CHAPTER

6

The Biosphere
Biogeochemical Cycling on Land

OUTLINE

INTRODUCTION

Living tissue is primarily composed of carbon, hydrogen, and oxygen in the approximate proportion of CH_2O, but more than 25 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 enzymes

and structural proteins found in plants and animals contain about 16% nitrogen (N) by weight. Earlier we saw that the enzyme ribulose bisphosphate carboxylase determines the rate of photosynthesis—carbon uptake—by 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) (Reiners 1986, Sterner and Elser 2002). For instance, the ratio of C to N in leaf tissue ranges from 25 to 50 (i.e., 1–2% N). At the global level, our estimate of net primary production (NPP), 60×10^{15} g C/yr, implies that at least 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 controls the rate of net primary production in many terrestrial ecosystems (Reich et al. 1997, LeBauer and Treseder 2008, Elser et al. 2007, Xia and Wan 2008).

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 stream waters. 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 found that the atmosphere is the dominant source of C, N, and S in terrestrial ecosystems. Except on old, highly weathered soils, rock weathering is the major source for most of the remaining biochemical elements (e.g., Ca, Mg, K, Fe, and 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 on 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).[2] This large internal, or *intrasystem*, *cycle* is achieved by the long-term retention and recycling of elements derived 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 (Vitousek and Reiners 1975).

In this chapter, we analyze the cycles of biochemical elements in terrestrial ecosystems. We begin by examining aspects of plant uptake, allocations during growth, and losses due to the death of plants and plant tissues. Then we see how elements such as N, P, and S in dead organic matter are transformed in the soil, leading to their release for plant uptake or for loss from the ecosystem. The yearly uptake, allocation, return, and release of nutrient elements in an ecosystem constitute the nutrient cycle. Throughout, we stress interactions between

[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).

[2] Volk (1998) defines the recycling ratio as the ratio of the amount cycling in a system to the amount exiting it, which is 6 for N and 4 for P in terrestrial ecosystems (see Chapter 12).

TABLE 6.1 Percentage of the Annual Requirement of Nutrients for Plant Growth in the Northern Hardwoods Forest at Hubbard Brook, New Hampshire, Which Could Be Supplied by Various Sources of Available Nutrients

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

Note: Calculated using Eqs. 6.2 and 6.3.
Source: 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).

carbon and other biochemical elements and examine how land plants have adapted to the widespread limitations of N and P in terrestrial ecosystems. We deduce changes in the sources of nutrients that determine plant growth during ecosystem development.

BIOGEOCHEMICAL CYCLING IN LAND PLANTS

Nutrient Uptake

It is easy to forget the essential, initial role played by plants in all of biochemistry. Plants obtain essential elements from the soil (e.g., N from NO_3^-) and incorporate them into biochemical molecules (e.g., amino acids) (Oaks 1994). Animals may eat plants, and each other, and synthesize new amino acids, but the building blocks of the amino acids in animal protein are those originally synthesized in plants. Only in isolated instances, for example, in animals at natural salt licks, do we find a direct transfer of elements from inorganic form to animal biochemistry—geophagy (Jones and Hanson 1985). There are few vitamin pills in the natural biosphere!

Soil chemical characteristics, including mineralogy and ion exchange, set the initial constraints on the availability of essential elements for plant uptake. However, when plant uptake of an element is rapid, plants can release organic compounds that enhance the solubility of elements, such as P, from soil minerals (Chapter 4). Thus, plants can affect the availability of nutrients needed for their own growth and adapt to a wide range of soil fertility (Forde and Lorenzo 2001). Although foliar uptake is known, the vast majority of plant nutrient uptake passes through roots. A few unusual, insectivorous plants obtain N and P by digesting captured organisms (Adamec 1997, Wakefield et al. 2005). For instance, Dixon et al. (1980) found that 11 to 17% of the annual uptake of N in *Drosera erythrorhiza* (sundew) can be obtained from captured insects.

Delivery of ions to plant roots can occur by several pathways (Barber 1962). The concentration of some elements in the soil solution is such that their passive uptake with water is adequate for plant nutrition (Turner 1982). In some cases, the delivery is excessive, and the ions must be actively excluded at the root surface. For example, it is not unusual to see accumulations of Ca, as $CaCO_3$, surrounding the roots of desert shrubs growing in calcareous soils (Klappa 1980, Wullstein and Pratt 1981). In contrast, for N, P, and K, the concentration in the soil solution is often much too low for adequate delivery in the transpiration stream, and plant uptake is enhanced by enzymes—transporters—that carry ions through channels in the root membrane using active transport (Hirsch et al. 1998, Khademi et al. 2004, Williams and Miller 2001). Indeed, in a process known as signal transduction, NO_3^- appears to activate the enzymes that promote its own uptake (Zhang and Forde 1998, Tischner 2000). These ion transporters account for the large portion of root respiration that is associated with nutrient uptake (Chapter 5).

The transporter systems embedded in root membranes achieve increasing rates of nutrient uptake as a function of increasing concentrations in the soil solution until the activity of the enzyme system is saturated. Chapin and Oechel (1983) found that populations of the arctic sedge, *Carex aquatilis*, from colder habitats have higher rates of uptake than those from warmer habitats, presumably reflecting adaptation to the lower availability of phosphorus in cold soils (Figure 6.1). In comparative studies, root physiologists define the specific absorption rate (SAR) as the rate of uptake of a nutrient from the soil per unit of root mass over a specified period of time.

Normally, the uptake of N and P is so rapid and the concentrations in the soil solution are so low that these elements are effectively absent in the soil solution surrounding roots,

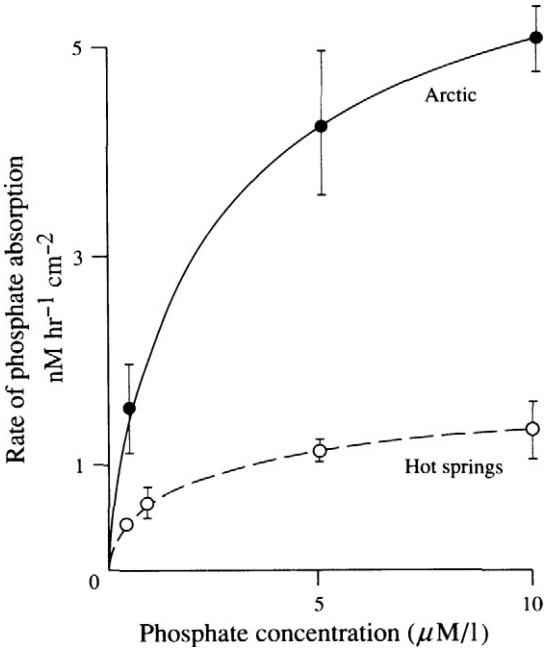

FIGURE 6.1 Rate of phosphate absorption per unit of root surface area in populations of *Carex aquatilis* from cold (arctic) and warm (hot springs) habitats, measured at 5°C. *Source: From Chapin (1974). Used with permission of the Ecological Society of America.*

and the rate of uptake is determined by diffusion to the root from other areas (Nye 1977). Phosphate is particularly immobile in most soils, and the rate of diffusion strongly limits P supply to plant roots (Robinson 1986). Although adaptations for more efficient root enzymes are seen in some species (Pennell et al. 1990), the most apparent response of plants to low nutrient concentrations is an increase in the root/shoot ratio, which increases the volume of soil exploited and decreases diffusion distances (Aerts and Chapin 2000, Clarkson and Hanson 1980, Robinson 1994). In many species, the relative growth rate of roots determines the uptake of nitrogen and phosphorus (Newman and Andrews 1973; Figure 6.2). Enhanced root growth is found in low phosphorus soils (Bates and Lynch 1996, Ma et al. 2001), and roots rapidly proliferate in nutrient-rich patches (Jackson et al. 1990, Black et al. 1994).

Plants and soil microbes exude enzymes into the soil that can release inorganic phosphorus from organic matter. These extracellular enzymes are known as *phosphatases*, which have different forms in acid and alkaline soils (Malcolm 1983, Tarafdar and Claassen 1988, Dinkelaker and Marschner 1992, Duff et al. 1994). In many cases, root phosphatase activity is inversely proportional to available soil P (Fox and Comerford 1992a, Treseder and Vitousek 2001). For example, phosphatase activity rises with the accumulation of organic matter in soils during the development of *Eucalyptus* plantations after fire (Polglase et al. 1992). Phosphatase activity associated with root surfaces is particularly significant to plants in phosphorus-poor habitats, and it may supply up to 75% of the annual phosphorus

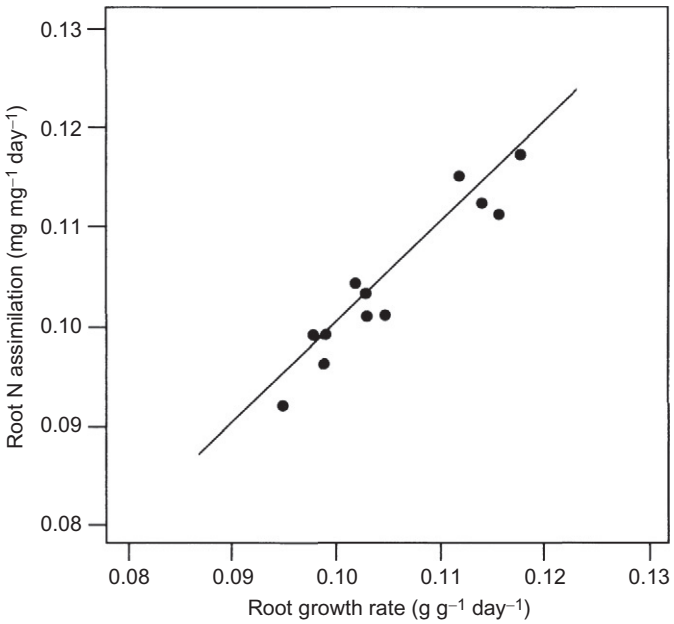

FIGURE 6.2 The rate of N uptake in tobacco as a function of the relative growth rate of roots. *Source: From Raper et al. (1978). Used with permission of the University of Chicago Press.*

demand of some tundra and boreal forest species (Kroehler and Linkins 1991, Firsching and Claassen, 1996).

Nutrient Balance

In addition to an adequate supply of nutrient elements, plant growth is affected by the balance of nutrients in the soil (Shear et al. 1946). For seedlings of several tree species, Ingestad (1979b) found that a solution containing 100 parts N, 15 parts P, 50 parts K, 5 parts Ca and Mg, and 10 parts S was ideal for maximum growth. In a compilation of data from nearly 10,000 species, leaf N and P contents were related by a 2/3-power-law function, with a mean N/P ratio of 10.9 (by mass; Reich et al. 2010; compare Kerkhoff et al. 2005). Despite wide variations in nutrient availability in the environment, most plants show an N:P ratio of about 14 to 15 (by mass) in leaf tissues (Gusewell 2004, McGroddy et al. 2004, Han 2005, Koerselman and Meuleman 1996), with N deficiency at lower and P deficiency at higher values. However, unless the supply of a nutrient reaches very low levels, plants usually do not show deficiency symptoms; they simply grow more slowly (Clarkson and Hanson 1980). Inherent slow growth is a characteristic of plants adapted to infertile habitats, and it often persists even when nutrients are added experimentally (Chapin et al. 1986a).

Because more nutrients occur as positively charged ions than as negatively charged ions in the soil solution, one might expect that plant roots would develop a charge imbalance as a result of nutrient uptake. When ions such as K^+ are removed from the soil solution in excess of the uptake of negatively charged ions, the plant releases H^+ to maintain an internal balance of charge (Maathuis and Sanders 1994). This H^+ may, in turn, replace K^+ on a cation exchange site, driving another K^+ into the soil solution. The high concentration of N in plant tissues causes the form in which N is taken up to dominate this process (Table 6.2). Oaks (1992) has shown how plants that use NH_4^+ as an N source tend to acidify the immediate zone around their roots (Figure 6.3). The uptake of NO_3^- has the opposite effect as a result of plant releases of HCO_3^- and organic anions to balance the negative charge (Nye 1981, Hedley et al. 1982a, Schöttelndreier and Falkengren-Grerup 1999).

TABLE 6.2 Chemical Composition and Ionic Balance for Perennial Ryegrass

	N	P	S	Cl	K	Na	Mg	Ca
Percent in leaf tissue	4.00	0.40	0.30	0.20	2.50	0.20	0.25	1.00
Equivalent weight (g)	14.00	30.98	16.03	35.46	39.10	22.99	12.16	20.04
mEq present	285.7	12.9	18.7	5.6	63.9	8.8	20.6	49.9
Sum of mEq	±285.7		−37.2			+143.1		

Imbalance in mEq %

(a) where ammonium nitrogen is taken up: 285.7 + 143.1 − 37.2 = +391.6

(b) where nitrate nitrogen is taken up: 143.1 − 285.7 − 37.2 = −179.8

Source: From Middleton and Smith (1979). Used with permission of Springer.

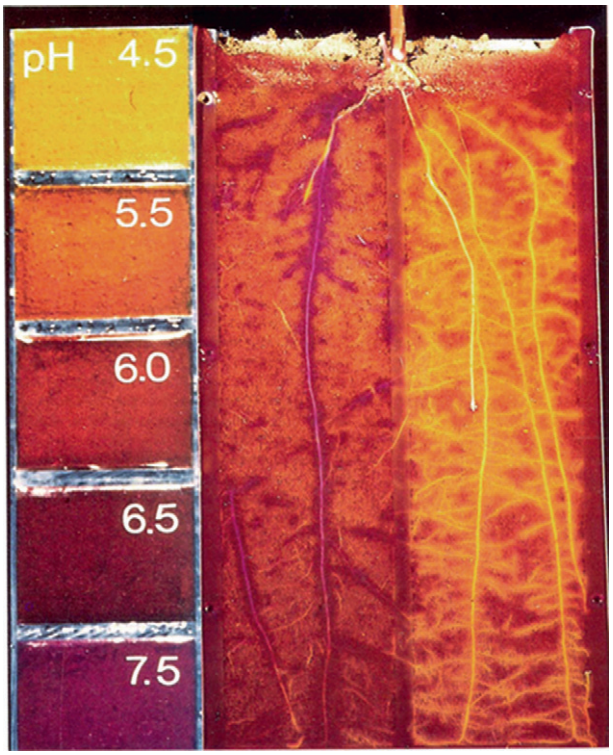

FIGURE 6.3 The pH of the soil in plants fertilized with nitrate (left) and ammonium (right), shown with a dye that changes color as a function of acidity. *Source: From Oaks (1994). Used with permission of NRC Research Press.*

Nitrogen Assimilation

Among various habitats, the availability of soil nitrogen as NH_4^+ or NO_3^- differs largely depending on the environmental conditions that affect the conversion of NH_4^+ to NO_3^- in the microbial process known as nitrification (Eqs. 2.17 and 2.18). For example, in waterlogged soils, almost all nitrogen is found as NH_4^+ (Barsdate and Alexander 1975), whereas in some deserts and forests, nearly all mineralized NH_4 is converted to NO_3^- (Virginia and Jarrell 1983, Nadelhoffer et al. 1984). Many species show a preference for NO_3^-, although species occurring in sites where nitrification is slow or inhibited often tend to show superior growth with ammonium (Haynes and Goh 1978, Adams and Attiwill 1982, Falkengren-Grerup 1995, Kronzucker et al. 1997, Wang and Macko 2011).

Derived from the breakdown of proteins, amino acids are found in many soils (Yu et al. 2002, Hofmockel et al. 2010) and used as a source of N by plants in a wide range of habitats, including tundra (Kielland 1994, Schimel and Chapin 1996, Nordin et al. 2004), boreal and temperate forest (Nasholm et al. 1998, Finzi and Berthrong 2005), and desert ecosystems (Jin and Evans 2010). Direct uptake of amino acids has been demonstrated using isotopically labeled amino acids (Nasholm et al. 1998) and nanoscale labels known as "quantum dots," which are attached to amino acids (Whiteside et al. 2009). Generally, the uptake of amino acids is greatest when the availability of inorganic N is low (Finzi and Berthrong 2005). In a British grassland, most species showed preferential uptake of inorganic N over amino acids (Harrison et al. 2007).

Once inside the plant, NO_3^- and NH_4^+ are converted to amino groups ($-NH_2$) that are attached to soluble organic compounds. In many woody species these conversions occur in the roots, and N is transported to the shoot as amides, amino acids, and ureide compounds in the xylem stream (Andrews 1986, Tischner 2000). However, in some species, N in the xylem is found as NO_3^-, and the reduction of NO_3^- to $-NH_2$ occurs in leaf tissues (Smirnoff et al. 1984). Eventually, most plant N is incorporated into protein, and the amino acid arginine is used for storage of excess N (Llácer et al. 2008).

The conversion of NO_3^- to $-NH_2$ is a biochemical reduction reaction that requires metabolic energy and is catalyzed by an enzyme, *nitrate reductase*. One might puzzle why most plants do not show a clear preference for NH_4^+, which is assimilated more easily. Several explanations have been offered. Recall that NH_4^+ interacts with soil cation exchange sites, whereas NO_3^- is extremely mobile in most soils. The rate of delivery of NO_3^- to the root by diffusion or mass flow is much higher than that of NH_4^+ under otherwise equivalent conditions (Raven et al. 1992). Plants that utilize NH_4^+ may have to compensate for the differences in diffusion by investing more energy in root growth (Gijsman 1990, Oaks 1992, Bloom et al. 1993).

Uptake of NO_3^- also avoids the competition that occurs in root enzyme carriers between NH_4^+ and other positively charged nutrient ions. For example, the presence of large amounts of K^+ in the soil solution can reduce the uptake of NH_4^+ (Haynes and Goh 1978). Finally, relatively low concentrations of NH_4^+ are potentially toxic to plant tissues. These potential disadvantages in the uptake of NH_4^+ may explain why many plants take up NO_3^- when thermodynamic calculations suggest that the metabolic costs of reducing NO_3^- are greater than for plants that assimilate NH_4^+ or amino acids directly (Middleton and Smith 1979, Gutschick 1981, Bloom et al. 1992, Zerihun et al. 1998).

It is unclear why so many woody species concentrate nitrate reductase in their roots, when the same reaction performed in leaf tissues, where it can be coupled to the photosynthetic reaction, is energetically much less costly (Gutschick 1981, Andrews 1986). Addition of NO_3^- to the soil often induces the production of root enzymes for NO_3^- uptake and the synthesis of more nitrate reductase in plant tissues (Lee and Stewart 1978, Hoff et al. 1992, Oaks 1994, Tischner 2000). There is some evidence that the proportion of nitrate reductase in the shoot increases at high levels of available NO_3^- (Andrews 1986). Both photosynthetic rates and nitrate uptake increase when plants are grown at high CO_2, but the response is not universal (Bassirirad 2000).

Nitrogen Fixation

Several types of bacteria possess the enzyme *nitrogenase*, which converts atmospheric N_2 to NH_3 in local conditions of cellular anoxia (see Eq. 2.10). Some of these exist as free-living (asymbiotic) forms in soils, but others, such as *Rhizobium* and *Frankia*, form symbiotic associations with the roots of higher plants. The symbiotic bacteria reside in root nodules that are easily recognized in the field. Nitrogen fixation is especially well known among species of legumes (Leguminosae) (Bryan et al. 1996).

