Water-Quality Principles
QW1022–TEL

Lesson 9—Environmental Microbiology

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A Model for the Earth as a Biogeochemical System

Garrels and Lerman (1981) developed a simple model for the biogeochemistry of the Earth's surface which includes interactions between the atmospheric, oceanic, and crustal compartments and the biosphere (Fig. 1.1). The model assumes that the atmosphere and the oceans have not shown large changes in their composition during geologic time. Of course, we know that this has not always been true, but for the last 60 million years or so, there is good geologic evidence that this assumption is reasonable (Holland et al. 1986). With these constraints, the model couples reactions in the atmosphere and oceans to seven compartments that represent major crustal minerals, such as gypsum ($CaSO_4 \cdot 2H_2O$), pyrite (FeS_2), and calcium carbonate ($CaCO_3$). For instance, if the weathering of limestone transfers

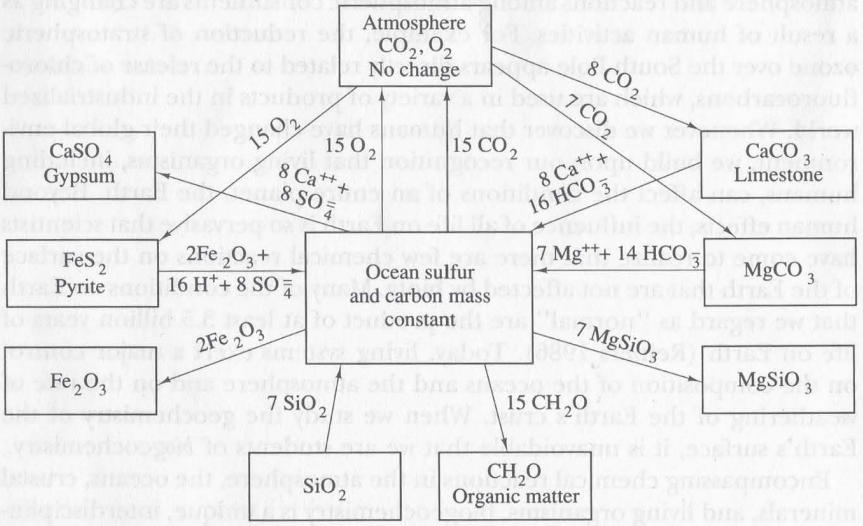

Figure 1.1 A model of major sedimentary reservoirs and the transfers between them that are associated with an increase in the mass of the biosphere by 15 moles. From Garrels and Lerman (1981).

8 units of Ca^{2+} to the world's oceans and the Ca content of seawater does not change, then the same amount of Ca must be deposited in a sedimentary mineral on the seafloor.

Organic materials, living and dead, constitute the biosphere, which appears in the model compartment labeled CH_2O, representing the approximate stoichiometric composition of living tissues. Changes in the mass of the biosphere through geologic time are indicated by net transfers of material into and out of that compartment.

Consider the increase in the total mass of organic matter that must have occurred during the Carboniferous Period, when large areas of land were covered by swamps. Here, dead vegetation accumulated as peat that was later transformed into coal. Storage of carbon in dead materials, detritus, represents an increase in the mass of the biosphere. With no change in the CO_2 content of the atmosphere or the CO_2 dissolved in the oceans as HCO_3^-, the carbon added to the biosphere must have been derived from the weathering of carbonate minerals. Weathering of carbonate minerals, however, would also transfer Ca and Mg to the oceans, and to maintain constant seawater chemistry the model predicts that Ca must be deposited as $CaSO_4$ and that Mg must be deposited in silicate minerals by various reactions that occur in ocean sediments (Chapter 9). To deposit $CaSO_4$ with no change in the SO_4^{2-} content of the world's oceans, sulfur must be derived from another pool. Oxidative weathering of pyrite (FeS_2) would supply SO_4 to the oceans, also consuming some of the oxygen that would have been added to the atmosphere by photosynthesis. The remaining oxygen would be consumed in the deposition of Fe_2O_3. Note that the total O_2 consumed by these reactions is in molar stoichiometric balance with the carbon stored in organic matter by photosynthesis, so the atmospheric content of O_2 does not change.

