dioxide concentration in the atmosphere, are discussed in Chapter 3.

Another important part of the carbon cycle is the continual exchange of carbon dioxide between the atmosphere and the oceans, a process that is important in maintaining the carbon dioxide concentration of the atmosphere at a constant level. The amount of carbon dioxide that dissolves in the oceans depends mainly on the temperature of the ocean water and the relative concentrations of carbon dioxide in the atmosphere and the water. When the temperature falls or when the carbon dioxide concentration in the water becomes relatively low, more atmospheric carbon dioxide dissolves. Only the surface layer of the ocean is at equilibrium with the atmosphere. A very small portion of the dissolved carbon dioxide reacts with chemicals in the water, such as calcium, to form carbonates. The carbonates, primarily limestone ($CaCO_3$), are insoluble (do not dissolve) in water and settle on the ocean floor.

Rock formation and weathering are other aspects of the carbon cycle. Sedimentary rocks such as limestone and dolomite ($CaMg[CO_3]_2$) were formed millions of years ago from the skeletal remains of coral and other marine creatures that were rich in calcium carbonates. When chemically weathered by rain with a slight natural acidity, limestone rocks very gradually dissolve, releasing carbon dioxide into the atmosphere. This recycling of carbon through rock is a very slow process.

The **solubility product** is the equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution. The solution is saturated; that is, some of the undissolved solute is in contact with the solution. For example, when limestone (calcium carbonate) is placed in water, the dissociation process is described with this equation:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

The equilibrium constant, K for this reaction, can be written as follows:

$$K = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3(s)]}$$

remember that [ ] means "molar concentration"
M in mol/L or mmol/mL

The solid $CaCO_3$ is not dissolved. It is considered to be in a standard state and is omitted from the equilibrium constant. The solubility product equilibrium constant, K_{sp} for this reaction, is defined as follows:

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

This equation describes the equilibrium concentration of the calcium and carbonate ions in solution. The K_{sp} for various solid compounds are listed in Appendix A.

If calcium carbonate ($CaCO_3$) is placed in water, the equilibrium concentration of calcium ion in solution is calculated as follows:

The K_{sp} of $CaCO_3$ is 4.9×10^{-9}

This equilibrium shows that every $CaCO_3$ that dissolves produces one Ca^{2+} and one CO_3^{2-}.

$$[Ca^{2+}] = [CO_3^{2-}]$$

Therefore,

$$K_{sp} = [Ca^{2+}]^2 = 4.9 \times 10^{-9}$$

Take the square root of both sides.

$$[Ca^{2+}] = 6.8 \times 10^{-5}\ M$$

This is a molar concentration, M, expressed as mol/L or mmol/mL.

The mass of dissolved calcium ion is (40.08 g/mol) (6.8×10^{-5} mol/L) = 2.8×10^{-3} g/L or 2.8 mg/L. This corresponds to 2.8 ppm (mg/L). The Ksp indicates that the equilibrium concentration of calcium ion should be 2.8 ppm. This means that if a limestone rock is in contact with pure water (carbon dioxide free), it will dissolve until the concentration of calcium ion reaches 2.8 ppm. Once this concentration is attained, dissolution will stop and the limestone will no longer dissolve, even though it is in contact with the solution. This calculation ignores the fact that dissolved carbon dioxide can react with calcium carbonate.

Calcium ion is the most common metal ion in rivers and lakes. When measured in lakes, the concentration is much higher than the 2.8-ppm concentration that the Ksp indicates. In natural waters, Ca^{2+} is produced by the dissolution of calcium carbonate by the action of dissolved CO_2 to produce 2 moles of bicarbonate (HCO_3^-) for each mole of Ca^{2+}.

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

If the pH is near neutral, most of the product is bicarbonate, not CO_3^{2-} or H_2CO_3. Measurements of Ca^{2+} and HCO_3^- in many rivers confirm that there is one calcium ion for every two bicarbonate ion. This process raises the $[Ca^{2+}]$ to 20 ppm (for an average atmospheric carbon dioxide concentration). As can be seen in Figure 1.12, the concentration of calcium and bicarbonate in river water has been measured across the world. Rivers such as the Congo, the Mississippi, and the Danube all show a relationship of $2[Ca^{2+}] = [HCO_3^-]$ and appear to be saturated with calcium carbonate. Rivers such as the Nile and the Amazon for which $2[Ca^{2+}]$ is less than $[HCO_3^-]$ are not saturated with calcium carbonate.