Nitrogen that enters terrestrial ecosystems by fixation is a "new" input in the sense that it is derived from outside the boundaries of the ecosystem—that is, from the atmosphere. The reduction of N_2 to NH_3 has large metabolic costs that require the respiration of organic carbon.

Nevertheless, Gutschick (1981) suggests that symbiotic fixation in higher plants is not greatly less efficient than the uptake of NO_3^- for those species in which the nitrate reductase is located in plant roots. Only a few land plants support symbiotic nitrogen fixation, and it is interesting to speculate why nitrogen fixation is not more widespread, when nitrogen limitations of net primary production are so frequent (Vitousek and Howarth 1991, Crews 1999). Globally, plants "spend" only about 2.5% of NPP on nitrogen fixation (Gutschick 1981).

The energy cost of nitrogen fixation links this biogeochemical process to the availability of organic carbon, provided by net primary production. In plants with symbiotic nitrogen fixation, the rate of N fixation is often directly related to the rate of photosynthesis and the efficiency of plant growth (Bormann and Gordon 1984). N fixation is stimulated in seedlings of various species grown at high CO_2 (Tissue et al. 1997, Millett et al. 2012), but it is unclear if this initial effect is persistent in long-term field experiments (Hungate et al. 2004). Free-living heterotrophic bacteria that conduct asymbiotic nitrogen fixation are usually found in organic soils or local areas with high levels of organic matter that provide a ready source of energy (Granhall 1981, Billings et al. 2003). Organic-rich environments also foster the development of cellular anaerobiosis required by the nitrogenase enzyme (Marchal and Vanderleyden 2000). For instance, nitrogen fixation is frequently observed in rotten logs (Roskoski 1980, Silvester et al. 1982, Griffiths et al. 1993), where it is probably associated with anaerobic cellulolytic bacteria (Leschine et al. 1988). N-fixing symbioses are found in a wide variety of local microenvironments where other organisms provide abundant organic matter, such as the root zone of desert grasses (Herman et al. 1993), the hind-gut of termites (Breznak et al. 1973, Yamada et al. 2006, Hongoh et al. 2008), the interior of pineapples (Tapia-Hernandez 2000), feathermoss carpets in the boreal forest (DeLuca et al. 2002), and the fungus gardens of leaf-cutter ants in tropical rainforests (Pinto-Tomas 2009). Studies of nitrogen fixation in these habitats are often aided by the identification of the genes coding for nitrogenase (nifH) using molecular techniques (Widmer et al. 1999, Reed et al. 2010).

In both symbiotic and asymbiotic forms, nitrogen fixation is generally inhibited at high levels of available nitrogen (Cejudo et al. 1984). In many cases, the rate of fixation appears to be controlled by the N:P ratio in the soil (Chapin et al. 1991, Smith 1992a), and added phosphorus stimulates asymbiotic N fixation (Figure 6.4). In bacteria, phosphorus appears to activate the gene for the synthesis of nitrogenase (Stock et al. 1990), illustrating how the linkage between the global cycles of nitrogen and phosphorus has a basis in molecular biology. Requirements for Mo and Fe as structural components of nitrogenase also link nitrogen fixation to the availability of these elements in natural ecosystems (Kim and Rees 1994, O'Hara et al. 1988). Low availability of Mo may limit asymbiotic N fixation in many forests (Silvester 1989, Barron et al. 2009). Some plants with symbiotic N-fixing bacteria appear to acidify their rooting zone to make Fe and P more available (Ae et al. 1990, Raven et al. 1990, Gillespie and Pope 1990), and legumes appear to have several mechanisms to aid the uptake and retention of P in phosphorus-poor soils (He et al. 2011, Venterink 2011).

The isotopic ratio of N in plant tissues is expressed as $\delta^{15}N$, using a calculation analogous to what we saw for the isotopes of carbon in Chapter 5 (Robinson 2001). In the case of nitrogen, the standard is the atmosphere, which contains 99.63% ^{14}N and 0.37% ^{15}N. Nitrogenase shows only a slight discrimination between the isotopes of N, that is, between $^{15}N_2$ and $^{14}N_2$ (Handley and Raven 1992, Hogberg 1997), so differences in the isotopic ratio of nitrogen among plant species growing in the same soil can be used to suggest which species may be

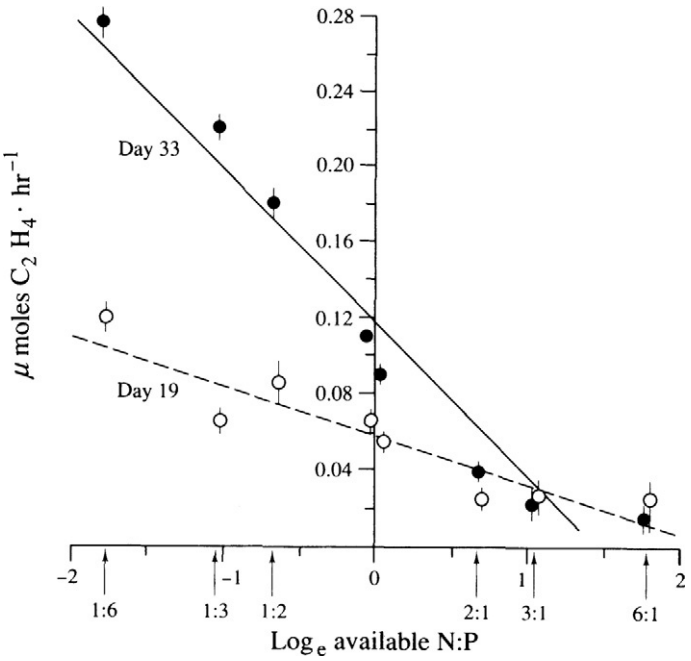

FIGURE 6.4 Acetylene reduction as an index of nitrogen fixation in asymbiotic N-fixing bacteria as a function of the ratio of N to P in the soil. *Source: From Eisele et al. (1989). Used with permission of Springer.*

involved in nitrogen fixation (Virginia and Delwiche 1982, Yoneyama et al. 1993). Nitrogen-fixing species typically show values of $\delta^{15}N$ that are slightly negative or close to the atmospheric ratio ($\delta^{15}N = 0$), whereas nonfixing species show a wide range of values (usually positive) depending on various N transformations in the soil (Garten and Van Miegroet 1994, Hogberg 1997; Figure 6.5) (see also pp. 202–203).

Shearer et al. (1983) used the difference in isotopic ratio between *Prosopis* grown in the laboratory without added N (i.e., all nitrogen was derived from fixation) and the same species in the field to estimate that the field plants derived 43 to 61% of their nitrogen from fixation. Of course, when nitrogen-fixing plants die, their nitrogen content is available for other species in the ecosystem (Huss-Danell 1986, van Kessel et al. 1994). Lajtha and Schlesinger (1986) found that the desert shrub *Larrea tridentata*, growing adjacent to nitrogen-fixing *Prosopis,* had lower $\delta^{15}N$ than when *Larrea* was growing alone.

Nitrogenase activity can be measured using the acetylene-reduction technique, which is based on the observation that this enzyme also converts acetylene to ethylene under experimental conditions. Plants or nodules are placed in small chambers or small chambers are placed over field plots, and the conversion of injected acetylene to ethylene over a known time period is measured using gas chromatography. The conversion of acetylene (in moles) is not exactly equivalent to the potential rate of fixation of N_2 because the enzyme has different affinities for these substrates. However, appropriate conversion ratios can be determined using other techniques (Schwintzer and Tjepkema 1994, Liengen 1999). For instance, investigators have added $^{15}N_2$, the heavy stable isotope of N, to closed chambers and used the increase in organic compounds containing ^{15}N in test plants or soil as a measure of nitrogen fixation (e.g., Silvester et al. 1982, Zechmeister-Boltenstern and Kinzel 1990).

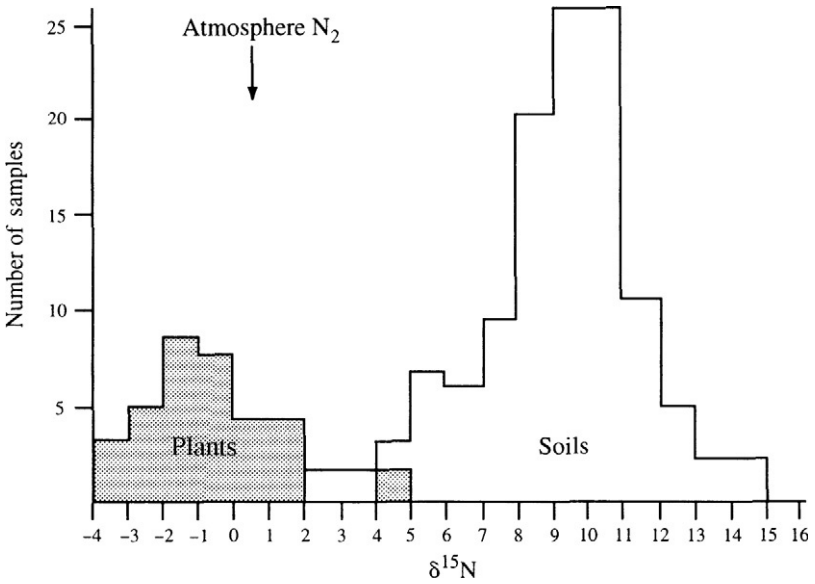

FIGURE 6.5 Frequency distribution of $\delta^{15}N$ in the tissues of 34 nitrogen-fixing plants and in the organic matter of 124 soils from throughout the United States. *Source: Plotted using data from Shearer and Kohl (1988, 1989).*

Heterotrophic N-fixing bacteria and cyanobacteria (blue-green algae) are widespread, and their nitrogen fixation can be an important source of N for some terrestrial ecosystems (Reed et al. 2011). Exceptionally high rates of fixation have been recorded in cyanobacterial crusts that cover the soil surface in some desert ecosystems (Rychert et al. 1978), but in most cases, the total input from these sources of asymbiotic N fixation is in the range of 1 to 5 kg N ha^{-1} yr^{-1} (Boring et al. 1988, Cushon and Feller 1989, Son 2001, Cleveland et al. 2010). This input is usually less than the annual deposition of nitrogen in wetfall and dryfall from the atmosphere (Schwintzer and Tjepkema 1994).

The importance of symbiotic nitrogen fixation in terrestrial ecosystems varies widely depending on the presence of species that harbor symbiotic bacteria (Reed et al. 2011). Grazed pastures with clover routinely show N fixation at rates of 100 to 200 kg N ha^{-1} yr^{-1} (Bolan et al. 2004). In natural ecosystems, some of the greatest rates of N fixation are seen in species that invade after disturbance, where high light levels allow maximum photosynthesis (Vitousek and Howarth 1991). For example, in the recovery of Douglas fir forests after fire, Youngberg and Wollum (1976) found that the nodulated shrub *Ceanothus velutinus* contributed up to 100 kg N ha^{-1} yr^{-1} on some sites. Invasion of the exotic, nitrogen-fixing tree *Myrica fay*, provides important inputs of nitrogen (18 kg ha^{-1} yr^{-1}) on fresh volcanic ashflows in Hawaii (Vitousek et al. 1987). In most cases the importance of plants with symbiotic nitrogen fixation declines with the recovery of mature vegetation, and their occurrence in undisturbed communities is limited. In this regard, the widespread occurrence of leguminous species in tropical forests is deserving of further study (Kreibich et al. 2006, Vitousek et al. 2002). The sporadic occurrence of symbiotic nitrogen fixation in terrestrial ecosystems makes it difficult to extrapolate from local studies to provide a global estimate of its importance.

The global rate of N fixation (asymbiotic + symbiotic) in natural ecosystems may supply 60 to 100 $\times$ 10^{12} g N/yr, or about 10% of the annual plant demand for nitrogen on land (Chapter 12).

Mycorrhizal Fungi

Symbiotic associations between fungi and higher plants are found in most ecosystems (Allen 1992). This symbiosis is important for the nutrition of plants and may have even determined the origin of land plants (Simon et al. 1993, Courty et al. 2010). There are several forms of symbiosis. In temperate regions, many trees harbor ectotrophic mycorrhizal fungi. These fungi form a sheath around the active fine roots and extend additional hyphae into the surrounding soil. In many areas, especially the tropics, plants possess endotrophic mycorrhizal fungi in which the hyphae actually penetrate cells of the root.

By virtue of their large surface area and efficient absorption capacity, mycorrhizal fungi are able to obtain soil nutrients and transfer these to the higher plant root. Recent work has elucidated the genetic development of the symbiosis and the molecular structure of a transporter protein in mycorrhizae that moves phosphorus into the roots (Harrison and van Buuren 1995, Bucher 2007). Mycorrhizal fungi are directly involved in the decomposition of soil organic materials through the release of extracellular enzymes such as cellulases and phosphatases (Antibus et al. 1981, Dodd et al. 1987, Hodge et al. 2001) and in the weathering of soil minerals through the release of organic acids (Bolan et al. 1984, Illmer et al. 1995, Van Breemen et al. 2000, van Scholl et al. 2008, Blum et al. 2002; see also Chapter 4). It is important to remember that most of these reactions are also associated with plant roots; mycorrhizae simply enhance their occurrence in the rhizosphere, increasing the overall rate of plant nutrient uptake (Bolan 1991). In return, mycorrhizal fungi depend on the host plant for supplies of carbohydrate.

The importance of mycorrhizae in infertile sites is well known. Treseder and Vitousek (2001) show greater mycorrhizal colonization, greater extracellular phosphatase, and greater phosphorus uptake by plants on P-deficient soils in Hawaii. Many species of pine require ectotrophic mycorrhizae, which perhaps accounts for the success of pines in nutrient-poor soils. Most tropical trees appear to require endotrophic mycorrhizal associations for proper growth (Janos 1980), and mycorrhizal fungi are widespread among the *Eucalyptus* species growing in the low-phosphorus soils of Australia. Berliner et al. (1986) report the complete exclusion of *Cistus incanus* from basaltic soils in Israel due to a failure of mycorrhizal development. The same species grows well on adjacent calcareous soils or on basaltic soils supplied with fertilizer.

Mycorrhizal fungi are especially important in the transfer of those soil nutrients with low diffusion rates in the soil. A large number of studies document the importance of mycorrhizae in P nutrition (Koide 1991), but absorption of N and other nutrients is also known (Bowen and Smith 1981, Ames et al. 1983, Govindarajulu et al. 2005). In forests, mycorrhizae mediate the uptake of amino acids by trees. Mycorrhizae appear responsible for 61 to 86% of N uptake in Arctic tundra (Hobbie and Hobbie 2006).

Some plants with mycorrhizal fungi show higher levels of various nutrients in foliage, but frequently the enhanced uptake of nutrients results in higher rates of growth (Schultz

et al. 1979). Rose and Youngberg (1981) provide an insightful experiment with *Ceanothus velutinus* growing in nitrogen-deficient soils with and without mycorrhizae and symbiotic nitrogen-fixing bacteria (Table 6.3). The highest rates of growth were seen when both of these symbiotic associations were present, which also allowed a decrease in the root/shoot ratio. Nitrogen fixation enhanced the uptake of phosphorus by mycorrhizal fungi. These results illustrate the strong interactions between N, P, and C in the nutrition of higher plants.

Under conditions of nutrient deficiency, plant growth usually slows, whereas photosynthesis continues at relatively high rates (Chapin 1980) and the content of soluble carbohydrate in the plant increases. Marx et al. (1977) found that high concentrations of carbohydrate in root tissues of loblolly pine (*Pinus taeda*) stimulated mycorrhizal infection (Figure 6.6). Plants grown at high CO_2 also appear to allocate additional carbohydrate to fine roots to support mycorrhizal development (DeLucia et al. 1997, Pritchard et al. 2008a, Phillips et al. 2011a). Thus, internal plant allocation of carbohydrates to roots may result in increased nutrient uptake by mycorrhizae and an alleviation of nutrient deficiencies (Bucking and Shachar-Hill 2005, Ryan et al. 2012).

Mycorrhizal fungi use a fraction of the carbon fixed by the host plant, representing a drain on net primary production that might otherwise be allocated to growth (Rygiewicz and Andersen 1994). That the cost of symbiotic fungi is significant is underscored by experiments in which the degree of colonization declined and plant growth increased when plants were fertilized (e.g., Blaise and Garbaye 1983). Across a wide variety of species, the carbon allocation to mycorrhizae appears to lower net primary productivity by about 15% (Hobbie 2006; see also Table 5.1).

TABLE 6.3 Effects of Mycorrhizae and N-Fixing Nodules on Growth and Nitrogen Fixation in *Ceanothus velutinus* Seedlings

	Control	**+ Mycorrhizae**	**+ Nodules**	**+ Mycorrhizae and nodules**
Mean shoot dry weight (mg)	72.8	84.4	392.9	1028.8
Mean root dry weight (mg)	166.4	183.4	285.0	904.4
Root/shoot	2.29	2.17	0.73	0.88
Nodules per plant	0	0	3	5
Mean nodule weight (mg)	0	0	10.5	44.6
Acetylene reduction (mg/nodule/hr)	0	0	27.85	40.46
Percent mycorrhizal colonization	0	45	0	80
Nutrient concentration (in shoot, %)				
N	0.32	0.30	1.24	1.31
P	0.08	0.07	0.25	0.25
Ca			1.07	1.15

Source: From Rose and Youngberg (1981). Used with permission of NRC Research Press.

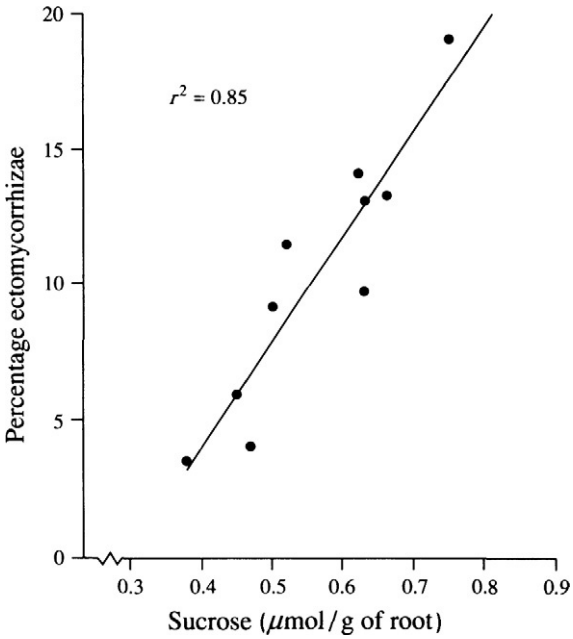

FIGURE 6.6 Relationship between infection of the roots of loblolly pine (*Pinus taeda*) by ectomycorrhizal fungi and the sucrose concentration in the root. *Source: From Marx et al. (1977).*

NUTRIENT ALLOCATIONS AND CYCLING IN LAND VEGETATION

The Annual Intrasystem Cycle

The plant uptake of nutrients from the soil is allocated to the growth of new tissues. Although short-lived tissues (leaves and fine roots) compose a small fraction of total plant biomass, they receive the largest proportion of the annual nutrient uptake (Pregitzer et al. 2010). Growth of leaves and roots received 87% of the N and 79% of the P allocated to new tissues in a deciduous forest in England (Cole and Rapp 1981, p. 404). In a perennial grassland dominated by *Bouteloua gracilis* in Colorado, new growth of aboveground tissues accounted for 67% of the annual uptake of N (Woodmansee et al. 1978).