This model illustrates how minerals such as magnesium silicates, not traditionally the focus of biological studies, are linked to the activities of the biosphere. Certainly, it is legitimate to ask whether this is a reasonable model for the linkage of chemical reactions on Earth. Support for the model would be found if large geologic deposits of gypsum are associated with periods in which there were large net stores of organic carbon, since the model predicts a coupled balance,

$$\text{pyrite} + \text{carbonates} \rightleftarrows \text{gypsum} + \text{organic carbon}, \tag{1.1}$$

through geologic time. Indeed, Garrels and Lerman (1981) show that the molar ratio of organic carbon to gypsum has remained fairly constant through geologic time, with large deposits of gypsum associated with the Carboniferous Period, when large amounts of organic carbon were stored in coal (Fig. 1.2).

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Origins

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Origin of Life
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Introduction

Six elements, C, H, O, N, P, and S, are the major constituents of living tissue and account for 95% of the biosphere. At least 20 other elements (see inside front cover) are known to be essential to life, and it is possible that this list may grow slightly as we come to recognize the role of additional trace elements in biochemistry (McDowell 1992). In the periodic table all of the biologically relevant elements are found at atomic numbers less than that of iodine at 53. Even though living organisms affect the distribution and abundance of some of the heavier elements, we can speak of the chemistry of life as the chemistry of "light" elements (Deevey 1970a). One initial constraint on the composition of life must have been the relative abundance of chemical elements in our galaxy. Later as the Sun and its planets formed and differentiated, the chemical composition of the Earth's surface determined the environment in which life arose.

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The Biosphere: The Carbon Cycle of Terrestrial Ecosystems

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Photosynthesis is the biogeochemical process that acts to transfer carbon from its oxidized form, CO_2, in the atmosphere to the reduced (organic) forms that result in plant growth. Directly or indirectly, photosynthesis provides the energy for all other forms of life in the biosphere, and the use of plant products for food, fuel, and shelter brings photosynthesis into our daily lives. The growth of plants affects the composition of the atmosphere (Chapter 3) and the development of soils (Chapter 4), linking photosynthesis to other aspects of global biogeochemistry. Indeed, the

presence of organic carbon in soils and O_2 in our atmosphere provides the striking contrast between the *bio*geochemistry on Earth and the simple geochemistry that characterizes our neighboring planets.

In this chapter we will consider the measurement of net primary production—the rate of accumulation of organic carbon in the tissues of land plants. A similar treatment of photosynthesis in the world's oceans is given in Chapter 9. The rate of plant growth varies widely over the land surface. Deserts and continental ice masses may have little or no net primary production, while tropical rainforests can show annual production of >1000 g C/m^2.

Various environmental factors affect the global rate of net primary productivity on land and the total storage of organic carbon in plant tissues (biomass), dead plant parts (detritus), and soil organic matter. As any home gardener knows, light and water are important, but plant growth is also determined by the stock of available nutrients in the soil. These nutrients are ultimately derived from the atmosphere or from the underlying bedrock (Table 4.5). The overall storage of carbon on land is determined by the balance between primary production and decomposition, which returns carbon to the atmosphere as CO_2 (Schlesinger 1977).

Photosynthesis

Containing a central atom of magnesium, the chlorophyll molecule is a prime example of how plants have incorporated an abundant product of rock weathering as an essential element in biochemistry. When photosynthetic pigments absorb sunlight, a few of the chlorophyll molecules are oxidized—passing an electron to a sequence of electron transfer proteins that ultimately lead to the reduction of a high-energy molecule, known as nicotinamide adenine dinucleotide phosphate (NADP), to NADPH. These chlorophyll molecules regain an electron from a water molecule, which is split by an enzyme containing manganese, calcium, and chlorine in a recently postulated asymmetrical three-dimensional structure (Pecoraro 1988, Yachandra et al. 1993). This reaction is the origin of O_2 in the Earth's atmosphere:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \uparrow . \qquad (5.1)$$

In all cases, the photosynthetic pigments and proteins are embedded in a cell membrane, which allows protons (e.g., H^+ of Eq. 5.1) to build up to high concentrations on one side of the membrane and for this potential energy to be used to synthesize another high-energy compound, adenosine triphosphate or ATP. In higher plants, the accumulation of protons occurs within the chloroplasts of leaf cells, whereas in photosynthetic bacteria, the reaction is conducted across the external cell membrane.