In principle, it may be possible to use the Ksp of a solid to estimate the solubility of a solid. In practice, the solubility of the solid is affected by the presence of other solutes. As was shown previously here, the presence of an acid can greatly increase the solid solubility. The presence of complexing agents or common ions also dramatically affects the solubility of solids.

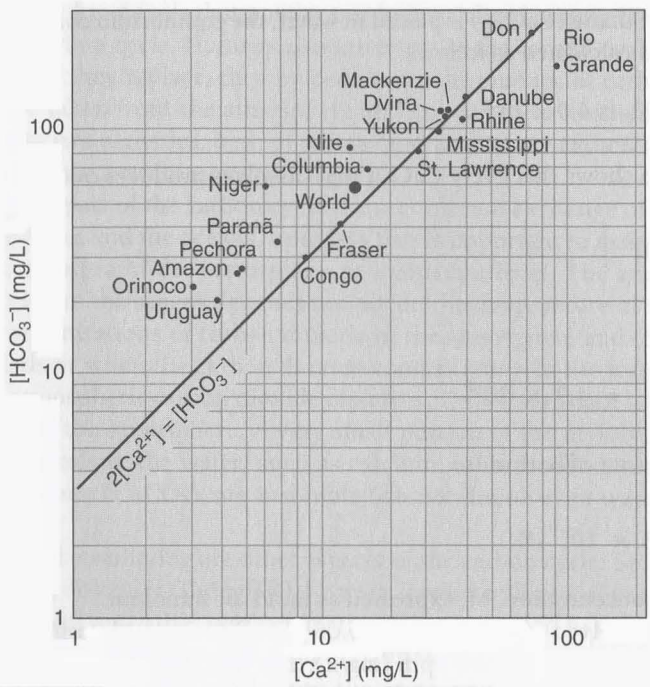

Figure 1.12 Concentrations of bicarbonate and calcium in many rivers conform to the mass balance for the reaction: $[HCO_3^-] = 2[Ca^{2+}]$. Data from W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3rd ed. (New York: Wiley Interscience, 1996), p. 189, and H. D. Holland, *The Chemistry of the Atmosphere and Oceans*. (New York: Wiley Interscience, 1978).

The Nitrogen Cycle

The **nitrogen cycle** is illustrated in Figure 1.13. Nitrogen is an essential component of proteins and of the genetic material that makes up DNA (deoxyribonucleic acid) and is a constant supply that is vital for all living organisms. Although 78%* of the Earth's atmosphere is composed of nitrogen gas (N_2), plants and animals cannot use this nitrogen directly. Atmospheric nitrogen must be converted to other nitrogen compounds before it can be absorbed through the roots of plants. This change is achieved by **nitrogen fixation**, a process that is carried out by specialized bacteria that have the ability to transform atmospheric nitrogen into ammonia (NH_3). Some nitrogen-fixing bacteria live in soil, whereas others live in nodules on the roots of leguminous plants such as peas, beans, clover, and alfalfa. The ammonia produced in root nodules is converted into a variety of nitrogen compounds that are then transported through the plant as needed.

Another means by which atmospheric nitrogen is converted to a usable form is lightning. The electric discharges in lightning cause nitrogen and oxygen in the atmosphere to combine and form oxides of nitrogen, which in turn react with water in the atmosphere to form nitric acid (HNO_3). The nitric acid, which reaches the Earth's surface dissolved in rainwater, reacts with materials in soil and water to form nitrates (NO_3^-) that are directly absorbed through plant roots. Compared with biological fixation, lightning accounts for only a small fraction of the usable nitrogen in soil.

* (F.D. Wilde, USGS 2011)