When leaf buds break and new foliage begins to grow, the leaf tissues often have high concentrations of N, P, and K. As the foliage matures, these concentrations often decrease (van den Driessche 1974). Some of these changes are due to the increasing accumulation of photosynthetic products with time and to leaf thickening during development. Leaf mass per unit area (mg/cm^2) may increase as much as 50% during the growing season and then decline as the leaf senesces (Smith et al. 1981). The initial concentrations of N and P are diluted as the leaf tissues accumulate carbohydrates and cellulose. In contrast, the concentrations of some nutrients (e.g., Ca, Mg, and Fe) often increase with leaf age (van den Driessche 1974). Increases in calcium concentration with leaf age result from secondary thickening, including calcium pectate deposition in cell walls, and from increasing storage of calcium oxalate in cell vacuoles.

Although there are variations among species, nutrient concentrations in mature foliage are related to the rate of photosynthesis (Chapter 5) and plant growth (e.g., Tilton 1978), and analysis of foliage is often a good index of site fertility (van den Driessche 1974, Ordonez et al. 2009). Leaf concentrations of trace metals often reflect the content of the underlying soil, such that leaf tissues are useful for mineral prospecting in some areas (Cannon 1960, Brooks 1973). Among tropical forests, concentrations of major nutrients in leaves are significantly higher on more fertile soils (Vitousek and Sanford 1986). Yin (1993) found that concentration of N and P in the foliage of deciduous trees varied systematically with higher values among species in colder habitats than in the tropics. The higher leaf nutrient contents in colder climates may allow for higher photosynthetic rates and rapid growth of these species in response to a short growing season (Mooney and Billings 1961, Körner 1989, Reich and Oleksyn 2004).

After fertilization with a specific nutrient, the concentrations of other leaf nutrients can show surprising changes. For example, leaf N increased when Miller et al. (1976) fertilized Corsican pine (*Pinus nigra*) with N, but in the same samples, concentrations of P, Ca, and Mg declined. When nitrogen fertilization of N-deficient stands stimulates photosynthesis, the concentrations of other nutrients in foliage may be diluted by new accumulations of carbohydrate (Fowells and Krauss 1959, Timmer and Stone 1978, Jarrell and Beverly 1981). In some cases, uptake of P from the soil may fall behind the rates needed for maximum growth at the newly established levels of N availability. In other cases, improvements in plant nitrogen status enhance the uptake of other elements as well (e.g., Table 6.3). Plant response to multiple element fertilizations are illustrative of the importance of considering balanced nutrition for maximum plant growth.

Once leaves are fully expanded, changes in the nutrient content per unit of leaf area indicate movements of nutrients between the foliage and the stem. Woodwell (1974) found that oak leaves rapidly accumulated N during the early summer, presumably as a component of photosynthetic enzymes. The leaf content of N, P, and K remained relatively constant at high levels throughout the growing season, but concentrations of all three elements declined rapidly in autumn prior to leaf abscission. Such losses often represent active withdrawal of nutrients from foliage for reuse during the next year. Some trace micronutrients are also withdrawn before leaf-fall (Killingbeck 1985), but usually reabsorption of foliar Ca and Mg is limited. Fife and Nambiar (1984) observed that reabsorption of N, P, and K was not just related to leaf senescence in *Pinus radiata*; these nutrients could also move from tissues produced early and later during the same growing season.

Leaf nutrient contents are also affected by rainfall that leaches nutrients from the leaf surface (Tukey 1970, Parker 1983). In particular, seasonal changes in the content of K, which is highly soluble and especially concentrated in cells near the leaf surface, may represent leaching. The losses of nutrients in leaching often follow the order

$$K >> P > N > Ca. \tag{6.1}$$

Leaching rates generally increase as foliage senesces before abscission; thus, care must be taken to recognize changes due to leaching versus changes due to active nutrient withdrawals (Ostman and Weaver 1982).

Nutrient losses by leaching differ among leaf types. Luxmoore et al. (1981) calculated lower rates of leaching loss from pines than from broad-leaf deciduous species in a forest in

Tennessee. Such differences may be the result of variation in leaf nutrient concentration, surface-area-to-volume ratio, surface texture, and leaf age. Among the trees of the humid tropics, the smooth surface of broad sclerophylls may be an adaptive response to reducing leaching by minimizing the length of time that rainwater is in contact with the leaf surface (Dean and Smith 1978). Species-specific differences in rates of leaching from potential host trees may explain differences in their epiphyte loads (Benzing and Renfrow 1974, Awasthi et al. 1995), with many epiphytes showing P deficiency (Wanek and Zotz 2011).

Rainwater that passes through a vegetation canopy is called *throughfall*, which is usually collected in funnels or troughs placed on the ground. Throughfall contains nutrients leached from leaf surfaces and is most important in the cycling of nutrients such as K (Parker 1983, Schaefer and Reiners 1989). In forests, rainwater that travels down the surface of stems is called *stemflow* (Levia and Frost 2003). The concentrations of nutrients in stemflow waters are high, but usually much more water reaches the ground as throughfall. Stemflow is significant to the extent that it returns highly concentrated nutrient solutions to the soil at the base of plants (Gersper and Holowaychuk 1971).

Leaching varies seasonally depending on forest type and climate. Not surprisingly, in temperate deciduous forests, the greatest losses are during the summer months (Lindberg et al. 1986). Some of the nutrient content in throughfall is derived from aerosols that are deposited on leaf surfaces (Chapter 3). Indeed, Lindberg and Garten (1988) found that about 85% of the apparent loss of sulfate from a forest canopy was due to dry deposition on leaf surfaces, and some studies have used the SO_4^{2-} content of throughfall to estimate dry deposition in the canopy (Garten et al. 1988, Ivens et al. 1990, Neary and Gizyn 1994).

For most elements, however, leaching of nutrients from vegetation makes it difficult to use nutrient concentrations in the rainfall collected under a canopy to calculate dry deposition on leaf surfaces (Chapter 3). In some cases, leaves appear to take up nutrients from rainfall, particularly soluble forms of N (Carlisle et al. 1966, Miller et al. 1976, Garten and Hanson 1990, Lovett and Lindberg 1993). Various reactive nitrogen gases (e.g., NH_3, NO_x, and peroxyacetyl nitrate) are also absorbed at the leaf surface (Gessler et al. 2000, Sparks et al. 2003).

Litterfall

When the biomass of vegetation is not changing, the annual production of new tissues is balanced by the senescence and loss of plant parts (Chapter 5). In the intrasystem cycle, plant litterfall is the dominant pathway for nutrient return to the soil, especially for N and P (Figure 6.7). Below ground, root death also makes a major contribution of nutrients to the soil each year (Cox et al. 1978, Vogt et al. 1983, Burke and Raynal 1994).

The nutrient concentrations in litterfall differ from the nutrient concentrations in mature foliage by the reabsorption of constituents during leaf senescence (Killingbeck 1996). In the tundra shrub *Eriophorum vaginatum*, Chapin et al. (1986b) found that all organic N and P compounds decreased to a similar extent during leaf senescence, suggesting that reabsorption is not simply limited to certain biochemical compounds that are particularly susceptible to hydrolysis. Nutrient reabsorption is also known during the senescence of fine roots (Freschet et al. 2010) and during the aging of sapwood to heartwood in trees (Laclau et al. 2001).

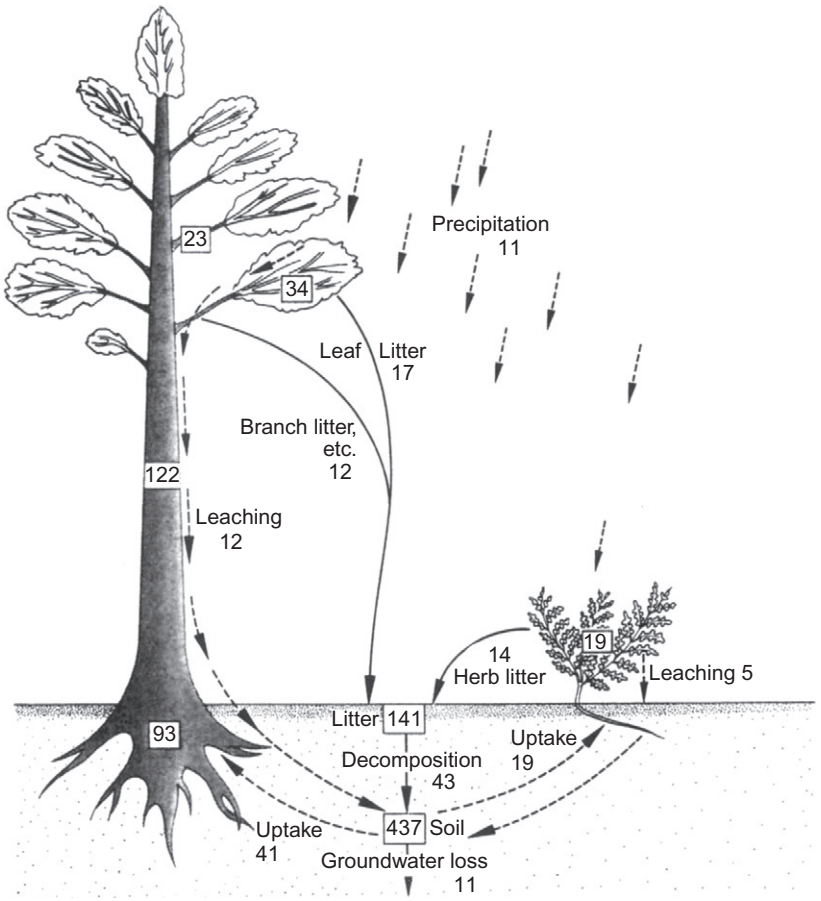

FIGURE 6.7 The intrasystem cycle of Ca in a forest ecosystem in Great Britain. Pools are shown in kg/ha and annual flux in kg ha^{-1} yr^{-1}. *Source: From Whittaker, R.H., Communities and Ecosystems (1970, p. 110). Reprinted by permission of Prentice Hall, Upper Saddle River, New Jersey.*

Nutrient reabsorption potentially confers a second type of nutrient-use efficiency on vegetation (see Chapter 5 for a discussion of nutrient-use efficiency in photosynthesis). Nutrients that are reabsorbed can be used in net primary production in future years, increasing the carbon fixed per unit of nutrient uptake (Salifu and Timmer 2003).

Compiling data from a wide range of species, Aerts (1996) found a mean fractional reabsorption of 50% N and 52% P during leaf senescence. A recent report by Vergutz et al. (2012) suggests that N and P resorption from leaves frequently may exceed 60%. Somewhat lower values are seen in a California shrubland (Table 6.4), in the Hubbard Brook forest (Table 6.1), and in grassland ecosystems (Woodmansee et al. 1978). Lajtha (1987) found exceptionally high values for P reabsorption (72–86%) in the desert shrub *Larrea tridentata* growing in calcareous soils in which P availability is limited due to the precipitation of calcium phosphate

TABLE 6.4 Nutrient Cycling in a 22-Year-Old Stand of the Chaparral Shrub (*Ceanothus megacarpus*) near Santa Barbara, California

	Biomass	N	P	K	Ca	Mg
Atmospheric input ($g\ m^{-2}\ yr^{-1}$)						
Deposition		0.15		0.06	0.19	0.10
N-fixation		0.11				
Total input		0.26		0.06	0.19	0.10
Compartment pools (g/m^2)						
Foliage	553	8.20	0.38	2.07	4.50	0.98
Live wood	5929	32.60	2.43	13.93	28.99	3.20
Reproductive tissues	81	0.92	0.08	0.47	0.32	0.06
Total live	6563	41.72	2.89	16.47	33.81	4.24
Dead wood	1142	6.28	0.46	2.68	5.58	0.61
Surface litter	2027	20.5	0.6	4.7	26.1	6.7
Annual flux ($g\ m^{-2}\ yr^{-1}$)						
Requirement for production						
Foliage	553	9.35	0.48	2.81	4.89	1.04
New twigs	120	1.18	0.06	0.62	0.71	0.11
Wood increment	302	1.66	0.12	0.71	1.47	0.16
Reproductive tissues	81	0.92	0.08	0.47	0.32	0.07
Total in production	1056	13.11	0.74	4.61	7.39	1.38
Reabsorption before abscission		4.15	0.29	0	0	0
Return to soil						
Litterfall	727	6.65	0.32	2.10	8.01	1.41
Branch mortality	74	0.22	0.01	0.15	0.44	0.02
Throughfall		0.19	0	0.94	0.31	0.09
Stemflow		0.24	0	0.87	0.78	0.25
Total return	801	7.30	0.33	4.06	9.54	1.77
Uptake (= increment + return)		8.96	0.45	4.77	11.01	1.93
Stream-water loss ($g\ m^{-2}\ yr^{-1}$)		0.03	0.01	0.06	0.09	0.06
Comparisons of turnover and flux						
Foliage requirement/total requirement (%)		71.3	64.9	61.0	66.2	75.4
Litter fall/total return (%)		91.1	97.0	51.7	84.0	79.7
Uptake/total live pool (%)		21.4	15.6	29.0	32.6	45.5
Return/uptake (%)		81.4	73.3	85.1	86.6	91.7
Reabsorption/requirement (%)		31.7	39.0	0	0	0
Surface litter/litter fall (yr)	2.8	3.1	1.9	1.2	3.3	4.8

Source: Modified from Gray (1983) and Schlesinger et al. (1982b).

minerals (see Figure 4.10). DeLucia and Schlesinger (1995) report 94% reabsorption of leaf P in *Cyrilla racemiflora* in a P-limited bog in the southeastern United States.

Plants grown with low nutrient availability or occurring on infertile sites tend to have low nutrient concentrations in mature leaves and litter; they generally reabsorb a smaller *amount* but a larger *proportion* of the nutrient pool in senescent leaves, compared to individuals of the same species under conditions of greater nutrient availability (Chapin 1988, Boerner 1984,

Pugnaire and Chapin 1993, Killingbeck 1996, Kobe et al. 2005). In most cases, however, species appear to have only a limited ability to adjust the efficiency of reabsorption of leaf nutrients as a function of site fertility (Chapin and Kedrowski 1983, Birk and Vitousek 1986, Chapin and Moilanen 1991, Enoki and Kawaguchi 1999).

Differences in nutrient-use efficiency in reabsorption between nutrient-rich and nutrient-poor sites are not as likely to be due to a direct response of plants as to the tendency for species with higher inherent capabilities for nutrient reabsorption to dominate nutrient-poor sites (Pastor et al. 1984, Chapin et al. 1986b, Schlesinger et al. 1989). Among tropical forests, reabsorption of P varies as an inverse function of site fertility (Kitayama et al. 2000; Figure 6.8). As a result of mycorrhizal associations and internal conservation of P, it appears that tropical trees are well adapted to P-deficient soils, which are widespread in these regions (Cuevas and Medina 1986, Paoli et al. 2005, Cleveland et al. 2011).

Mass Balance of the Intrasystem Cycle

The annual circulation of nutrients in land vegetation, the intrasystem cycle (Figure 6.7), can be modeled using the mass-balance approach. Nutrient requirement is equal to the peak nutrient content in newly produced tissues during the growing season (refer to Table 6.1). Nutrient uptake cannot be measured directly, but uptake must equal the annual storage in

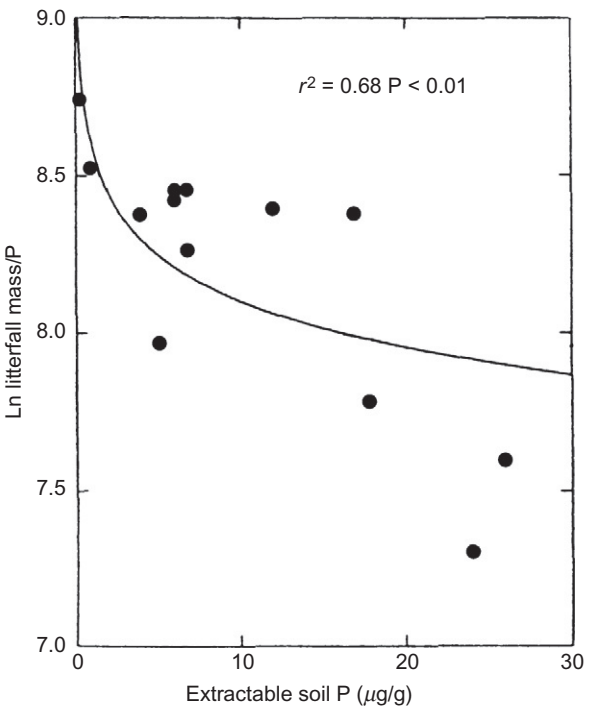

FIGURE 6.8 Litterfall mass/P ratio as a function of soil phosphorus availability measured in 13 humid tropical forests. *Source: From Silver (1994). Used with permission of Springer.*

perennial tissues, such as wood, plus the replacement of losses in litterfall and leaching; thus, the following equation:

$$\text{Uptake} = \text{Retained} + \text{Returned}. \tag{6.2}$$

Uptake is less than the annual requirement by the amount reabsorbed from leaf tissues before abscission; namely:

$$\text{Requirement} = \text{Uptake} + \text{Retranslocation}. \tag{6.3}$$

The requirement is the nutrient flux needed to complete a mass balance; it should not be taken as indicative of biological requirements. In fact, this equation can be solved for nonessential elements such as Na. For a forest in Tennessee, the mass-balance approach was used to show that net accumulations of Ca and Mg in vegetation were directly related to decreases in the content of exchangeable Ca and Mg in the soil during 11 years of growth (Johnson et al. 1988). Similarly, during 100 years of forest growth on abandoned agricultural land, Hooker and Compton (2003) showed that the nitrogen accumulation by vegetation was largely supplied from the soil N pool—not new inputs. Mass-balance studies also show that some dissolved silicon (Si), which is often used as an index of rock weathering, is retained and recycled by terrestrial vegetation (Markewitz and Richter 1998, Conley 2002, Derry et al. 2005, Cornelis et al. 2010).

The mass-balance approach was used to analyze the internal storage and the annual transfers of nutrients in the aboveground portion of a California shrubland (Table 6.4). These data serve to summarize many aspects of the intrasystem cycle. Note that 71% of the annual requirement of N is allocated to foliage, whereas much less is allocated to stem wood. Nevertheless, total nutrient storage in short-lived tissues is small compared to storage in wood, which has lower nutrient concentrations than leaf tissue but has accumulated during 22 years of growth. For most nutrients in this ecosystem, the storage in wood increases by about 5% each year.

In this community the nutrient flux in stemflow is unusually large but the total annual return in leaching is relatively small, except for K. Despite substantial reabsorption of N and P before leaf abscission, litterfall is the dominant pathway of return of these elements to the soil from the aboveground vegetation. Ca is actively exported to the leaves before abscission (i.e., requirement $<$ uptake). In this shrubland, annual uptake is 16 to 46% of the total storage in vegetation, but 73 to 92% of the uptake is returned each year. As in most studies, some of these calculations would be revised if belowground transfers were better understood.