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The Biosphere: Biogeochemical Cycling on Land

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Living tissue is primarily composed of carbon, hydrogen, and oxygen in the approximate proportion of CH_2O, but more than 20 other elements

are necessary for biochemical reactions and for the growth of structural biomass. For example, phosphorus (P) is required for adenosine triphosphate (ATP), the universal molecule for energy transformations in organisms, and calcium (Ca) is a major structural component in both plants and animals. The proteins found in plants and animals contain about 16% nitrogen (N) by weight. Earlier we saw that the protein ribulose bisphosphate carboxylase (RuBP) controls the rate of carbon fixation during photosynthesis in many plant species (Chapter 5). The link between C and N that begins in cellular biochemistry extends to the global biogeochemical cycles of these elements.

The various elements essential to biochemical structure and function are often found in predictable proportions in living tissues (e.g., wood, leaf, bone, and muscle; Garten 1976, Reiners 1986). For instance, the ratio of C to N in leaf tissue is about 50. At the global level, our estimate of net primary production (NPP), 60×10^{15} g C/yr, implies that about 1200×10^{12} g of nitrogen must be supplied to plants each year through biogeochemical cycling to achieve the level of NPP that we observe. As we shall see, the availability of some elements, such as N and P, is often limited, and the supply of these elements may control the rate of net primary production in terrestrial ecosystems. Conversely, for elements that are typically available in greater quantities, e.g., Ca and S, the rate of net primary production often determines the rate of cycling in the ecosystem and losses to streamwaters. In every case, the biosphere exerts a strong control on the geochemical behavior of the major elements of life. Much less biological control is seen in the cycling of elements such as sodium (Na) and chloride (Cl), which are less important constituents of biomass (Gorham et al. 1979).

In earlier chapters we saw that the atmosphere is the dominant source of C, N, and S in terrestrial ecosystems, and that rock weathering is the major source for most of the remaining biochemical elements (e.g., Ca, Mg, K, Fe, P). In any terrestrial ecosystem, the receipt of elements from the atmosphere and the lithosphere represents an input of new quantities of nutrients for plant growth.[1] However, as a result of internal cycling and retention of past inputs, plant growth is not solely dependent upon new inputs to the system. In fact, the annual circulation of important elements such as N within an ecosystem is often 10 to 20× greater than the amount received from outside the system (Table 6.1). This large internal, or *intrasystem cycle,* is achieved by the long-term retention of elements received from the atmosphere and the lithosphere. Important biochemical elements are accumulated in terrestrial ecosystems by biotic uptake, whereas nonessential elements pass through these systems under simple geochemical control (Johnson 1971, Vitousek and Reiners 1975).

[1] Unlike the well-known models developed for the Hubbard Brook Ecosystem (e.g., Likens and Bormann 1995), the nutrient budgets in this book consider rock weathering as an *external* source of nutrients that enter a terrestrial ecosystem each year (Gorham et al. 1979).

Table 6.1 Percentage of the Annual Requirement of Nutrients for Growth in the Northern Hardwoods Forest at Hubbard Brook, New Hampshire, That Could Be Supplied by Various Sources of Available Nutrients[a]

Process	N	P	K	Ca	Mg
Growth requirement (Kg ha^{-1} yr^{-1})	115.4	12.3	66.9	62.2	9.5
Percentage of the requirement that could be supplied by:					
Intersystem inputs					
Atmospheric	18	0	1	4	6
Rock weathering	0	1	11	34	37
Intrasystem transfers					
Reabsorptions	31	28	4	0	2
Detritus turnover (includes return in throughfall and stemflow)	69	67	87	85	87

[a] Calculated using Eqs. 6.2 and 6.3. Reabsorption data are from Ryan and Bormann (1982). Data for N, K, Ca, and Mg are from Likens and Bormann (1995) and for P from Yanai (1992).