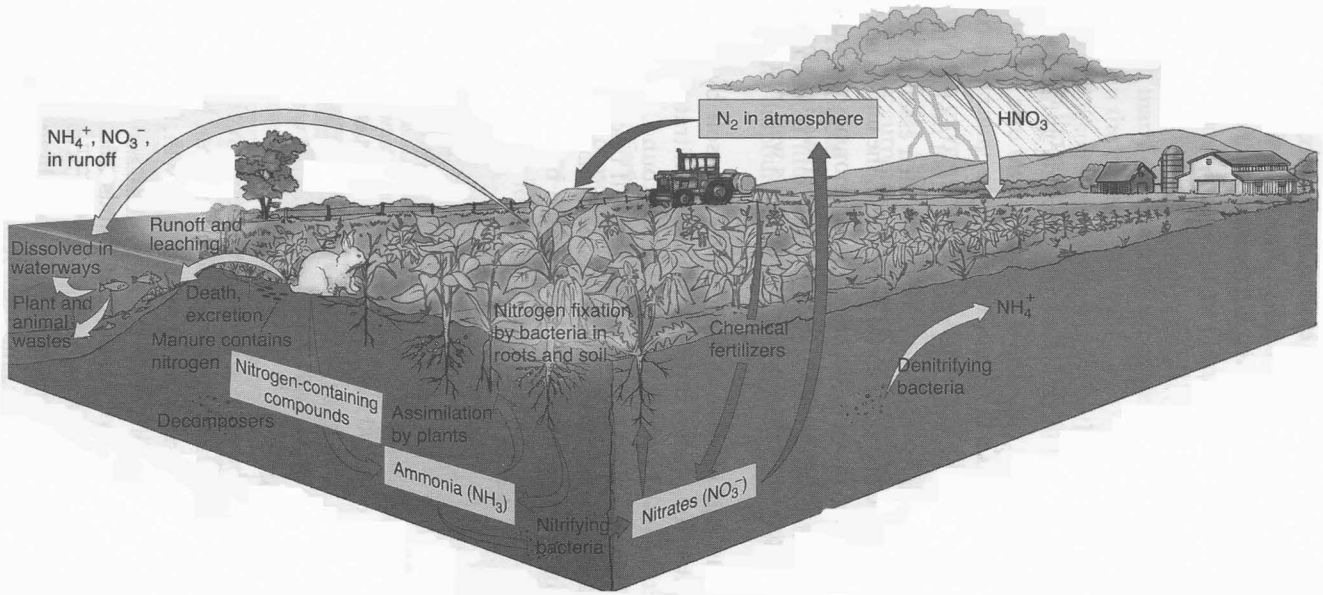

Figure 1.13 The nitrogen cycle: In nitrogen fixation, specialized bacteria convert atmospheric nitrogen to ammonia and nitrates, which plants absorb through their roots. Some nitrogen gas is fixed by lightening. Animals obtain the nitrogen they need to make tissues from plants. The wastes animals produce and their dead bodies return nitrogen to the soil in forms plants can use. In denitrification, bacteria convert nitrates in soil back to nitrogen gas.

Although some trees and grasses can absorb ammonia produced by nitrogen-fixing bacteria directly from the soil, most plants can use only nitrogen that is in the form of nitrates. The transformation of ammonia into nitrates is carried out by specialized soil bacteria in the process known as **nitrification.** A soil pH of 6.5 to 8 is optimum, and the reaction rate decreases when the pH is below 6. The two-step nitrification reaction is as follows:

$$2\,NH_4^+ + 3\,O_2 + 2\,H_2O \rightarrow 2\,NO_2^- + 4\,H_3O^+$$

$$2\,NO_2^- + O_2 + H_2O \rightarrow 2\,NO_3^-$$

When these two reactions are added together, they yield this overall reaction:

$$NH_4^+ + 2\,O_2 + H_2O \rightarrow NO_3^- + 2\,H_3O^+$$

Plants convert ammonia or nitrates that they get from soil or root nodules into proteins and other essential nitrogen-containing compounds. Animals get their essential nitrogen supplies by eating plants. When plants and animals die and decompose, the nitrogen-containing compounds in their tissues are broken down by decomposers; ammonia is eventually formed and returned to the soil. Nitrogen is also returned to the soil in animal wastes. Both urine and feces have a high content of nitrogen-containing compounds. In this way, nitrogen is continually cycled through food chains.

Not all of the ammonia and nitrates that are formed in soil by the processes just described become available for plants. Both ammonia and nitrates are very soluble in water. As rainwater percolates downward through the ground, these compounds are leached out of topsoil. They are often carried away in runoff into nearby streams, rivers, and lakes, where they are recycled through aquatic food chains. Another process that removes nitrates from the soil is **denitrification,** in which bacteria carry out a series of reactions that convert nitrates back to nitrogen gas. One of the denitrification reactions can be written as follows:

$$4\,NO_3^- + 5\,CH_2O + 4\,H_3O^+ \rightarrow 2\,N_2 + 5\,CO_2 + 11\,H_2O$$

In a few locations around the world, nitrates have accumulated in large mineral deposits. In Chile, for example, as mountain streams originating in the Andes Mountains flowed across dry, hot desert toward the sea over thousand of years, much of the water evaporated, leaving behind huge deposits of sodium nitrate.