There are changes in the nutrient cycles in vegetation, which accompany changes in the allocation of net primary production with stand age. During forest regrowth after disturbance, leaf area develops rapidly and the nutrient movements dependent on leaf area (i.e., litterfall and leaching) are quickly reestablished (Marks and Bormann 1972, Boring et al. 1981, Davidson et al. 2007). Gholz et al. (1985) found that the proportion of the annual requirement met by internal cycling (i.e., nutrient reabsorption from leaves) increased with time during the development of pine forests in Florida. Nutrients are accumulated most rapidly during the early development of forests and more slowly as the aboveground biomass reaches a steady state (Gholz et al. 1985, Pearson et al. 1987, Reiners 1992). Percentage turnover in vegetation declines as the mass and nutrient storage in vegetation increase. In mature forests, leaf biomass is $<5\%$ of the total and leaves contain only 5 to 20% of the total nutrient pool in vegetation (Waring and Schlesinger 1985).

TABLE 6.5 Biomass and Element Accumulations in Biomass of Mature Forests

Forest biome	Number of stands	Total biomass (t/ha)	Percent of total biomass				Mass ratio		
			Leaf	Branch	Bole	Roots	C/N	C/P	N/P
Northern/subalpine conifer	12	233	4.5	10.2	62.8	22.6	143	1246	8.71
Temperate broadleaf deciduous	13	286	1.1	16.2	63.1	19.5	165	1384	8.40
Giant temperate conifer	5	624	2.5	10.2	66.4	20.8	158	1345	8.53
Temperate broadleaf evergreen	15	315	2.7	14.7	66.2	16.5	159	1383	8.73
Tropical/subtropical closed forest	13	494	1.9	21.8	59.8	16.4	161	1394	8.65
Tropical/subtropical woodland and savanna	13	107	3.6	19.1	60.4	16.9	147	1290	8.80

Source: From Vitousek et al. (1988). Used with permission of Springer.

Vitousek et al. (1988) have compiled data showing the proportions of biomass (i.e., carbon) and major nutrient elements in various types of mature forest (Table 6.5). The nutrient ratios vary over a surprisingly small range, so the global pattern of element stocks in vegetation is similar to that for biomass; that is, tropical > temperate > boreal forests (Table 5.3). It is important to remember that these ratios are calculated for the total plant biomass; the concentrations of nutrients in leaf tissues are higher, and C/N and C/P ratios in leaves are correspondingly smaller. Thus, nutrient ratios for whole-plant biomass increase with time as the vegetation becomes increasingly dominated by structural tissues with lower nutrient content (Vitousek et al. 1988, Reiners 1992).

Nutrient Use Efficiency

A mass balance for the intrasystem cycle of vegetation allows us to calculate an integrated measure of nutrient-use efficiency by vegetation—net primary production per unit nutrient uptake (Pastor and Bridgham 1999). This measure is affected by various factors that we have examined individually, including the rate of photosynthesis per unit leaf nutrient (Chapter 5), uptake per unit of root growth (refer to Figure 6.2), and leaching and nutrient retranslocations from leaves. As a result of changes in these factors, net primary production per unit of nitrogen or phosphorus taken from the soil increased by factors of 5 and 10, respectively, during the growth of pine forests in central Florida (Gholz et al. 1985).

Among temperate forests, the annual circulation of nutrients in coniferous forests is much lower than the circulation in deciduous forests, largely as a result of lower leaf nutrient concentrations and lower leaf turnover in coniferous forest species (Cole and Rapp 1981, Aerts 1996). The foliage of some coniferous species persists for 8 to 10 years. Also, leaching losses are lower in coniferous forests (Parker 1983), and photosynthesis per unit of leaf nitrogen tends to be greater in coniferous species (Reich et al. 1995). Together these mechanisms result in greater nutrient-use efficiency in coniferous forests compared to deciduous forests of the

TABLE 6.6 Net Primary Production (kg ha^{-1} yr^{-1}) per Unit of Nutrient Uptake, as an Index of Nutrient-Use Efficiency in Deciduous and Coniferous Forests

	Production per unit nutrient uptake				
Forest type	**N**	**P**	**K**	**Ca**	**Mg**
Deciduous	143	1859	216	130	915
Coniferous	194	1519	354	217	1559

Source: From Cole and Rapp (1981).

world (Table 6.6). Higher nutrient-use efficiency in coniferous species may explain their frequent occurrence on nutrient-poor sites and in boreal climates where soil nutrient turnover is slow. Significantly, larch (*Larix* sp.), one of the few deciduous species in the boreal forest, has exceptionally high fractional reabsorption of foliar nutrients (Carlyle and Malcolm 1986).

The high nutrient-use efficiency of most conifers may also extend to the occurrence of broad-leaf evergreen vegetation on nutrient-poor soils in other climates (Monk 1966; Beadle 1966; Goldberg 1982, 1985; DeLucia and Schlesinger 1995). Escudero et al. (1992) suggest that leaf longevity was the most important factor increasing nutrient-use efficiency among various trees and shrubs in central Spain (compare Reich et al. 1992), since deciduous and evergreen species have roughly similar amounts of nutrient reabsorption during leaf senescence (del Arco et al. 1991, Aerts 1996, Eckstein et al. 1999).

For biogeochemical cycling in vegetation, we have seen that the leaves and fine roots contain only a small portion of the nutrient content in biomass, but the growth, death, and replacement of these tissues largely determine the annual intrasystem cycle of nutrients. Net primary production is positively correlated to soil N availability in both coniferous and deciduous forests (Zak et al. 1989, Reich et al. 1997), but differences in nutrient-use efficiency tend to weaken the correlation, so that light and moisture are the primary determinants of net primary production on a global basis (Figures 5.13 and 5.14). When nutrient concentrations in litter are low, as might be expected after reabsorption of nutrients, decomposition is slower (Scott and Binkley 1997, Lovett et al. 2004). Thus, intrasystem cycling contains a positive feedback to the extent that an increase in nutrient-use efficiency by vegetation may reduce the future availability of soil nutrients for plant uptake (Shaver and Melillo 1984).

Because of the uptake of nutrients from the soil and the intrasystem cycling of nutrients, terrestrial vegetation leaves a marked imprint on the nutrient distribution in soils. Some nutrients are actively accumulated from deep in the soil profile and deposited at the surface (Marsh et al. 2000, Lawrence and Schlesinger 2001, Jobbágy and Jackson 2004). This effect is most pronounced for nutrients that are strongly recycled within the plant community, while others are more evenly distributed through the soil profile. As a result, a global compilation of 10,000 soil profiles shows the following rank-order of nutrient concentrations with depth (shallow to deep) (Jobbágy and Jackson 2001):

$$P > K > Ca > Mg > Na = Cl = SO_4. \quad (6.4)$$

Nutrient uplift by plants is mediated by precipitation—if the site is very wet, leaching tends to dominate over plant uplift (Porder and Chadwick 2009). In deserts and other areas where there is patchy vegetation, plant nutrients are strongly concentrated under shrubs, whereas nonlimiting or nonessential nutrients accumulate in the barren spaces between

shrubs (Schlesinger et al. 1996, Gallardo and Parama 2007). Even in forests individual trees can leave an imprint on soil chemistry (Boettcher and Kalisz 1990, Rodriguez et al. 2011).

BIOGEOCHEMICAL CYCLING IN THE SOIL

Despite new inputs from the atmosphere and from rock weathering, and adaptations in plants to minimize their loss of nutrients, most of the annual nutrient requirement of land plants is supplied from the decomposition of dead materials in the soil (refer to Table 6.1). Decomposition of dead organic matter completes the intrasystem cycle by returning nutrient elements to the soil where they are available for plant uptake.

Soil Microbial Biomass and the Decomposition Process

Decomposition is a general term that refers to the breakdown of organic matter. *Mineralization* is a more specific term[3] that refers to processes that release carbon as CO_2 and nutrients in inorganic form (e.g., N as NH_4^+ and P as PO_4^{3-}).

A variety of soil animals, including earthworms, fragment and mix fresh litterfall (Swift et al. 1979, Wolfe 2001); however, the main biogeochemical transformations are performed by fungi and bacteria in the soil. Most of the mineralization reactions are the result of the activity of extracellular degradative enzymes, released by soil microbes and mycorrhizae (Burns 1982; Linkins et al. 1990; Sinsabaugh et al. 1993, 2002, 2008). The release of a wide variety of extracellular enzymes, including cellulases and proteases, increases in response to the amount of freshly deposited organic matter available for decomposition.

Microbial biomass (bacteria + fungi) typically comprises $<3\%$ of the organic carbon found in soils (Wardle 1992, Zak et al. 1994). High levels of microbial biomass are found in most forest soils and lower levels in deserts (Insam 1990, Gallardo and Schlesinger 1992). Fungi dominate over bacteria in most well-drained, upland soils (Anderson and Domsch 1980). Ruess and Seagle (1994) found a direct correlation between soil microbial biomass and soil respiration in the grasslands of the African Serengeti, and microbial biomass is often measured as an index of its activity (Andersson et al. 2004a, Booth et al. 2005).

Determination of microbial biomass is often performed by one of several techniques involving fumigation with chloroform (Jenkinson and Powlson 1976, Martens 1995, Joergensen et al. 2011). For instance, in a subdivided soil sample, total soluble nitrogen (NH_4^+, NO_3^-, and dissolved organic N) is measured before and after fumigation with chloroform. A higher content in the fumigated sample is assumed to result from the lysis of microbes that were killed by chloroform (Brookes et al. 1985, Joergensen 1996). Microbial biomass is then calculated by assuming a standard nitrogen content in microbial tissue and a correction factor, *K*n, to account for microbial N that is not immediately released by fumigation (Voroney and Paul 1984, Shen et al. 1984, Joergensen and Mueller 1996). The technique is justified by the observation of relatively constant C/N and C/P ratios in soil microbial biomass from many

[3] This use of the term *mineralization* differs from its common usage in the literature of geology, in which mineralization refers to various processes (e.g., precipitation from hydrothermal fluids) that result in the deposition of metals in an ore deposit of economic significance.

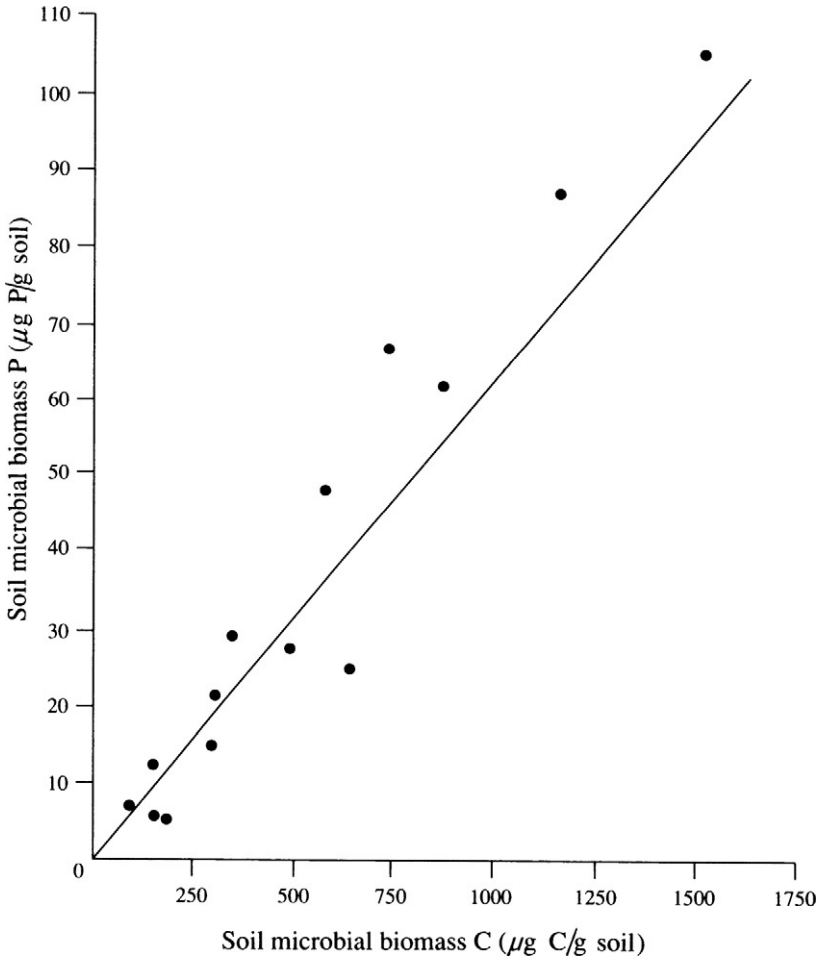

FIGURE 6.9 Relationship between the phosphorus and carbon contained in the microbial biomass of 14 soils. *Source: From Brookes et al. (1984).*

different environments (e.g., Figure 6.9). Microbial biomass is also measured by changes in respiration on the addition of glucose (i.e., substrate-induced respiration; Anderson and Domsch 1978, Lin and Brookes 1999) and extractions of the phospholipid fatty acid (PLFA) content from soil samples (Leckie et al. 2004, Bailey et al. 2002).

Soil microbes have high nutrient concentrations relative to the organic matter they decompose (Diaz-Ravina et al. 1993, Cleveland and Liptzin 2007). Microbial biomass contained 2.5 to 5.6% of the organic carbon but up to 19.2% of the organic phosphorus in tropical soils of central India (Srivastava and Singh 1988). During the decomposition of plant material, respiration of soil microbes converts organic carbon to CO_2, while the N and P content are initially retained in microbial biomass. When the decomposition of fresh litter is observed in litterbags (Chapter 5), the C/N and C/P ratios decline as decomposition proceeds and as the remaining

TABLE 6.7 Ratios of Nutrient Elements to Carbon in the Litter of Scots Pine (*Pinus sylvestris*) at Sequential Stages of Decomposition

	C/N	C/P	C/K	C/S	C/Ca	C/Mg	C/Mn
Needle litter							
Initial	134	2630	705	1210	79	1350	330
After incubation of:							
1 year	85	1330	735	864	101	1870	576
2 year	66	912	867	ND	107	2360	800
3 year	53	948	1970	ND	132	1710	1110
4 year	46	869	1360	496	104	704	988
5 year	41	656	591	497	231	1600	1120
Fungal biomass							
Scots pine forest	12	64	41	ND	ND	ND	ND

Note: C/N and C/P ratios decline with time, which indicates retention of these nutrients as C is lost, whereas C/Ca and C/K ratios increase, which indicates that these nutrients are lost more rapidly than carbon.
Source: From Staaf and Berg (1982). Used with permission of NRC Research Press.

materials are progressively dominated by microbial biomass that has colonized and grown on the substrate (Table 6.7; Sinsabaugh et al. 1993, Manzoni et al. 2010, Fahey et al. 2011).

The accumulation of N, P, and other nutrients in soil microbes is known as *immobilization*. Immobilization is most significant for N and P, which are limiting to microbial growth and usually less obvious for Mg and K, which are available in greater quantities (Jorgensen et al. 1980, Staaf and Berg 1982). In the process of immobilization, soil microbes not only retain the nutrients released from their substrate but also accumulate nutrients from the soil solution—net immobilization (Figure 6.10; Drury et al. 1991). Microbial uptake of NH_4^+ is rapid, sequestering available NH_4^+ that might otherwise be available for plant uptake or nitrifying bacteria

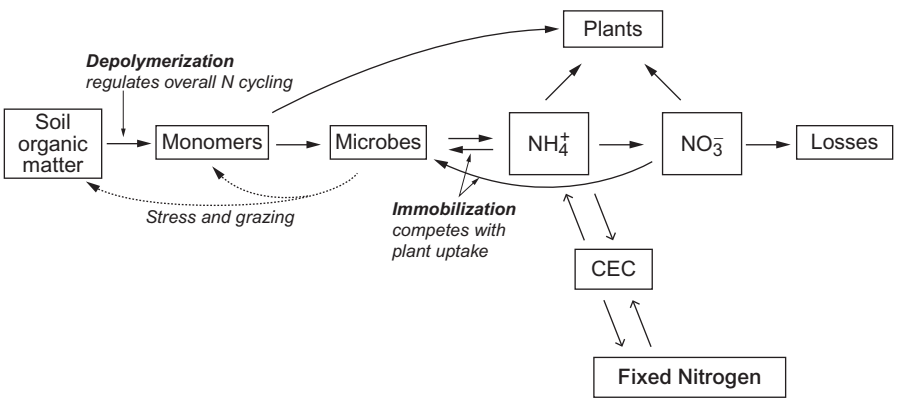

FIGURE 6.10 A conceptual model for the soil nitrogen cycle. *Source: Modified from Schimel and Bennett (2004); see also Drury et al. (1991).*

(Jackson et al. 1989, Schimel and Firestone 1989). In a beech forest near Vienna, Austria, microbial uptake exceeded mineralization during the winter (Kaiser et al. 2011). In cases of net accumulation by microbes, the total nutrient content of the substrate appears to increase during the initial phases of decomposition (e.g., Aber and Melillo 1980, Berg 1988).

Mineralization slows when fresh residues with high C/N ratio are added to the soil (Turner and Olson 1976, Gallardo and Merino 1998). Fallen logs have low N contents, and long-term immobilization of N is especially evident during log decay (Lambert et al. 1980, Fahey 1983, Schimel and Firestone 1989). In contrast, leaf tissues decompose more readily. Ecologists have long used the C/N ratio of litterfall as an index of its potential rate of decomposition (Taylor et al. 1989, Enriquez et al. 1993). Lignin/nitrogen (Melillo et al. 1982) and lignin/phosphorus (Wieder et al. 2009) ratios in litter are also good predictors of the rate of decomposition in various ecosystems (Figure 6.11). These relationships allow us to predict the rate of decomposition and mineralization over large regions using remote sensing (Fan et al. 1998a, Ollinger et al. 2002).

When microbial growth slows, there is little further nutrient immobilization. Thus, immobilization of nutrients predominates in the layer of fresh litter on the soil surface, while net mineralization of N, P, and S is usually greatest in the lower forest floor (Federer 1983). Net mineralization of N often begins with C/N ratios near 30:1, but this can vary depending on the substrate and the assimilation efficiency of the decomposer (Manzoni et al. 2010). Immobilization is least rapid and the release of nitrogen is most rapid in substrates of greatest initial nitrogen content (Parton et al. 2007, Manzoni et al. 2008).