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The Global Cycles of Nitrogen and Phosphorus

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Linking the Global Cycles of C, N, and P
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The availability of nitrogen and phosphorus controls many aspects of local ecosystem function and global biogeochemistry. Nitrogen often limits the rate of net primary production on land and in the sea (Vitousek and Howarth 1991). In living tissues, nitrogen is an integral part of enzymes, which mediate the biochemical reactions in which carbon is reduced (i.e., photosynthesis) or oxidized (respiration). Phosphorus is an essential component of DNA, ATP, and the phospholipid molecules of cell membranes. Changes in the availability of N and P are likely to have controlled the size and activity of the biosphere through geologic time.

A large number of biochemical transformations of nitrogen are possible, since nitrogen is found at valence states ranging from -3 (in NH_3) to $+5$ (in NO_3^-). A variety of microbes capitalize on the potential for transformations of N among these states and use the energy released by the changes in redox potential to maintain their life processes (Rosswall 1982). Collec-

tively, these microbial reactions drive the cycle of nitrogen (Fig. 12.1). In contrast, whether it occurs in soils or in biochemistry, phosphorus is almost always found in combination with oxygen (i.e., as PO_4^{3-}). Most metabolic activity is associated with the synthesis or destruction of high-energy bonds between a phosphate ion and various organic molecules, but in nearly all cases the phosphorus atom remains at a valence of +5 in these reactions.

The most abundant form of nitrogen at the surface of the Earth, N_2, is the least reactive species. Nitrogen fixation converts atmospheric N_2 to one of the forms of "fixed" (or "odd," Chapter 3) nitrogen that can be used by biota. Nitrogen-fixing species are most abundant in nitrogen-poor habitats, where their activity increases the availability of nitrogen for the biosphere (Eq. 2.12). At the same time, denitrifying bacteria return N_2 to the atmosphere (Eq. 2.18), lowering the overall stock of nitrogen available for life on Earth.

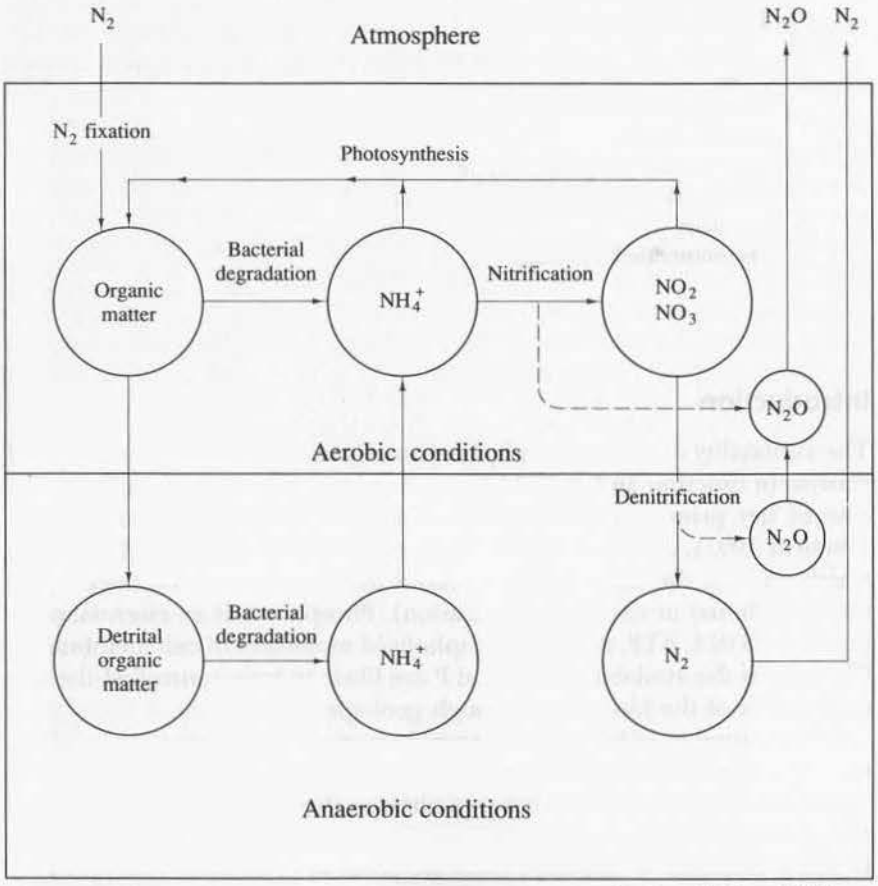

Figure 12.1 Microbial transformations in the nitrogen cycle. From Wollast (1981).