In the natural environment, a balance is maintained between the amount of nitrogen removed from the atmosphere and the amount returned. However, because most soils contain an insufficient amount of nitrogen for maximum plant growth, farmers frequently apply synthetic inorganic fertilizers containing ammonia and nitrates. As a result of runoff from fertilized farmland, the extra nitrogen-containing compounds reaching rivers and lakes may upset the natural balance, sometimes with damaging consequences for the environment.

An alternative to the use of synthetic fertilizers for replenishing nitrogen in the soil is to plant a nitrogen-fixing crop, such as clover, and plow it back into the soil. Another method is to spread manure and allow the natural soil bacteria to degrade it and release the nitrogen-containing compounds that plants can absorb.

The Oxygen Cycle

Oxygen is all around us. As O_2, it makes up 21% of the atmosphere and is a component of all of the important organic compounds in living organisms. Oxygen is a very reactive element that combines readily with many other elements. It is a component of CO_2, nitrate (NO_2^-), and phosphate (PO_4^{3-}), and thus is an integral part of the recycling of carbon, nitrogen, and phosphorus. Oxygen is also a constituent of most rocks and minerals, including silicates, limestone ($CaCO_3$), and iron ores (Fe_2O_3, Fe_3O_4). The **oxygen cycle** is very complex and is interconnected with many other cycles. Here we briefly consider only some of the more important pathways in the cycle.

Photosynthesis and respiration are the basis of both the carbon cycle and the oxygen cycle. Oxygen is released during photosynthesis and is consumed during respiration. The oxygen and carbon cycles are also interconnected when coal, wood, or any other organic materials are burned. During burning, oxygen is consumed, and carbon dioxide is released.

Another part of the oxygen cycle is the constant exchange of oxygen between the atmosphere and bodies of water, especially oceans. Oxygen dissolved at the surface of water is carried to deeper levels by currents. Dissolved oxygen is essential for fish and other aquatic life.

The Phosphorus Cycle

The **phosphorus cycle** is illustrated in Figure 1.14. Phosphorus is a component of many important biological compounds, including DNA and enzymes that play an essential role in

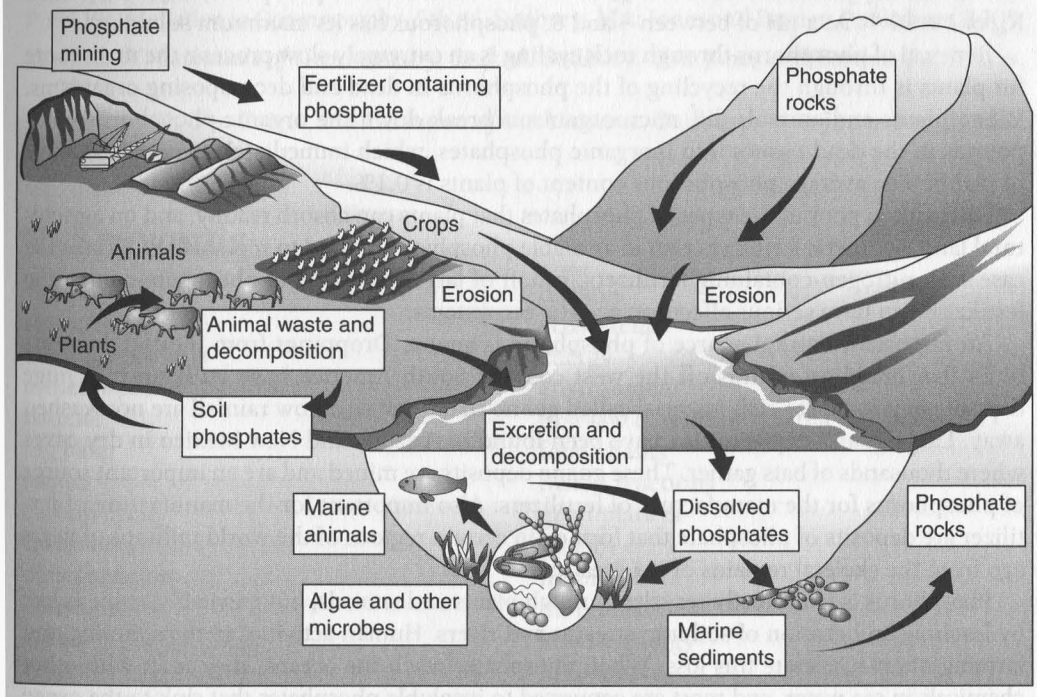

Figure 1.14 The phosphorus cycle. The main reservoir of phosphorus is phosphate rock. Phosphate released to the soil during weathering is absorbed through plant roots. Animals obtain phosphorus form plants and return it to soil in wastes and dead tissue. Phosphates leached from the soil enter waterways and are carried to the ocean.

the transfer of energy in living cells. It is a major constituent of cell membranes and is present in high concentration in bones, teeth, and shells.