During the decomposition process, fulvic acids and other dissolved organic compounds carry nutrients to the lower soil horizons (Schoenau and Bettany 1987, Qualls and Haines 1991), where they add to the nutrient pool in humus. Sollins et al. (1984) found that the "light" fraction of soil organic matter, representing fresh plant residues, had a higher C/N ratio and lower mineralization than the "heavy" fraction, composed of humic substances. A small fraction of the substrate is converted to humic compounds (Chapter 5) that paradoxically have high N content (Schulten and Schnitzer 1993) but long-term stability in the soil profile (Chapter 5). Decaying plant litter appears to adsorb Al and Fe (Rustad 1994,

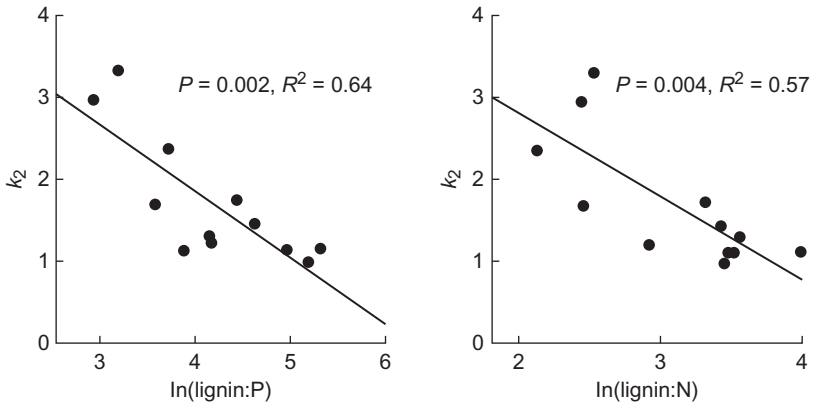

FIGURE 6.11 Fractional decomposition of leaf litter from wet tropical forests as a function of the lignin-to-P and lignin-to-N ratio in newly fallen litter. *Source: From Wieder et al. (2009). Used with permission of the Ecological Society of America.*

TABLE 6.8 Mean Residence Time, in Years, of Organic Matter and Nutrients in the Surface Litter of Forest and Woodland Ecosystems

	Mean residence time (year)					
Region	**Organic matter**	**N**	**P**	**K**	**Ca**	**Mg**
Boreal forest	353	230	324	94	149	455
Temperate forest						
Coniferous	17	17.9	15.3	2.2	5.9	12.9
Deciduous	4	5.5	5.8	1.3	3.0	3.4
Mediterranean	3.8	4.2	3.6	1.4	5.0	2.8
Tropical rainforest	0.4	2.0	1.6	0.7	1.5	1.1

Note: Values are calculated by dividing the forest floor mass by the mean annual litterfall.
Sources: Boreal and temperate values are from Cole and Rapp (1981); tropical values are from Edwards and Grubb (1982) and Edwards (1977, 1982); Mediterranean values are from Gray and Schlesinger (1981).

Laskowski et al. 1995), perhaps in compounds that are precursors to fulvic acids that carry Al and Fe to the lower soil profile in the process of podzolization (Chapter 4).

Differential losses of nutrients and nutrient immobilizations mean that the loss of mass from litterbags cannot be directly equated with the proportional release of its original nutrient content (Jorgensen et al. 1980, Rustad 1994). Table 6.8 shows the mean residence time for organic matter and its nutrient content in the surface litter of various ecosystems. Some nutrients, such as K, that are easily leached from litter may show mineralization rates in excess of the loss of litter mass. Others, such as N, turn over more slowly due to immobilization in microbial tissues. Pregitzer et al. (2010) used experimental additions of $^{15}NO_3$ to a sugar maple forest in Michigan to measure a mean residence time of 6.5 years for N in the forest floor.

Vogt et al. (1986) suggest that immobilization of N is greatest in temperate and boreal forests, whereas the immobilization of P is more important in tropical forests. Given the nutrient limitations facing soil microbes, it is perhaps not surprising that their activity increases with nutrient additions (e.g., Cleveland and Townsend 2006, Allen and Schlesinger 2004), leading to losses of organic matter from the soil profile (Neff et al. 2002b, Mack et al. 2004). Paradoxically, most nutrient-addition experiments show decreased soil microbial biomass (Wallenstein et al. 2006, Treseder 2008, Lu et al. 2010, Liu and Greaver 2010).

In Chapter 5 we saw that the pool of soil organic matter greatly exceeds the mass of vegetation in most ecosystems. As a result of its high nutrient content, humus also dominates the storage of biogeochemical elements in most ecosystems. Aboveground biomass contains only 4 to 8% of the total quantity of N in temperate forests (Cole and Rapp 1981) and 3 to 32% in tropical forests (Edwards and Grubb 1982). Generally, the ratio of C, N, P, and S in humus is close to 140:10:1.3:1.3 (Stevenson 1986, Schulten and Schnitzer 1993; compare Cleveland and Liptzin 2007), so the global pool of nitrogen in soil, estimated at 95 to 140 $\times$ 10^{15} g (Post et al. 1985, Batjes 1996), dwarfs the pool of nitrogen in vegetation, 3.8 $\times$ 10^{15} g.[4] Owing to the

[4] Calculated using the global biomass of 615 $\times$ 10^{15} g C (Table 5.3) and a C/N ratio in vegetation of 160 (Table 6.5).

stability of humus substances in the soil, the large nutrient pool in humus turns over very slowly. Typically soil microbes mineralize about 1 to 3% of the pool of nitrogen in the soil each year (Connell et al. 1995).

Simple measurements of extractable nutrients, such as NH_4^+ or PO_4^{3-}, are unlikely to give a good index of nutrient availability in terrestrial ecosystems. These nutrients are subject to active uptake by plant roots, immobilization by soil microbes, and a variety of other processes that rapidly remove available forms from the soil solution. At any moment, the quantity extractable from a soil sample may be only a small fraction of what is made available by mineralization during the course of a growing season (Davidson et al. 1990). Thus, studies of biogeochemical cycling in the soil need to be based on measurements that record the dynamic nature of nutrient turnover.

Nitrogen Cycling

The mineralization of N from decomposing materials begins with the release of amino acids and other simple organic-N molecules by the microbes involved in decomposition (Schimel and Bennett 2004, Geisseler et al. 2010; Figure 6.10). Some of the amino acids are taken up directly by plants and soil microbes. Using ^{15}N as a tracer, Marumoto et al. (1982) have shown that much of the N mineralized in the soil is released from dead microbes. The presence of soil animals that feed on bacteria and fungi can increase the rates of release of N and P from microbial tissues (Cole et al. 1978, Anderson et al. 1983). The release, or mineralization, of NH_4^+ from organic forms is known as *ammonification*.

Subsequently, a variety of abiotic and biotic processes may remove NH_4^+ from the soil solution, including uptake by plants, immobilization by microbes, and fixation in clay minerals (Johnson et al. 2000a). Some of the remaining NH_4^+ may undergo nitrification, in which the oxidation of NH_4^+ to NO_3^- is coupled to the fixation of carbon by chemoautotrophic bacteria, traditionally classified within the genera *Nitrosomonas* and *Nitrobacter* (Meyer 1994; see Eqs. 2.17 and 2.18). Recent work suggests that nitrification is also performed by prokaryotes in the more primitive group archaea, although it is unclear whether they normally achieve the same level of activity in soils as bacteria (Leininger et al. 2006, Di et al. 2009). In some cases, NH_4^+ is also oxidized by heterotrophic nitrification, producing NO_3^- (Schimel et al. 1984, Duggin et al. 1991, Brierley and Wood 2001, Pedersen et al. 1999).

Nitrate may be taken up by plants and microbes or lost from the ecosystem in runoff waters or in emissions of N-containing gases during denitrification. An intermediate product in the nitrification reaction (see Eq. 2.17), NO_2^- appears to bind to soil organic matter by abiotic processes (Dail et al. 2001, Fitzhugh et al. 2003, Davidson et al. 2003). Nitrate taken up by soil microbes (immobilization) is reduced to NH_4^+ by nitrate reductase and used in microbial growth (Davidson et al. 1990, DeLuca and Keeney 1993, Downs et al. 1996). This process is known as *assimilatory reduction*. Nitrate can also be utilized by dissimilatory nitrate-reducing bacteria to produce NH_4^+, which can cycle back through these pathways. Dissimilatory nitrate reduction to ammonium (DNRA) is best known from its occurrence in wet tropical soils, where it can exceed denitrification—the conversion of NO_3^- to N_2 (Silver et al. 2001, Rutting et al. 2008, Templer et al. 2008). DNRA potentially reduces the loss of NO_3^- to stream waters.

At any time, the extractable quantities of NH_4^+ and NO_3^- in the soil represent the net result of all of these processes. A low concentration of NH_4^+ is not necessarily an indication of

low mineralization rates; it can also indicate rapid nitrification or plant uptake (Rosswall 1982, Davidson et al. 1990). A variety of techniques are available to study the transformations of nitrogen in the soil (Binkley and Hart 1989). Many workers have used the "buried-bag" approach to examine net mineralization. A soil sample is subdivided and part is extracted immediately, usually with KCl, to measure the available NH_4^+ and NO_3^-. The remaining soil is replaced in the field in a polyethylene bag, which is permeable to O_2 but not to H_2O. After a short period, usually 30 days, the bag is retrieved and its contents analyzed for the forms of available N. An increase in the quantity of available N in the buried bag is taken to represent *net* mineralization (i.e., the mineralization in excess of microbial immobilization) in the absence of plant uptake. Repeated samples taken through an annual cycle allow an estimate of annual net mineralization, which can be correlated with plant uptake and cycling (Pastor et al. 1984).

Field measurements can also be performed in tubes (Raison et al. 1987) or trenched plots (Vitousek et al. 1982). In the latter, a block of soil, often 1 m^2, is isolated on all sides by trenching and the trenches are lined with plastic to prevent the invasion of roots. Plants rooted in this plot are removed, but the area is not otherwise disturbed. Periodic measurements of NH_4^+ and NO_3^- indicate rates of mineralization and nitrification in the absence of plant uptake. Trenching also eliminates the plant uptake of water, so this approach measures microbial activity at artificially high soil moisture content, with potentially greater losses from the ecosystem due to leaching and denitrification.

A more expensive approach involves the use of $^{15}NH_4^+$ to label the initial pool of available NH_4^+ in the soil (Van Cleve and White 1980, Davidson et al. 1991a, Di et al. 2000). After a period of time, the pool is remeasured for the ratio of $^{15}NH_4^+$ to $^{14}NH_4^+$. A decline in proportion of $^{15}NH_4^+$ is assumed to result from the microbial mineralization of NH_4^+ from the pool of N in soil organic matter. This technique gives a measure of total (gross) mineralization under natural field conditions. Using this approach, Davidson et al. (1992) found that net mineralization was only 14% of the total in a coniferous forest; the remainder was immobilized by the microbial community. Known as the isotope-pool dilution technique, this approach has also been applied to determine turnover of amino acids (Wanek et al. 2010) and NO_3^- (Stark and Hart 1997). For instance, $^{15}NO_3$ is used to label the pool of NO_3^- in the soil, and gross nitrification is measured as the label is diluted by $^{14}NO_3^-$. Net nitrification can also be studied by measuring changes in the concentration of NH_4^+ and NO_3^- after application of compounds that specifically inhibit nitrification, including nitrapyrin (Bundy and Bremner 1973), acetylene (Berg et al. 1982), or chlorate (Belser and Mays 1980).

Mineralization and nitrification have been studied in a wide variety of ecosystems (Vitousek and Melillo 1979, Robertson 1982a, Vitousek and Matson 1988, Davidson et al. 1992). Net mineralization typically ranges from 20 to 120 kg N ha^{-1} yr^{-1} in forests (Pastor et al. 1984, Fan et al. 1998b, Perakis and Sinkhorn 2011), 40 to 90 kg N ha^{-1} yr^{-1} in grasslands (Hatch et al. 1990), and 10 to 30 kg N ha^{-1} yr^{-1} in deserts (Schlesinger et al. 2006). Generally, net mineralization is directly related to the total content of organic nitrogen in the soil (e.g., Marion and Black 1988, McCarty et al. 1995, Accoe et al. 2004, Perakis and Sinkhorn 2011), but mineralization is also closely linked to the availability of carbon (Booth et al. 2005). Vegetation with a high C/N ratio in litterfall often shows low rates of mineralization in the soil (Gosz 1981, Vitousek et al. 1982). When field plots are fertilized with sugar, net mineralization and nitrification slow because of increased immobilization of NH_4^+ by soil microbes

(DeLuca and Keeney 1993, Zagal and Persson 1994). Fertilization of a Douglas fir forest with sugar resulted in lower N content in leaves and greater nutrient reabsorption before leaf-fall (Turner and Olson 1976), showing a direct link between microbial processes in the soil and the nutrient-use efficiency of vegetation.

Although soil microbial populations may adapt to a wide variety of field conditions, nitrification is generally lower at low pH, low O_2, low soil moisture content, and high litter C/N ratios (Wetselaar 1968, Rosswall 1982, Robertson 1982b, Bramley and White 1990, Booth et al. 2005). Compared to mineralization, nitrification is more sensitive to low soil water content, so NH_4^+ accumulates in seasonally dry desert soils (Hartley and Schlesinger 2000). Generally, however, nitrification rates are high whenever NH_4^+ is readily available (Robertson and Vitousek 1981, Vitousek and Matson 1988).

A large amount of effort has been directed toward understanding the control of nitrification following disturbances, such as forest harvest or fire (Vitousek and Melillo 1979, Vitousek et al. 1982). When vegetation is removed, soil temperature and moisture content are generally higher, and rapid ammonification increases the availability of NH_4^+. Subsequently, nitrification may be so rapid that uptake by regrowing vegetation and immobilization by soil microbes are insufficient to prevent large losses of NO_3^- in stream water. However, not all disturbed sites show large losses of NO_3^-. In pine forests in the southeastern United States, microbial immobilization in harvest debris accounted for 83% of the uptake of ^{15}N that was applied as an experimental tracer following forest harvest (Vitousek and Matson 1984). Immobilization of nitrate accounts for a large fraction of the nitrogen turnover in coniferous forests (Stark and Hart 1997), and microbial immobilization also retards the loss of nitrate following burning of tallgrass prairie (Seastedt and Hayes 1988).

In general, nitrification and losses of NO_3^- in stream water after disturbance are greatest in forests with high nitrogen availability (Krause 1982, Vitousek et al. 1982). Rates of nitrification decline during the early recovery of vegetation, and only minor differences are seen between middle- and old-age forests (Robertson and Vitousek 1981, Christensen and MacAller 1985, Davidson et al. 1992). There is some evidence that nitrification is inhibited by terpenoid and tannin compounds released by some types of vegetation (Olson and Reiners 1983, White 1988, Subbarao et al. 2009).

Increases in nitrification following disturbance affect other aspects of ecosystem function. Nitrification generates acidity (Eq. 2.17), so losses of NO_3^- in stream water are often accompanied by increased losses of cations, which are removed from cation exchange sites in favor of H^+ (Likens et al. 1970b). Stream-water losses of nearly all biogeochemical elements increased following harvest of the Hubbard Brook forest in New Hampshire. Sulfate was a curious exception (Figure 6.12). Nodvin et al. (1988) showed that the decline in stream water SO_4^{2-} concentrations after forest harvest was a result of the acidity generated from nitrification, which increased soil anion adsorption capacity (Chapter 4; Mitchell et al. 1989). These observations are a good example of a link between the biogeochemical cycles of N and S in terrestrial ecosystems.

Since the various transformations of N in the soil favor ^{14}N over ^{15}N (Hogberg 1997), ^{15}N increases in the undecomposed residues (Nadelhoffer and Fry 1988), with depth in the soil profile (Koba et al. 1998, Hobbie and Ouimette 2009, Piccolo et al. 1996, Kramer et al. 2003), and with time of ecosystem development (Brenner et al. 2001, Billings and Richter 2006). In contrast, nitrate in runoff waters is depleted in ^{15}N (Spoelstra et al. 2007). Nearly all soils

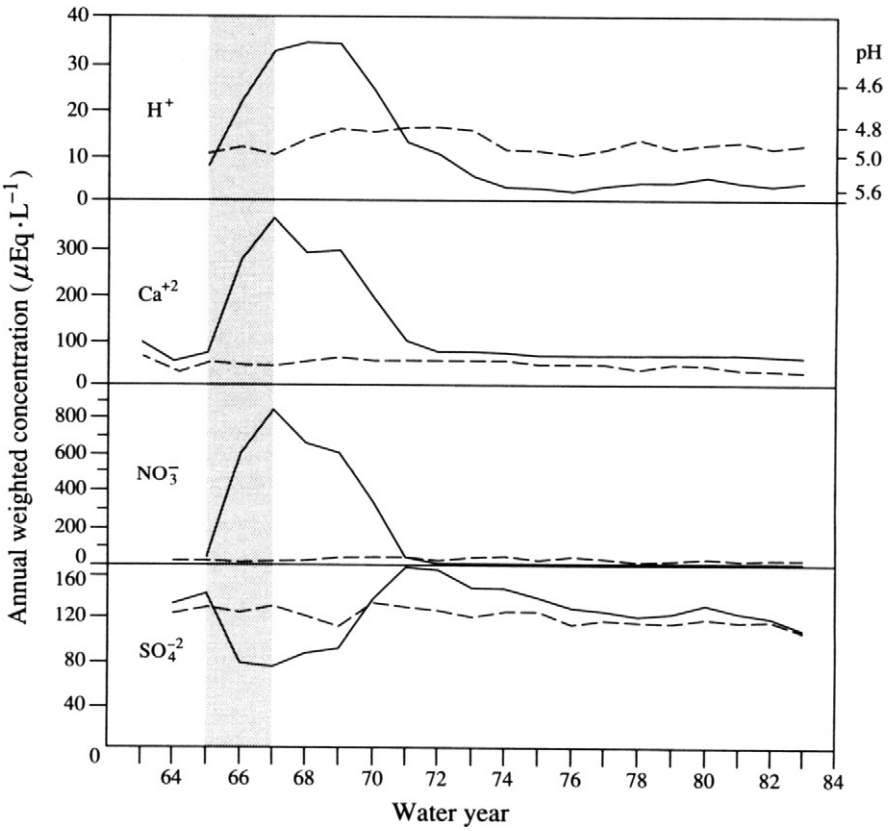

FIGURE 6.12 Concentration of H^+, Ca^{2+}, NO_3^-, and SO_4^{2-} in streams draining the Hubbard Brook Experimental Forest for the years 1964–1984. Streams draining undisturbed forest are shown with the dashed line. The solid line depicts the concentrations in a stream draining a single watershed that was disturbed between 1965 and 1967 (*shaded*). Losses of Ca and NO_3 increased strongly during the period of disturbance, and then recovered to normal values as the vegetation regenerated. The budget for SO_4 shows greater retention during and after the period of disturbance, presumably as a result of increased acidity and anion adsorption in the soil. *Source: Modified from Nodvin et al. (1988).*

show $\delta^{15}N > 0$, with the greatest values seen in ecosystems with rapid nitrogen cycling (Templer et al. 2007) and with substantial losses of NO_3^- in runoff and emissions of nitrogen gases from the ecosystem (Amundson et al. 2003, Pardo et al. 2002). Since plants depend on nitrogen mineralization for uptake, plant $\delta^{15}N$ is usually lower than that of soil organic matter, but $\delta^{15}N$ in plants increases as a function of soil nitrogen cycling, which progressively enriches ^{15}N remaining in the soil (Garten and Van Miegroet 1994, Templer et al. 2007).

Emission of Nitrogen Gases from Soils

During transformations of nitrogen in the soil, a variety of nitrogen gases, including NH_3, NO, N_2O, and N_2, are produced as products and byproducts of microbial activity (Figure 6.13). Some of these may escape from the ecosystem, contributing to a loss of local

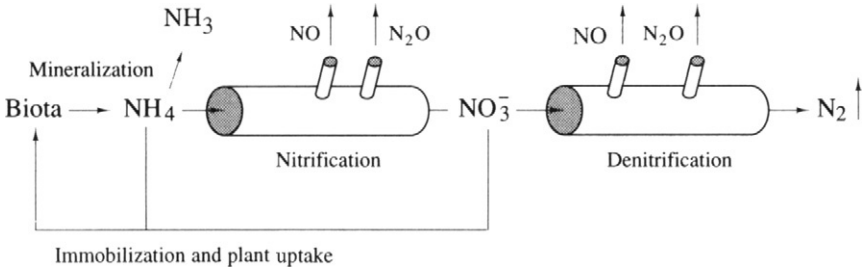

FIGURE 6.13 Microbial processes that yield nitrogen gases during nitrification and denitrification in the soil. *Source: Modified from Firestone and Davidson (1989).*

soil fertility. More significantly, terrestrial ecosystems are a significant source of these gases in the atmosphere (Chapters 3 and 12).