Rocks of the continental crust hold the reservoir of phosphorus that becomes available to the biosphere through rock weathering. Land plants can increase the rate of rock weathering in P-deficient habitats (Chapter 4), but in nearly all cases the phosphorus content of rocks is relatively low. Subsequent reactions between dissolved P and other minerals reduce the availability of P in soil solutions or seawater. Thus, in most habitats—both on land and in the sea—the availability of P is controlled by the degradation of organic forms of P (e.g., Fig. 6.17). This *bio*geochemical cycle temporarily retains and recycles some P from the unrelenting flow of P from weathered rock to ocean sediments. The global P cycle is complete only when sedimentary rocks are lifted above sea level and the weathering begins again.

In this chapter we will examine our current understanding of the global cycles of N and P. We will attempt to balance N and P budgets for the world's land area and the sea. For N, the balance between N-fixation and denitrification through geologic time determines the nitrogen available to biota and the global nitrogen cycle. One of the by-products of nitrification and denitrification is N_2O (nitrous oxide), which is both a greenhouse gas and a cause of ozone destruction in the stratosphere (Chapter 3). We will formulate a tentative budget for N_2O based on our current, limited understanding of the sources of this gas in the atmosphere.

large source of N_2O in the atmosphere (Kaplan et al. 1978). Anthropogenic sources of N_2O are more than enough to explain its rate of increase in the atmosphere, but the total compilation of sources—both natural and anthropogenic—is slightly less than the known sinks, including the rate of N_2O accumulation in the atmosphere (Table 12.3). Clearly, more research is needed to refine the budget for atmospheric N_2O.

Cores extracted from the Antarctic ice cap show that the concentration of N_2O was much lower during the last glacial period (Leuenberger and Siegenthaler 1992). At the end of the Pleistocene, concentrations rose from 185 ppb to about 280 ppb and remained fairly constant until the Industrial Revolution, when they increased to the present-day value of about 311 ppb (Fig. 12.5; Zardini et al. 1989). Relatively high rates of N_2O emission have been observed in a variety of wetlands (Bowden 1986), and deglaciation uncovered large areas of boreal peatland, perhaps accounting for the increase in atmospheric N_2O at the end of the last glaciation. Concentrations of atmospheric N_2O may now be increasing as global warming affects wetlands in tundra and boreal regions (Khalil and Rasmussen 1989, 1992a).

The Global Phosphorus Cycle

The global cycle of P is unique among the cycles of the major biogeochemical elements in having no significant gaseous component (Fig. 12.6). The redox potential of most soils is too high to allow for the production of

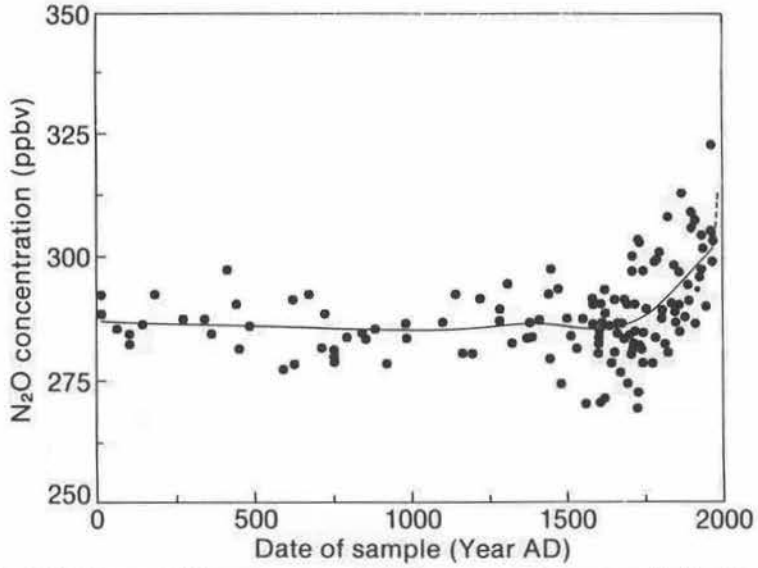

Figure 12.5 Nitrous oxide measurements from ice-core samples, as compiled by Watson et al. (1990).