Unlike the carbon and nitrogen cycles, the phosphorus cycle does not include an atmospheric phase, and the ultimate source of phosphorus for plants and animals is rock, nearly all of which contains small amounts of phosphorus, mostly in the form of phosphates (PO_4^{3-}). Two examples are apatite, $Ca_5(PO_4)_3(F)$, and vivianite, $Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$. The phosphorus cycle is primarily a sedimentary cycle. As rocks weather, phosphates are very slowly dissolved and released to the soil. The crustal average abundance of apatite is 1.2 mg/g.

Plants absorb dissolved phosphate directly from the soil through their roots and transport it to their leaves, where it is incorporated into large biological molecules. Animals get their phosphorus by eating plants. Not all of the phosphate formed from rock by weathering becomes available to plants. Some of it becomes tightly bound to elements such as aluminum, iron, and calcium in compounds that are not very soluble in water.

In water, phosphorus solubility is largely controlled by pH. The phosphate ion has three forms: $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

$$H_3PO_4 \xrightarrow{pK_a\ 2.15} H_2PO_4^- + H^+ \xrightarrow{pK_a\ 7.2} HPO_4^{2-} + H^+ \xrightarrow{pK_a\ 12.3} PO_4^{3-} + H^+$$

At a pH of less than 4, insoluble iron and aluminum phosphates are formed. At a pH of greater than 8, almost insoluble calcium phosphates are formed. Iron phosphate, $Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$, has a solubility product constant (K_{sp}) of 1×10^{-36}, and calcium phosphate, $Ca_3(PO_4)_2$, has a K_{sp} of 1×10^{-24}. At a pH of between 4 and 8, phosphorous has its maximum solubility.

Renewal of phosphorus through rock cycling is an extremely slow process; the main route for plants is through the recycling of the phosphorus in dead and decomposing organisms. When plants and animals die, microorganisms break down the organic phosphorus compounds in the dead tissues into inorganic phosphates, which immediately become available to plants. The average phosphorous content of plants is 0.1%.

Soil is often poor in the types of phosphates that plants can absorb readily, and on agricultural land, synthetic fertilizers rich in available phosphate are used to replenish it. As was the case with nitrogen-containing fertilizers, runoff of large quantities of phosphate-containing fertilizers can have serious effects on aquatic ecosystems.

An important natural source of phosphates is **guano.** Droppings from thousands of sea birds that breed on islands off the west coast of South America have built up into huge deposits of phosphate-rich material called guano that because of low rainfall are not washed away. Large guano deposits also have been found in Arizona and New Mexico in dry caves where thousands of bats gather. These guano deposits are mined and are an important source of phosphorus for the manufacture of fertilizers. Also important for the manufacture of fertilizer are deposits of phosphate that formed in certain regions of the world millions of years ago from the skeletal remains of sea creatures.

Phosphorus is continually recycled through plants and animals, but inevitably, some is lost by leaching and erosion of soil into streams and rivers. Human activities such as mining and farming often accelerate this loss. When phosphates reach the oceans, they react with other chemicals in sea water, and most are converted to insoluble phosphates that sink to the ocean floor and, for all practical purposes, are permanently lost. It can take millions of years for phosphate lost to the oceans to be replenished by weathering of rock. Humans add to the problem of

phosphorus loss by disposing of large amounts of their wastes—which contain significant quantities of phosphorus—into waterways instead of recycling them and returning them to the land.

Reserves of phosphorus in high-grade phosphate ores are estimated to be sufficient for several hundred years. We do not have an immediate problem, but we would be wise to conserve the reserves of phosphorus that we still have and reduce phosphorus loss as far as possible.

Nature's Cycles in Balance

Life on Earth depends on a continual supply of energy from the sun and a continual recycling of materials. As you have learned here, the numerous and complex processes that sustain life are interlinked and interdependent. Because all aspects of an ecosystem are so completely interwoven, human intervention in any part of the system can easily lead to widespread disturbances of the natural balance in the environment.