In soils, ammonium may be converted to ammonia gas (NH_3), which is lost to the atmosphere. The reaction

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O \tag{6.5}$$

is favored in dry soils and deserts, where accumulations of $CaCO_3$ maintain alkaline pH. Low cation exchange capacity and low rates of nitrification also maximize the production and loss of NH_3 (Nelson 1982, Freney et al. 1983). Small losses of NH_3 have been measured in a variety of natural forest and grassland soils worldwide (Schlesinger and Hartley 1992; Figure 6.14). Losses of NH_3 are greatest in fertilized soils and during the decomposition of urea excreted by wild and domestic animals (Terman 1979). During the loss of NH_3

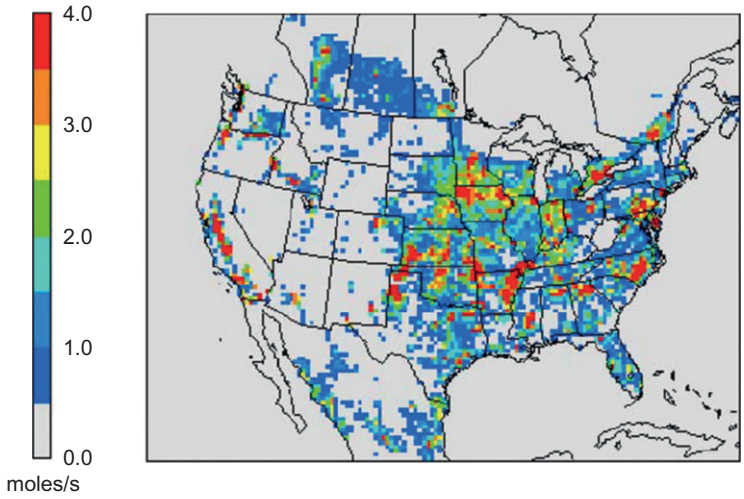

FIGURE 6.14 Soil emissions of NH_3 moles/m^2/sec for the continental United States, showing relatively high emissions from various agricultural regions and lower emissions from undisturbed ecosystems. *Source: From Gilliland et al. (2006).*

from soils, isotopic fraction occurs, leaving soils enriched in ^{15}N (Mizutani et al. 1986, Mizutani and Wada 1988).

Vegetation can also be a source of NH_3 during leaf senescence (Whitehead et al. 1988, Heckathorn and DeLucia 1995), but some of the NH_3 emitted by soils may be taken up by plants, so in many cases terrestrial ecosystems are only a small net source of NH_3 to the atmosphere (Langford and Fehsenfeld 1992, Sutton et al. 1993, Pryor et al. 2001). The loss of ammonia is typically <1 kg ha^{-1} yr^{-1} in soils that are not impacted by fertilizers or domestic animals. The global flux from natural soils is about 2.4×10^{12} g N/yr (Chapter 12). This flux to the atmosphere is significant inasmuch as NH_3 is the only substance that is a net source of alkalinity in the atmosphere, where it can reduce the acidity of rain (Eqs. 3.5 and 3.40). Extremely high NH_3 volatilization from barns and animal feedlots may result in enhanced atmospheric deposition of NH_4^+ in areas immediately downwind (Draaijers et al. 1989, Aneja et al. 2003, Theobald et al. 2006). Somewhat counterintuitively, these large inputs of NH_4^+ may acidify soils, as the NH_4^+ is nitrified and the nitrate is taken up by vegetation (van Breemen et al. 1982, Verstraten et al. 1990).

Both nitric oxide (NO) and nitrous oxide (N_2O) are generated as microbial byproducts of nitrification, with NO generally being the more abundant (Williams et al. 1992).[5] Specifically, NO is released during the oxidation of NO_2^- to NO_3^- by chemoautotrophic bacteria (Eq. 2.18; Venterea and Rolston 2000). Typically, about 1 to 3% of the nitrogen passing through the nitrification pathway is volatilized as NO each year (Baumgärtner and Conrad 1992, Hutchinson et al. 1993), and the net flux from soils to the atmosphere is estimated to be about 12×10^{12} g N/yr globally (Ganzeveld et al. 2002). Davidson et al. (1998) indicate that soils supply 10% of the NO_x emitted in the southeastern United States, with industrial and transportation sources accounting for the rest. (Recall that NO plays a major role in the chemistry of ozone in the troposphere—see Chapter 3.)

The flux of NO from soils is highest under conditions that stimulate nitrification, including fertilization with NH_4^+ (Skiba et al. 1993, Roelle et al. 1999). Soil NO efflux is directly related to nitrification in Chihuahuan desert soils (Figure 6.15). In various ecosystems, the flux

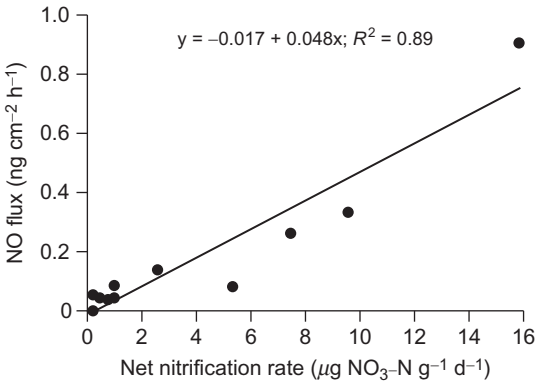

FIGURE 6.15 Emission of NO as a function of nitrification rates in soils of the Chihuahuan Desert, New Mexico. *Source: From Hartley and Schlesinger (2000).*

[5] The production of N_2O by several pathways during nitrification is sometimes called nitrifier denitrification (Wrage et al. 2001, Kool et al. 2011).

appears to increase as a function of soil temperature (Williams et al. 1992, Roelle et al. 1999, Van Dijk and Duyzer 1999) and immediately following the wetting of dry soils (Davidson et al. 1991b, 1993; Ghude et al. 2010; Hartley and Schlesinger 2000). When the atmospheric concentration of nitric oxide is high, some NO is taken up by plants and soils, reducing the net flux to the atmosphere (Rondón and Granat 1994, Slemr and Seiler 1991, Ganzeveld et al. 2002). The atmospheric concentration that produces no net uptake or loss is known as the *compensation point*. In most cases, the background concentration in the atmosphere, about 10 ppbv (refer to Table 3.5), is below the compensation point, so terrestrial ecosystems are a net source of NO to the atmosphere (Kaplan et al. 1988, Duyzer and Fowler 1994, Ludwig et al. 2001). In remote areas, the concentration of NO is greatest in the lower atmosphere, and it declines with altitude (Luke et al. 1992).

Losses of NO and N_2O increase with factors that increase the rate of nitrification in soils, including the clearing, cultivation, and fertilization of agricultural soils (Conrad et al. 1983, Mosier et al. 1991, Clayton et al. 1994, Bouwman et al. 2002a). Shepherd et al. (1991) report that 11% of fertilizer N was lost as NO and 5% as N_2O in some cultivated fields in Ontario. When tropical forests are cleared, the losses of NO and N_2O from soils increase dramatically (Sanhueza et al. 1994, Keller et al. 1993, Weitz et al. 1998), but older pastures often have lower N_2O emissions than uncut forest (Melillo et al. 2001, Verchot et al. 1999). Thus, fertilized and newly cleared fields may be responsible for the rising concentration of N_2O in Earth's atmosphere (Chapter 12).

Nitrate is also converted to NO, N_2O, and N_2 in the process of denitrification (Knowles 1982, Firestone 1982, Ye 1994, Goregues et al. 2005). This reaction (Eq. 2.20) is performed by soil bacteria that are aerobic heterotrophs in the presence of O_2 but facultative anaerobes at low concentrations of O_2. During anoxia, heterotrophic activity continues, with nitrate serving as the terminal electron acceptor in metabolism. The structure of the various denitrification enzymes, *nitrite reductases*, contains Fe and Cu (Godden et al. 1991, Tavares et al. 2006, Hino et al. 2010, Pomowski et al. 2011). Because NO_3^- is reduced, but not incorporated into microbial tissue, denitrification is also known as *dissimilatory nitrate reduction*. Bacteria in the genus *Pseudomonas* are the best known denitrifiers, but many others are reported (Knowles 1982, Tiedje et al. 1989).

For a long time, denitrification was thought to occur only in flooded, anoxic soils (Chapter 7), and its importance in upland ecosystems was overlooked. Indeed, the activity of denitrification enzymes is often greatest at low soil O_2 concentrations (Burgin et al. 2010). Now, soil scientists have shown that oxygen diffusion to the center of soil aggregates is so slow that anoxic microsites are common, even in well-drained soils (Figure 6.16; Tiedje et al. 1984, Sexstone et al. 1985a, van der Lee et al. 1999, Ju et al. 2011). Thus, denitrification is widespread in terrestrial ecosystems, especially those in which organic carbon and nitrate are readily available (Burford and Bremner 1975, Carter et al. 1995, Wagner et al. 1996, Wolf and Russow 2000).

Davidson and Swank (1987) found that additions of NO_3^- stimulated denitrification in the surface litter of forests in western North Carolina, and the addition of organic carbon stimulated denitrification in the mineral soil. Additions of organic carbon stimulated the expression of genes related to denitrification in some cultivated soils (Miller et al. 2012). Rainfall generally increases the rate of denitrification because the diffusion of oxygen is slower in wet soils (Sexstone et al. 1985b, Smith and Tiedje 1979, Rudaz et al. 1991, Peterjohn and Schlesinger 1991).

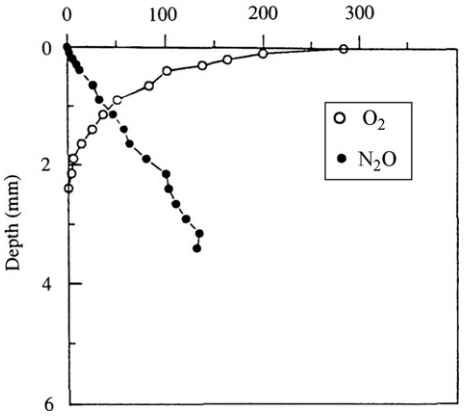

FIGURE 6.16 Concentration of O_2 and N_2O (μM) determined in a soil aggregate as a function of the depth of penetration of a microelectrode. *Source: From Hojberg et al. (1994).*

Typically the production of both NO and N_2O produced by nitrification declines with increasing soil moisture content (or declining O_2), and in anoxic conditions N_2O is entirely due to denitrification (Khalil et al. 2004, Wolf and Russow 2000, Wrage et al. 2001). In Germany, well-drained soils with near-neutral pH produced NO only from nitrification, whereas in acid, anoxic soils, NO was produced from denitrification (Remde and Conrad 1991). In studies of a semidesert ecosystem, Mummey et al. (1994) found that nitrification accounted for 61 to 98% of the N_2O produced in moist soils, but denitrification was the predominant reaction in saturated conditions. In the wet soils of Amazon rainforests, N_2O appeared to be mostly from denitrification (Livingston et al. 1988, Keller et al. 1988).

The relative importance of NO, N_2O, and N_2 as products of denitrification varies depending on environmental conditions (Firestone and Davidson 1989, Bonin et al. 1989). Typically, in denitrification, the production of N_2O dwarfs the production of NO, so the proportional and total loss (nitrification + denitrification) of NO from soils declines with increasing moisture content, while the flux of N_2O increases (Figure 6.17; Drury et al. 1992, Bollmann and

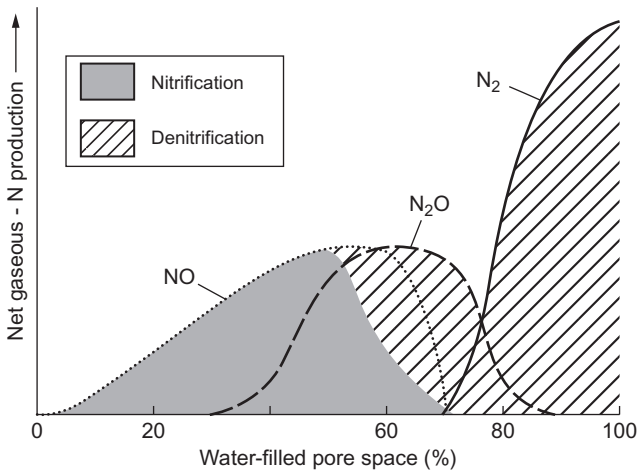

FIGURE 6.17 Relative emission of NO, N_2O, and N_2 from nitrification and denitrification as a function of the water content of soils. *Source: From Davidson et al. (2000). Used with permission of the American Institute of Biological Sciences. All rights reserved.*

Conrad 1998, Wolf and Russow 2000). Factors affecting the relative loss of N_2O and N_2 by denitrification are poorly understood, but they include soil pH and the relative abundance of NO_3^- and O_2 as oxidants and organic carbon as a reductant (Firestone et al. 1980, McKenney et al. 1994, Chen et al. 1995, Morley and Baggs 2010, Burgin and Groffman 2012, Zhang et al. 2009). When NO_3^- is abundant relative to the supply of organic carbon, N_2O can be an important product (Firestone and Davidson 1989, Mathieu et al. 2006, Huang et al. 2004). In studies of forest soils in New Hampshire (Melillo et al. 1983) and Michigan (Merrill and Zak 1992), N_2O was the only significant product of denitrification. In some circumstances, N_2O can diffuse into soils, where it is consumed by dentrifiers, producing N_2 (Frasier et al. 2010, Goldberg and Gebauer 2009).

The ratio of N_2O to N_2 produced in denitrification varies widely (Weier et al. 1993). The median ratio for the overall emission of these gases from upland soils appears to be about 1:1 (Schlesinger 2009), but the proportional emission of N_2O from wetter soils is much lower. The total loss of N from soils by denitrification is typically <2 kg ha^{-1} yr^{-1} in forests and grasslands. N_2O losses from croplands are typically 2 to 4 kg N ha^{-1} yr^{-1} (Roelandt et al. 2005), but occasional values as high as 13 kg N ha^{-1} yr^{-1} are reported from agricultural soils (Barton et al. 1999). Globally, the total loss of N_2 from soils ($\sim 44 \times 10^{12}$ g N/yr; Chapter 12) dwarfs the loss of N_2O ($<10 \times 10^{12}$ g N/yr) or NO (12×10^{12} g N/yr). Denitrification is a major process that returns N_2 to the atmosphere, completing the global biogeochemical cycle of nitrogen (Chapter 12). The flux of N_2O is significant inasmuch as its concentration in the atmosphere is increasing, and N_2O plays an important role as a greenhouse gas and as a catalyst of ozone chemistry in the stratosphere (Chapters 3 and 12).

Field measurements of denitrification are problematic, since the production of N_2 is difficult to measure against the background concentration of 78% in Earth's atmosphere. Recently, various workers have measured denitrification using an inert gas, such as helium or argon, to fill collection chambers in the field, allowing the efflux of N_2 from the soil to be observed more easily (Scholefield et al. 1997, Butterbach-Bahl et al. 2002, Dannenmann et al. 2008, Burgin et al. 2010).

Many laboratory studies have also measured denitrification using acetylene to block the conversion of the intermediate denitrification product, N_2O, to the final product, N_2 (refer to Figure 6.13; Yoshinari and Knowles 1976, Burton and Beauchamp 1984, Davidson et al. 1986, Tiedje et al. 1989). With the application of acetylene to laboratory soils or field plots, the sole product of denitrification is N_2O, which is easy to measure with gas chromatography against its background concentration of about 320 ppb in the atmosphere. Alternatively, many field workers have measured denitrification by the application of $^{15}NO_3^-$ to field plots and by measurements of the release of ^{15}N gases or the decline in $^{15}NO_3^-$ remaining in the soil (Parkin et al. 1985, Mosier et al. 1986, Mathieu et al. 2006, Zhang et al. 2009).

Field estimates of denitrification are complicated by high spatial variability. At the local scale, a large portion of the total variability is found at distances of <10 cm, which Parkin (1987) link to the local distribution of soil aggregates that provide anaerobic microsites. In one case, Parkin (1987) found that 85% of the total denitrification in a 15-cm-diameter soil core was located under a 1-cm^2 section of decaying pigweed (*Amaranthus*) leaf! In desert ecosystems, soil nitrogen content and nitrification rates are localized under shrubs, and denitrification is largely confined to those areas (Virginia et al. 1982, Peterjohn and Schlesinger 1991). Differences in the microbial communities between natural and disturbed ecosystems are also likely to contribute to variation in denitrification (Cavigelli and Robertson 2000).

Robertson et al. (1988) documented the pattern of mineralization, nitrification, and denitrification in a field in Michigan. All these processes showed large spatial variation, but the coefficient-of-variation for denitrification, 275%, was the largest measured. Significant correlations were found among these processes. Soil respiration and potential nitrification explained 37% of the variation in denitrification, presumably due to the dependence of denitrification on organic carbon and NO_3^- as substrates.

The high variability in these processes makes it difficult to use measurements from a few sample chambers to calculate a mean or total flux from an ecosystem (Ambus and Christensen 1994, Mathieu et al. 2006). High rates of denitrification are often confined to particular landscape positions, where conditions are favorable. For example, Peterjohn and Correll (1984) suggested that the runoff of nitrate from agricultural fields was largely denitrified in streamside forests, minimizing the losses in rivers (see also, Pinay et al. 1993, Schipper et al. 1993, Jordan et al. 1993, Ettema et al. 1999). In calculating regional averages for denitrification, investigators must evaluate the relative contributions from local areas of high and low activity (e.g., Groffman and Tiedje 1989, Matson et al. 1991, Yavitt and Fahey 1993, Morse et al. 2012).

As in the case of NH_3 volatilization, the losses of N gases as products and byproducts of nitrification and denitrification leave soils enriched in ^{15}N. Denitrifying bacteria fractionate among the isotopes of available nitrogen—that is, between $^{14}NO_3^-$ and $^{15}NO_3^-$ (Handley and Raven 1992, Robinson 2001, Snider et al. 2009). Preference for $^{14}NO_3^-$ leads to positive $\delta^{15}N$ in most soils (refer to Figure 6.5), as $^{14}N_2$ is lost from the soil by denitrification (Shearer and Kohl 1988, Knöller et al. 2011). Evans and Ehleringer (1993) show a strong inverse relation between $\delta^{15}N$ and the nitrogen content in soils (Figure 6.18), suggesting that soils with low nitrogen are enriched in ^{15}N as a result of the loss of N gases (Garten 1993). Strong enrichments in ^{15}N are also seen in saturated soils with low redox potential (Chapter 7) compared to

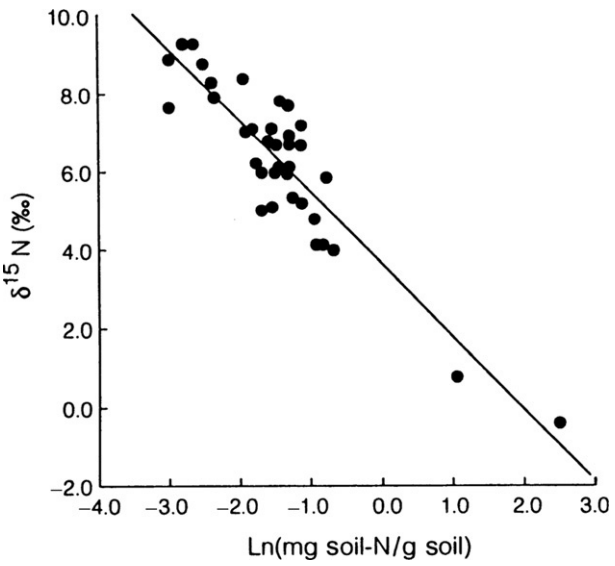

FIGURE 6.18 $\delta^{15}N$ of soil organic matter as a function of the total N content of the soil in juniper woodlands of Utah. *Source: From Evans and Ehleringer (1993).*

adjacent well-drained soils in the same field (Sutherland et al. 1993). Strong enrichments in tropical soils suggest that gaseous losses may be a major pathway of nitrogen loss (Martinelli et al. 1999, Houlton et al. 2006, Koba et al. 2012).