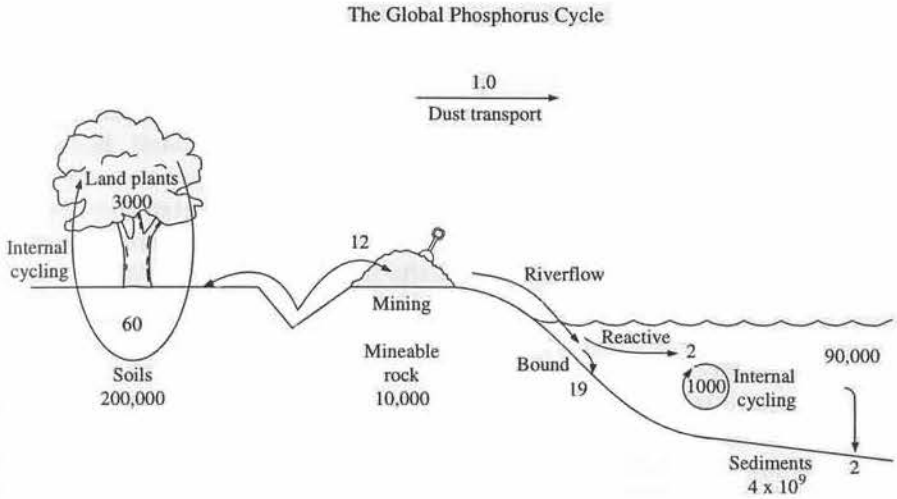

Figure 12.6 The global phosphorus cycle. Each flux is shown in units of 10^{12} g P/yr. Values are derived from the text and from Jahnke (1992). See also Fig. 9.17.

phosphine gas (PH_3; Bartlett 1986), except under very specialized, local conditions (e.g., Dévai et al. 1988, Dévai and DeLaune 1995). The global flux of P in phosphine is probably $<0.04 \times 10^{12}$g/yr (Gassmann and Glindemann 1993). The flux of P through the atmosphere in soil dust and seaspray (1×10^{12} g P/yr) is also much smaller than other transfers in the global P cycle (Graham and Duce 1979), although it is known to make a significant contribution to the supply of available P when it is deposited in some tropical forests (Swap et al. 1992, Newman 1995) and in the open ocean (Talbot et al. 1986).

Unlike transfers in the global nitrogen cycle, the major source of reactive P in the global P cycle is not provided by microbial reactions. Nearly all the phosphorus in terrestrial ecosystems is originally derived from the weathering of calcium phosphate minerals, especially apatite [$Ca_5(PO_4)_3OH$]. Root exudates and mycorrhizae may increase the rate of rock weathering on land (Chapter 4), but there is no process, equivalent to N-fixation, that can produce dramatic increases in phosphorus availability for plants in P-deficient habitats. The phosphorus content of most rocks is not large, and in most soils only a small fraction of the total P is available to biota (Chapter 4). Thus, on both land and at sea, the biota persist as a result of a well-developed recycling of phosphorus in organic forms (Figs. 6.17 and 9.17).

The main flux of P in the global cycle is carried by rivers, which transport about 21×10^{12} g P/yr to the sea (Meybeck 1982). Only about 10% of this

flux is potentially available to marine biota; the remainder is strongly bound to soil particles that are rapidly sedimented on the continental shelf (Chapter 9). The solubility product of apatite is only about 10^{-58} (Lindsay and Vlek 1977), so at a seawater pH of 8.0, the phosphorus concentration in equilibrium with apatite would be about 10^{-8} molar (cf. Fig. 4.4). In fact, organic and colloidal forms of P maintain its concentration in excess of that in equilibrium with respect to apatite; the average content of P in deep ocean water is about 3×10^{-6} *M* (Figs. 9.12 and 9.20). The concentration of PO_4^{3-} in the surface oceans is low, but the large volume of the deep sea accounts for a substantial pool of P (Fig. 12.6). The overall mean residence time for reactive P in the sea is about 25,000 years (Chapter 9).