Soil Phosphorus Cycling

Transformations of organic phosphorus in the soil are difficult to study because of the reaction of available phosphorus with various soil minerals (Figures 4.10 and 6.19). A few workers have examined phosphorus mineralization in soils using the buried-bag approach (e.g., Pastor et al. 1984), but in many cases there is no apparent mineralization because of the immediate complexation of P with soil minerals. Thus, most studies of phosphorus cycling have followed the decay of radioactively labeled plant materials (Harrison 1982) or measured the dilution of radioactive ^{32}P that is applied to the soil pool as a tracer (Walbridge and Vitousek 1987, Lopez-Hernandez et al. 1998). With the isotope-dilution technique, one must assume that ^{32}P equilibrates with all the chemical pools in the soil and that the only dilution of its concentration is by the mineralization of organic phosphorus (Kellogg et al. 2006). Unfortunately, these assumptions are not always valid, making the technique difficult to apply in many instances (Walbridge and Vitousek 1987, Di et al. 1997, Bunemann et al. 2007).

In the face of difficulty measuring P mineralization directly, many workers have used sequential extractions to quantify phosphorus availability in the soil (Hedley et al. 1982b, Stevenson 1986, Tiessen et al. 1984). Extraction with 0.5 M $NaHCO_3$ is a convenient index of labile inorganic and soluble organic phosphorus in many soils (Olsen et al. 1954, Sharpley

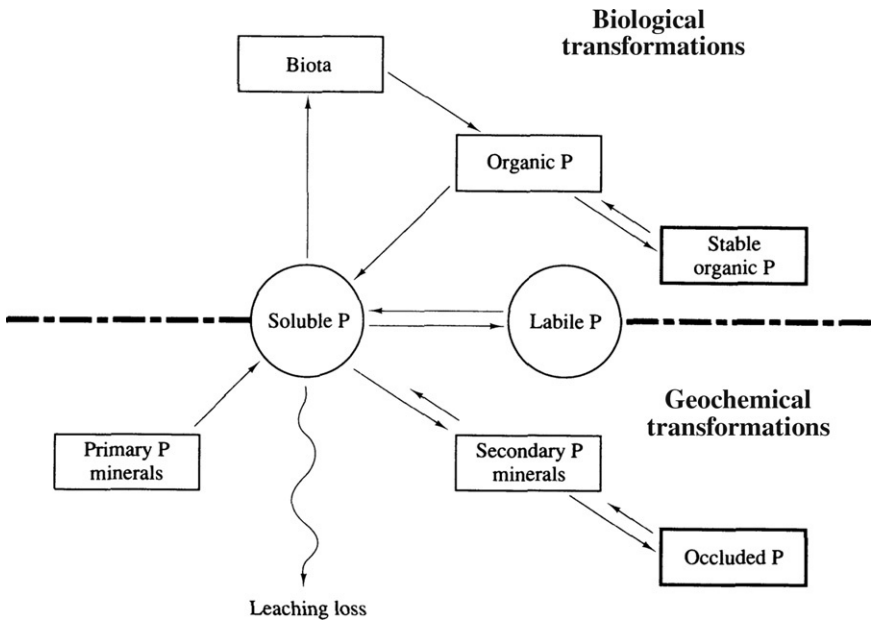

FIGURE 6.19 Phosphorus transformations in the soil. *Source: From Smeck (1985).*

et al. 1987). Organic P is often determined as the difference between PO_4 in a sample that has been combusted at high temperatures and an untreated sample (Stevenson 1986); microbial P, by the change in extractable phosphorus after fumigation with chloroform (Brookes et al. 1982, 1984).

Extraction with NaOH (to raise pH and lower anion adsorption capacity) indicates the amount of P that is held on Fe and Al minerals, while extraction with HCl releases P from many Ca-bound forms, including $CaCO_3$ (Tiessen et al. 1984, Cross and Schlesinger 1995). Acid-extractable phosphorus also includes P derived from apatite (Chapter 4), including secondary hydroxyapatite—$Ca_5OH(PO_4)_3$—from bones and fluoroapatite—$Ca_5F(PO_4)_3$—in teeth. These biominerals in soils are sometimes used by archeologists to determine the location of past human activity and settlements (Sjöberg 1976, Vitousek et al. 2004).

In most ecosystems, much of the phosphorus available for biogeochemical cycling is held in organic forms (Chapin et al. 1978, Wood et al. 1984, Yanai 1992, Gressel et al. 1996), especially inositol phosphates (Turner and Millward 2002). These organic forms can be isolated and identified using phosphorus-31 nuclear magnetic resonance spectroscopy (Turner et al. 2007, Turner and Engelbrecht 2011). Earlier we discussed the ability of soil microbes, mycorrhizae, and plant roots to release phosphatase enzymes and organic acids that mineralize P from organic and inorganic forms (see also Chapter 4).

Much of the P in decomposing materials is found in ester linkages (i.e., -C-O-P). These groups may be mineralized by the release of extracellular enzymes (e.g., phosphatases) in response to specific microbial demand for P (McGill and Cole 1981). Release of acid phosphatases by soil microbes is directly related to levels of soil organic matter (Tabatabai and Dick 1979, Polglase et al. 1992). During forest development, the phosphorus taken up from labile pools in the soil is replenished by P released from the anion adsorption and nonoccluded pools, which presumably equilibrate with the soil solution over longer periods (Richter et al. 2006).

Walbridge et al. (1991) found that up to 35% of the organic P in the undecomposed litter in a warm-temperate forest was held in microbial biomass, and Gallardo and Schlesinger (1994) found that additions of inorganic P increased the microbial biomass in the lower horizons of a forest soil in North Carolina, where the mineralogy is dominated by Fe and Al-oxide minerals with strong phosphorus adsorption capacity. Similar results are reported for tropical forests (Cleveland et al. 2002, Liu et al. 2012). P immobilization in microbial biomass also dominated P cycling in some European grasslands (Banemann et al. 2012). In the course of decomposition, organic phosphorus compounds move from the forest floor to the lower soil profile, where they accumulate in humus (Schoenau and Bettany 1987, Qualls and Haines 1991, Kaiser et al. 2003, Turner and Haygarth 2000).

Sulfur Cycling

Similar to phosphorus, the cycle of sulfur in the soil is affected by both chemical and biological reactions. Sulfur is derived from atmospheric deposition (Chapter 3) and from the weathering of sulfur-bearing minerals in rocks (Chapter 4), and the proportion from each source varies with location and soil development (Novak et al. 2005, Bern and Townsend 2008, Mitchell et al. 2011b). The concentration of SO_4^{2-} in the soil solution exists in equilibrium with sulfate adsorbed on soil minerals (Chapter 4). Plant uptake of SO_4^{2-} is followed by

assimilatory reduction and incorporation of sulfur into glutathione (Kostner et al. 1998) and the amino acids cysteine and methionine, which are incorporated into protein (Johnson 1984). The molecular structure of the S-reducing enzyme contains Fe as a cofactor (Crane et al. 1995). A small quantity of sulfur in plants is found in ester-bonded sulfates (-C-O-SO_4), and when soil sulfate concentrations are high, plants may accumulate SO_4 in leaf tissues (Turner et al. 1980).

In most soils, the majority of the S is held in organic forms (Bartel-Ortiz and David 1988, Mitchell et al. 1992, Houle and Carignan 1992) in a variety of compounds (Zhao et al. 2006, Schroth et al. 2007). Decomposition of plant tissues is accompanied by microbial immobilization of S (Saggar et al. 1981, Staaf and Berg 1982, Fitzgerald et al. 1984). Using ^{35}S as a radioisotopic tracer, Wu et al. (1995) found high rates of microbial immobilization of $^{35}SO_4^{2-}$ when glucose was added to soils (compare Houle et al. 2001). Downward movement of fulvic acids appears to transport organic sulfur compounds to the lower soil profile (Schoenau and Bettany 1987, Kaiser and Guggenberger 2005), where they are mineralized (Houle et al. 2001, Dail and Fitzgerald 1999). Typically, mineralization of SO_4^{2-} begins at C/S ratios <200 (Stevenson 1986). Sulfur in soil organic matter shows higher $\delta^{34}S$ than soil sulfate, suggesting that soil microbes discriminate against the heavy isotope of S in favor of ^{32}S during mineralization (Mayer et al. 1995). Most of the SO_4^{2-} in runoff waters appears to have passed through the organic pool (Likens et al. 2002, Novak et al. 2005).

In forest soils, the microbial immobilization of added SO_4^{2-} is greatest in the upper soil profile, and anion adsorption of inorganic SO_4^{2-} dominates the B horizons, where sesquioxide minerals are present (Schindler et al. 1986, Randlett et al. 1992, Houle et al. 2001). In most cases, the majority of microbial S is found in carbon-bonded forms (David et al. 1982, Watwood et al. 1988, Schindler et al. 1986, Mitchell et al. 1986, Dhamala and Mitchell 1995). Organic S appears to accumulate in areas of high inputs of SO_4^{2-} from acid rain (Likens et al. 2002, Armbruster et al. 2003). However, at the Coweeta Experimental Forest in North Carolina, a large portion of the immobilization of sulfur by soil microbes was accumulated as ester sulfates (Fitzgerald et al. 1985, Watwood and Fitzgerald 1988), yielding a significant sink for SO_4^{2-} deposited from the atmosphere (Swank et al. 1984). Despite the predominance of organic forms, the pool of SO_4^{2-} in most soils is not insignificant. In the study of a forest in Tennessee, Johnson et al. (1982) found that the pool of adsorbed SO_4^{2-} was larger than the total pool of S in vegetation by a factor of 15.

To maintain a charge balance, plant uptake and reduction of SO_4^{2-} consumes H^+ from the soil, whereas the mineralization of organic sulfur returns H^+ to the soil solution, producing no net increase in acidity (Binkley and Richter 1987). In contrast, reduced inorganic sulfur is found in association with some rock minerals (e.g., pyrite), and the oxidative weathering of reduced sulfide minerals accounts for highly acidic solutions draining mine tailings (Eqs. 2.16 and 4.6). This oxidation is performed by chemoautotrophic bacteria, generally in the genus *Thiobacillus*.

Production of reduced sulfur gases such as H_2S, COS (carbonyl sulfide), and $(CH_3)_2S$ (dimethylsulfide) is largely confined to wetland soils, since highly reducing, anaerobic conditions are required (Chapter 7). Globally, upland soils are only a small source of sulfur gases in the atmosphere (Lamb et al. 1987, Goldan et al. 1987, Staubes et al. 1989, Yi et al. 2010). However, many plants (e.g., garlic) produce a variety of volatile organic sulfur compounds that activate sensory receptors in humans and presumably other herbivores

(Bautista et al. 2005).[6] The smell of CS_2 (carbon disulfide) is often found when excavating the roots of the tropical tree *Stryphnodendron excelsum* (Haines et al. 1989), and many plant leaves are known to release sulfur gases during photosynthesis (Winner et al. 1981, Garten 1990, Kesselmeier et al. 1993).

Often the total net flux of sulfur gases from an ecosystem (soil + plant) is estimated by examining the vertical profile of gas concentrations in the atmosphere (e.g., Andreae and Andreae 1988). Hydrogen sulfide appears to dominate the release of sulfur gases from plants (Delmas and Servant 1983, Andreae et al. 1990, Rennenberg 1991). Terrestrial ecosystems also appear to be a source of $(CH_3)_2S$ during the day (Andreae et al. 1990, Berresheim and Vulcan 1992, Kesselmeier et al. 1993), but vegetation is a major sink for COS globally (Chapter 13).

Transformations in Fire

During fires, nutrients are lost in gases and in the particles of smoke (Andreae and Merlet 2001), and soil nutrient availability increases with the addition of ash to soil (Raison 1979, Giardina et al. 2000). Following fire, there is often increased runoff and erosion from bare, ash-covered soils. High rates of nitrification in these nutrient-rich soils can stimulate the loss of NO and N_2O after fire (Anderson et al. 1988, Levine et al. 1988).

Increases in the rate of forest burning worldwide have the potential to deplete the nutrient content of soils and add trace gases to the atmosphere (Mahowald et al. 2005a). However, before human intervention, fires were a natural part of the environment in many regions; thus, nutrient losses as a result of fire occurred at infrequent but somewhat regular intervals (Clark 1990). Using a mass-balance approach we can estimate the length of time it takes to replace the nutrients that are lost in a single fire. For instance, 11 to 40 kg/ha of N are lost in small ground fires in southeastern pine forests (Richter et al. 1982), equivalent to 3 to 12 times the annual deposition of N from the atmosphere in this region (Swank and Henderson 1976). In contrast, periodic losses of N in fires may dominate the long-term nitrogen budget in semi-arid forests—requiring hundreds of years of new inputs to replace the losses from a single fire (Johnson et al. 1998).

When leaves and twigs are burned under laboratory conditions, up to 90% of their N content can be lost, presumably as N_2 or as one or more forms of nitrogen oxide gases (DeBell and Ralston 1970, Lobert et al. 1990). Forest fires volatilize nitrogen in proportion to the heat generated and the organic matter consumed (DeBano and Conrad 1978, Raison et al. 1985, McNaughton et al. 1998); the rate of loss declines dramatically as fires pass from flaming to smoldering phases (Crutzen and Andreae 1990). Typically N losses in forest fires range from 100 to 600 kg/ha, or 10 to 40% of the amount in aboveground vegetation and surface litter (Johnson et al. 1998). Especially large losses are reported from slash fires in the Amazon rainforest (Kauffman et al. 1993).

Studies of the gaseous products of fires are often conducted by flying aircraft through the smoke plume to gather gas samples (e.g., Cofer et al. 1990, Nance et al. 1993, Hurst et al. 1994). The enrichment of CO_2 and CO over the atmospheric background is measured, as well as the

[6] The tasty compound in garlic is diallyl thiosulfinate or diallyl disulfide.

ratio of other gases to CO_2 in the smoke (e.g., NH_3/CO_2). Assuming that the carbon in the fuel is all converted to CO_2 and CO, the loss of other fuel constituents as gases and particles can be calculated from estimates of the carbon in the biomass consumed by fire and the ratio of the constituent in question to the total carbon ($CO_2 + CO$) in smoke (Laursen et al. 1992, Delmas et al. 1995). Thus, global estimates of the volatilization of nitrogen from forest fires can be calculated from global estimates of the amount of carbon lost in forest fires each year (Andreae and Merlet 2001, Schultz et al. 2008). N_2 dominates the gaseous loss of nitrogen (Kuhlbusch et al. 1991), constituting a form of "pyrodenitrification" that removes fixed nitrogen from the biosphere (Chapters 3 and 12).

The losses of other nitrogen gases in forest fires account for 6% of the N_2O, 15% of the NH_3, and 18% of the NO_x emitted annually to the atmosphere (Chapter 12). Tropospheric circulation can carry the plume of NO_x from fires in the boreal forest of Canada to Europe (Spichtinger et al. 2001). Forest fires are also a major global source of CO (Seiler and Conrad 1987; refer to Table 11.3) and smaller sources of CH_4 (Delmas et al. 1991, Quay et al. 1991), CH_3Br, CH_3Cl (refer to Table 3.7), and SO_2 in the atmosphere (Sanborn and Ballard 1991, Crutzen and Andreae 1990).

Air currents and updrafts during fire carry particles of ash that remove other nutrients from the site. These losses are usually much smaller than gaseous losses (Arianoutsou and Margaris 1981, Gaudichet et al. 1995). Expressed as a percentage of the amount present in aboveground vegetation and litter before fire, the total loss of plant nutrients in gases and particulates often follows the order $N \gg K > Mg > Ca > P > 0\%$. Differential rates of loss change the balance of nutrients available in the soil after fire (Raison et al. 1985), and nutrient losses to the atmosphere in fire may enhance the atmospheric deposition of nutrients in adjacent locations (Clayton 1976, Lewis 1981).

Depending on intensity, fire kills aboveground vegetation and transfers varying proportions of its mass and nutrient content to the soil as ash. There are a large number of changes in chemical and biological properties of soil as a result of the addition of ash (Raison 1979). Cations and P may be readily available in ash, which usually increases soil pH (Woodmansee and Wallach 1981). Burning increases extractable P, but reduces the levels of organic P and phosphatase activity in soil (DeBano and Klopatek 1988, Saa et al. 1993, Serrasolsas and Khanna 1995). Nitrogen in the ash is subject to rapid mineralization and nitrification (Christensen 1977, Dunn et al. 1979, Matson et al. 1987), so available NH_4^+ and NO_3^- usually increase after fire, even though total soil N may be unchanged (Wan et al. 2001). The increase in available nutrients as a result of ashfall is usually short-lived, as nutrients are taken up by vegetation or lost to leaching and erosion (Lewis 1974, Christensen 1977, Uhl and Jordan 1984). Enhanced emissions of NO and accumulations of nitrate after fire stimulate the germination of post-fire species (Keeley and Fotheringham 1997).

Stream-water runoff typically increases following fire because of reduced water losses in transpiration. High nutrient availability in the soil coupled with greater runoff can lead to large hydrologic losses of nutrients from ecosystems following burning. The loss of nutrients in runoff depends on many factors, including the season, rainfall pattern, and the growth of postfire vegetation (Dyrness et al. 1989). Wright (1976) noted significant increases in the loss of K and P from burned forest watersheds in Minnesota. These losses were greatest in the first 2 years after fire; by the third year there was actually less P lost from burned watersheds than from adjacent mature forests, presumably due to uptake by regrowing vegetation (McColl

and Grigal 1975; compare Saá et al. 1994). Although there are exceptions, the relative increase in the loss of Ca, Mg, Na, and K in runoff waters after fire often exceeds that of N and P (Chorover et al. 1994).

Ice cores and sediments contain a historical record of biomass burning. Layers of ice with buried ash often contain especially high concentrations of NH_4^+, indicating substantial NH_3 volatilization during fires (Legrand et al. 1992, Whitlow et al. 1994). Cores taken from the Greenland ice cap show episodes of increased biomass burning that appear to be related to the European colonization of North America (Whitlow et al. 1994, Savarino and Legrand 1998). Lake and ocean sediments contain layers of buried ash that indicate the frequency of fires (Mensing et al. 1999, Clark et al. 1996). It is likely that humans have significantly increased the rate of biomass burning worldwide, especially as a result of tropical deforestation (Crutzen and Andreae 1990, Cahoon et al. 1992).