The turnover of P through the organic pools in the surface ocean is only a few days. Nearly 90% of the phosphorus taken up by marine biota is regenerated in the surface ocean, and most of the rest is mineralized in the deep sea (Fig. 9.17). Eventually, however, phosphorus is deposited in ocean sediments, which contain the largest phosphorus pool near the surface of the Earth. About 2×10^{12} g P/yr are added to sediments of the open ocean—roughly equivalent to the delivery of reactive P to the oceans by rivers (Howarth et al. 1995). On a time scale of hundreds of millions of years, these sediments are uplifted and subject to rock weathering, completing the global cycle. Today, most of the phosphorus in rivers is derived from the weathering of sedimentary rocks, and it represents P that has made at least one complete journey through the global cycle (Griffith et al. 1977).

In many areas humans have enhanced the availability of P by mining phosphate rocks that can be used as fertilizer. Most of the economic deposits of phosphate are found in sedimentary rocks of marine origin, so the mining activity directly enhances the turnover of the global P cycle. In the United States, some of the largest deposits of phosphate rock are found in Florida and North Carolina. In many areas, the flux of P in rivers is significantly higher than it was in prehistoric times as a result of erosion, pollution, and fertilizer runoff (Howarth et al. 1995).

Linking the Global Cycles of C, N, and P

The cycles of important biogeochemical elements are linked at many levels. Stock et al. (1990) describe how P is used to activate a transcriptional protein, stimulating nitrogen fixation in bacteria when nitrogen is in short supply. In this case, an understanding of the interaction between these elements is gained through the study of molecular biology. In Chapter 5, we saw that the photosynthetic rate of land plants is related to the N and P content of their leaves, linking the availability of these elements in plant cells to the net production of organic C for plant growth. In marine ecosystems, net primary productivity is often

calculated from the Redfield ratio of C:N:P in phytoplankton biomass (Chapter 9). New production is predicted by estimating the mass of upwelling water and its nutrient content. Whatever our viewpoint—from molecules to whole ecosystems—the movements of N, P, and C are strongly linked in biogeochemistry (Reiners 1986).

Nitrogen fixation by free-living bacteria appears inversely related to the N/P ratio in soil (Fig. 6.3), and the rate of accumulation of N is greatest in soils with high P content (Walker and Adams 1958). Similarly, N/P ratios <29 appear to stimulate N-fixation in freshwater ecosystems (Chapter 7). One might speculate that the high demand for P by N-fixing organisms links the global cycles of N and P, with P being the ultimate limit on nitrogen availability and net primary production. Indeed, in many soils the accumulation of organic carbon is correlated to available P (Chapter 6). Despite these theoretical arguments for a phosphorus limitation of the biosphere through geologic time, net primary production in most terrestrial and marine ecosystems usually shows an immediate response to additions of N (Fig. 12.7). Denitrification appears to maintain small supplies of N in most ecosystems.

Summary

For both N and P, a small biogeochemical cycle with relatively rapid turnover is coupled to a large global pool with relatively slow turnover. For P, the large pool is found in unweathered rock and soil. For N, the major pool is found in the atmosphere.

The biogeochemical cycle of N begins with the fixation of atmospheric nitrogen, which transfers a small amount of inert N_2 to the biosphere. This transfer is balanced by denitrification, which returns N_2 to the atmosphere. The balance of these processes maintains a steady-state concentration of N_2 in the atmosphere with a turnover time of 10^7 years. In the absence of denitrification, most of the N inventory on the Earth would eventually be sequestered in the ocean and in organic sediments. Denitrification closes the global nitrogen cycle, and it causes nitrogen to cycle more rapidly than phosphorus, which has no gaseous phase. The mean residence time of phosphorus in sedimentary rocks is measured in 10^8 yr, and the phosphorus cycle is complete only as a result of tectonic movements of the Earth's crust.

Once within the biosphere, the movements of N and P are more rapid than in their global cycles, showing turnover times ranging from hours (for soluble P in the soil) to hundreds of years (for N in biomass). In response to nutrient limitations, biotic recycling in terrestrial and marine habitats allows much greater rates of net primary production than rates of N-fixation and rock weathering alone would otherwise support (Tables 6.1 and 9.3). The high efficiency of nutrient recycling may explain why, in the face of widespread nitrogen limitation, only about 2.5% of global net primary production is diverted to nitrogen fixation (Gutschick 1981).