The Role of Animals

Discussions of terrestrial biogeochemistry usually center on the role of plants and soil microbes. Having seen that animals harvest about 5% of terrestrial net primary production (Chapter 5), it is legitimate to ask if they might play a significant role in nutrient cycling. Certainly an impressive nutrient influx is observed in the soils below roosting birds (Gilmore et al. 1984, Mizutani and Wada 1988, Lindeboom 1984, Simas et al. 2007, Maron et al. 2006). In Yellowstone National Park, elk appear to redistribute plant materials among habitats in the landscape, increasing the nitrogen content and nitrogen mineralization in soils where they congregate (Frank et al. 1994, Frank and Groffman 1998). Soil $\delta^{15}N$ is higher in grazed soils, indicating greater N losses from the ecosystem (Frank and Evans 1997). Grazing in the Serengeti of Africa appears to stimulate nutrient cycling and plant productivity, providing better habitat for the animals (McNaughton et al. 1997).

Various workers have suggested that the grazing of vegetation, especially by insects, stimulates the intrasystem cycle of nutrients and might even be advantageous for terrestrial vegetation (Owen and Wiegert 1976). Trees that are susceptible to herbivory are often those that are deficient in minerals or otherwise stressed (Waring and Schlesinger 1985). Periodic herbivory may stimulate nutrient return to the soil via insect frass and alleviate nutrient deficiencies (Mattson and Addy 1975, Yang 2004). Risley and Crossley (1988) also noted significant premature leaf-fall in a forest that was subject to insect grazing. These leaves delivered large quantities of nutrients to the soil, since nutrient reabsorption had not yet occurred. In the same forest, Swank et al. (1981) noted an increase in stream-water nitrate when the trees were defoliated by grazing insects.

An enormous literature exists on the characteristics of plant tissues that are selected for food. Seasonal variations in the plants selected as food by large mammals may help these grazing animals avoid mineral deficiency (McNaughton 1990, Ben-Shahar and Coe 1992, Grasman and Hellgren 1993). Many studies report that herbivory is centered on plants with high nitrogen contents (Mattson 1980, Lightfoot and Whitford 1987, Griffin et al. 1998), suggesting that animal populations might be limited by N. However, the preference for such tissues may be related more to their high water (Scriber 1977) and low phenolic contents (Jonasson et al. 1986) than to a specific search for leaves with high amino acid content.

Grazing often reduces plant photosynthesis while nutrient uptake continues, resulting in high nutrient contents in the aboveground tissues that remain (McNaughton and Chapin 1985). Grazing may even enhance nitrogen uptake in some species (Jaramillo and Detling 1988). Thus, consumers sometimes increase the nutritional quality of the forage available for future consumption, although the quantity of defensive compounds may also increase (White 1984, Seastedt 1985).

In extreme cases, defoliations may be the dominant form of nutrient turnover in the ecosystem (Hollinger 1986). Usually, however, the role of grazing animals in terrestrial ecosystems is rather minor (Gosz et al. 1978, Woodmansee 1978, Pletscher et al. 1989), and certainly of limited benefit to plants (Lamb 1985). In fact, plants often show large allocations of net primary production to defensive compounds (Coley et al. 1985) and higher net primary production when they are relieved of pests (Cates 1975, Morrow and LaMarche 1978, Marquis and Whelan 1994).

At higher trophic levels, predators may also affect nutrient cycling in terrestrial ecosystems, inasmuch as they create local patches of nutrient-rich soil with the delivery of dead animals (Schmitz et al. 2010, Carter et al. 2007). Spawning salmon deliver nitrogen from the marine environment to streamside forests (Helfield and Naiman 2001, Ben-David et al. 1998), especially when bears prey on them (Hilderbrand et al. 1999). Similarly, sea turtles return nutrients to dune habitats, where they lay eggs (Bouchard and Bjorndal 2000, Hannan et al. 2007). When predators—foxes—were introduced to an Aleutian island, they disrupted nesting seabirds, which normally delivered nutrients from the marine environment to the soil (Maron et al. 2006).

The role of animals in litter decomposition is much more significant (Swift et al. 1979, Hole 1981, Seastedt and Crossley 1980). Nematodes, earthworms, and termites are particularly widespread and important in the initial breakdown of litter and the turnover of nutrients in the soil. Schaefer and Whitford (1981) found that termites were responsible for the turnover of 8% of litter N in a desert soil (Figure 6.20). An additional 2% of the pool of nitrogen in surface litter was transported belowground by their burrowing activities. When termites were excluded by the application of pesticides, decomposition slowed and surface litter accumulated. Because soil animals have short lifetimes, their nutrient contents are rapidly decomposed and returned to the intrasystem cycle (Seastedt and Tate 1981).

It is interesting to view the biogeochemistry of animals from another perspective: What is the role of biogeochemistry in determining the distribution and abundance of animals? The death of ducks and cattle feeding in areas of high soil selenium (Se) suggests that such interactions might be of widespread significance.

Plants have no essential role for sodium in their biochemistry, and naturally have low Na contents due to limited uptake and exclusion at the root surface (Smith 1976). On the other hand, sodium is an important, essential element for all animals. The wide ratio between the Na content of herbivores to that in their foodstuffs suggests that Na might limit mammal populations generally. Observations of Na deficiency are supported by the interest that many animals show in natural salt licks (Jones and Hanson 1985, Freeland et al. 1985, Smedley and Eisner 1995) and Na-rich plants (Botkin et al. 1973, Rothman et al. 2006). Weir (1972) suggested that the distribution of elephants in central Africa was at least partially dependent on sodium in seasonal waterholes, and McNaughton (1988) found that the abundance of ungulates in the Serengeti area was linked to Na, P, and Mg in plant tissues available

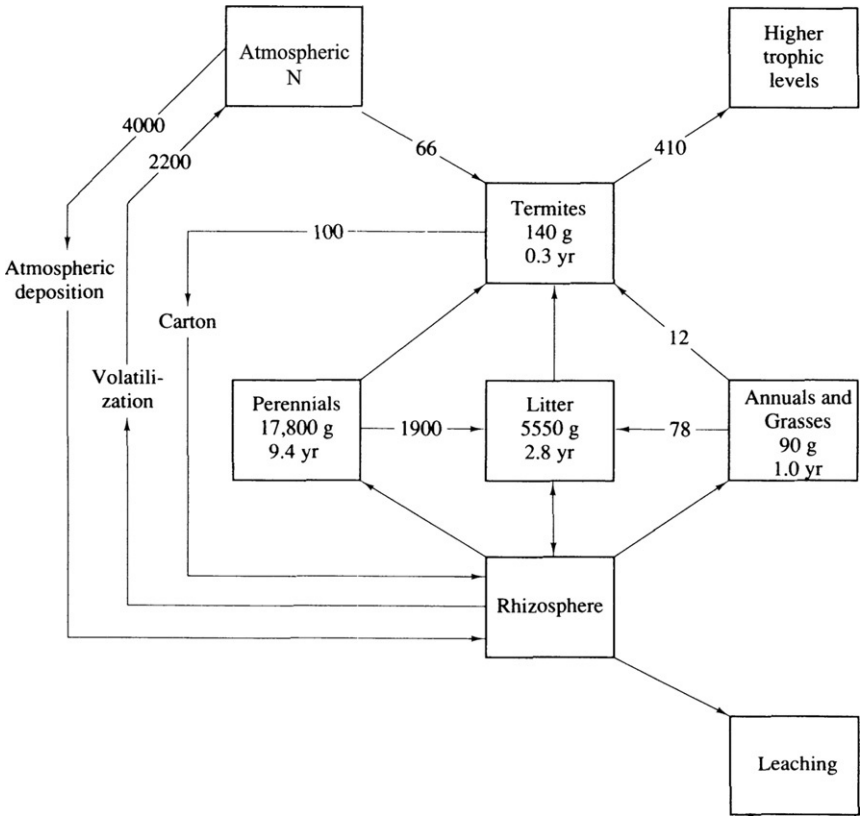

FIGURE 6.20 Nitrogen cycle in the Chihuahuan Desert of New Mexico, showing the role of termites in nitrogen transformations. Flux of nitrogen is shown along arrows in g N ha^{-1} yr^{-1}; nitrogen pools are shown in boxes with turnover time in years. *Source: From Schaefer and Whitford (1981). Used with permission of Springer.*

for grazing. Thus, animal populations may be affected by the availability of Na in natural ecosystems. Aumann (1965) found high rodent populations in areas of Na-rich soils, and speculated that the increased abundance of rodents in the eastern United States during the 1930s might have been due to a large deposition of Na-rich soil dust that was derived from the prairies during the "Dust Bowl." Such a case would link the abundance of animals to the biogeochemistry of soils and to soil erosion by wind in a distant region. Kaspari et al. (2009) suggest that the decomposition of litter by termites in tropical forests is mediated by the availability of sodium, derived from atmospheric deposition, which decreases inland from coastal areas.

CALCULATING LANDSCAPE MASS BALANCE

Elements are retained in terrestrial ecosystems when they play a functional role in biochemistry or are incorporated into organic matter. The pool of nutrients held in the soil and vegetation is many times larger than the annual receipt of nutrients from the atmosphere

and rock weathering (e.g., Table 6.4). In the Hubbard Brook Experimental Forest in New Hampshire, turnover times (mass/input) range from 21 years for Mg to >100 years for P in the vegetation and forest floor (Likens and Bormann 1995b, Yanai 1992). In contrast, for a nonessential element, sodium (Na), the turnover time is rapid (1.2 years), because Na is not retained by biota or incorporated into humus.

Because chlorine (Cl) is highly soluble, not strongly involved in soil chemical reactions (Chapter 4), and only a trace element in plant nutrition (White and Broadley 2001), chloride (Cl^-) has traditionally been used as a tracer of hydrologic flux through ecosystems (Juang and Johnson 1967). However, several studies (Oberg et al. 2005, Bastviken et al. 2007, Leri and Myneni 2010) show that some Cl is incorporated and retained in soil organic matter, partially compromising its use as a conservative tracer of geochemical processes when the overall Cl flux is small (Svensson et al. 2012). Some nonessential—even toxic—elements such as lead (Pb) that bind to organic matter may also accumulate in soils (Smith and Siccama 1981, Friedland and Johnson 1985, Dörr and Münnich 1989, Kaste et al. 2005). Even though Pb is not involved in biochemistry, its retention in the ecosystem is the result of the presence of biotic processes. Studies of the movement of Si, Cl, Pb, and mercury (Hg) in the Earth's terrestrial ecosystems all fall into the realm of biogeochemistry.

Annual mineralization, plant uptake, and litterfall result in a large internal cycle of elements in most ecosystems. Annual nitrogen inputs are typically 1 to 5 kg ha^{-1} yr^{-1}, while mineralization of soil nitrogen is 50 to 100 kg ha^{-1} yr^{-1} (Bowden 1986). Despite such large movements of available nutrients within the ecosystem, there are usually only small losses of N in streams draining forested landscapes (~3 kg N ha^{-1} yr^{-1}; Lewis 2002). The minor loss of nitrogen in stream water speaks strongly for the efficiency of biological processes that retain elements essential to biochemistry. Where plants are present, most nitrogen deposited from the atmosphere is taken up and recycled in the ecosystem (Durka et al. 1994), whereas in deserts, a substantial portion is lost (Michalski et al. 2004b).

Relatively few studies have included measurements of gaseous flux in ecosystem nutrient budgets (Schlesinger 2009). Losses of nitrogen in denitrification may explain why the retention of N applied in fertilizer is often somewhat lower than that of other elements (e.g., P and K), which have no gaseous phase (Stone and Kszystyniak 1977). Globally, denitrification may explain the tendency for the growth of most vegetation to be N limited, despite efficient plant uptake of N from the soil and only minor losses in stream water (Houlton et al. 2006; Chapter 12).

Allan et al. (1993) compared the mass balance of elements in small patches of forest occupying rock outcrops in Ontario. Areas of bare rock showed net losses of various elements, whereas adjacent patches of forest showed accumulations of N, P, and Ca in vegetation. We should not, however, expect that the essential biological nutrients will accumulate indefinitely in all ecosystems. The incorporation of N and P in biomass should be greatest when structural biomass and soil organic matter are accumulating rapidly—that is, in young ecosystems where there is positive net ecosystem production (Chapter 5). Losses of N should be higher in mature, steady-state ecosystems where the total biomass is stable (Vitousek and Reiners 1975, Davidson et al. 2007). The extent to which N is incorporated into biota may depend on its availability relative to other elements. For instance, lowland tropical rainforests forests, where vegetation growth is generally limited by P, appear to be "leaky" with respect to N relative to temperate forests (Martinelli et al. 1999, Brookshire et al. 2012).

Using the mass-balance approach, where

$$\text{Input} - \text{Output} = \Delta\text{Storage}, \tag{6.6}$$

Vitousek (1977) found greater losses of available N from old-growth forests than from younger sites in New Hampshire. Hedin et al. (1995b) confirmed high nutrient losses in old-growth forests of Chile, with forms of dissolved organic nitrogen being an important fraction of the total loss. The relatively high losses of N and P from the Caura River in Venezuela (Table 6.9) are consistent with the mature vegetation covering most of its watershed (Lewis 1986, compare Davidson et al. 2007).

In seasonal climates, losses of N and K in stream waters are usually minor during the growing season and greater during the winter period of plant dormancy (Likens and Bormann 1995, Likens et al. 1994). Often there is little seasonal variation in the loss of Na and Cl, which pass through the system under simple geochemical control (Johnson et al. 1969, Belillas and Rodà 1991b). Stream-water losses of nutrients give old-growth ecosystems the appearance of being "leaky," but it is important to recognize that outputs represent the excess of inputs over the seasonal demand for nutrients by vegetation and soil microbes (Gorham et al. 1979).

During long periods of soil development, chemical weathering depletes soils of the essential nutrients traditionally thought to be derived from bedrock, especially Ca and P (Figure 4.11). Thus, studying a 4-million-year-old sequence of soils in Hawaii, Chadwick et al. (1999) showed that small atmospheric inputs of phosphorus assume great importance to vegetation growing on ancient soils (Figure 6.21). Vegetation progressively shifts from N limitation to P limitation with soil age (Vitousek 2004, Richardson et al. 2004). Atmospheric inputs of phosphorus from the long-distance transport of desert dust seem essential to the continued productivity of tropical rainforests in Hawaii and the Amazon Basin (Gardner 1990, Okin et al. 2004, Bristow et al. 2010).

Indeed, using strontium (Sr) as a tracer, some workers have suggested that the vegetation in many regions is dependent on atmospheric inputs of elements traditionally associated with rock weathering (Graustein and Armstrong 1983, Miller et al. 1993, Kennedy et al. 1998). These observations are not universal; in areas of rapid geologic uplift and erosion, weathering is a persistent source of phosphorus and other plant nutrients that are derived from bedrock

TABLE 6.9 Annual Chemical Budgets for Undisturbed Forests in Various World Regions

		Chemical (kg ha^{-1} yr^{-1})			
Location and reference	**Precipitation (cm)**	**Ca**	**Cl**	**N**	**P**
British Columbia (Feller and Kimmins 1979)	240	15.8	2.9	−2.6	0
Oregon (Martin and Harr 1988)	219	41.2	—	−1.2	0.3
New Hampshire (Likens and Bormann 1995)	130	11.7	−1.6	−16.7	0
North Carolina (Swank and Douglass 1977)	185	3.9	1.7	−5.5	−0.1
Venezuela (Lewis et al. 1987, Lewis 1988)	450	14.2	−1.4	8.5	0.32
Brazil (Lesack and Melack 1996)	240	−0.52	3.58	−2.4	−0.04

Note: Total stream-water losses minus atmospheric deposition.

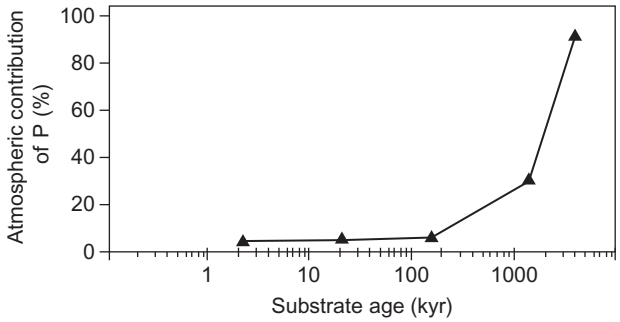

FIGURE 6.21 The relative importance of atmospheric inputs of phosphorus to ecosystems on the Hawaiian islands as a function of the age of the landscape. *Source: From Chadwick et al. (1999).*

(Bern et al. 2005, Porder et al. 2006). Generally, the long-term productivity of terrestrial vegetation may depend on periodic renewal of weatherable minerals (Wardle et al. 2004). Thus, biogeochemists must include both atmospheric and bedrock sources in ecosystem nutrient budgets, especially when these budgets are used to evaluate the impacts of changing levels of air pollution and atmospheric deposition on forest growth (e.g., Drouet et al. 2005, Mitchell et al. 2011a).

Among elements in short supply to biota, nitrogen is unique in that it is largely derived from the atmosphere (Table 4.5).[7] Net primary production in some temperate forests appears to show a correlation to N inputs in precipitation (Cole and Rapp 1981). Comparing forests from Oregon, Tennessee, and North Carolina, Henderson et al. (1978) noted strong N retention in each, despite a tenfold difference in N input from the atmosphere. The data suggest that plant growth is limited by N in each region. In contrast, losses of Ca were always a large percentage of the amount cycling in these forests. Especially on limestone soils, ample supplies of Ca were derived from rock weathering and Ca was not in short supply. Thus, abundant (e.g., Ca) and nonessential (e.g., Na) elements are most useful in estimating the rate of rock weathering (Chapter 4), whereas biogeochemistry controls the loss of scarce elements that are essential to life.

While most studies of ecosystem mass balance have considered watersheds, Baker et al. (2001) developed a nitrogen budget for the metropolitan ecosystem of Phoenix, Arizona, in which anthropogenic inputs (from food and pet food, combustion, and fertilizer) and gaseous outputs (NO_x and N_2) composed the largest movements of nitrogen (Table 6.10). Metson et al. (2011) formulated a similar assessment of the phosphorus budget for Phoenix. The ecosystem concept can even be applied to individual households to produce biogeochemical budgets for their inputs and outputs (Fissore et al. 2011). At the other extreme, Ti et al. (2012) compiled an input-output budget for nitrogen in all of mainland China. They found that chemical fertilizers, N fixation, and precipitation dominated the sources of nitrogen in this region, while denitrification, ammonia volatilization, and hydrologic export dominated the losses.

[7] Sedimentary and metasedimentary rocks usually contain a small amount of nitrogen, which can be released on weathering (Holloway and Dahlgren 2002). Nitrogen derived from bedrock can make a significant contribution to the nitrogen budget of some forests (Morford et al. 2011) and to the global sources of nitrogen for land plants (Chapter 12).

TABLE 6.10 Nitrogen Budget for the Phoenix Metropolitan Area

Inputs	**N flux (G g y^{-1})**
Surface water	1.2
Wet deposition	3.0
Human food	9.9
N-containing chemicals	5.8
Food for dairy cows	0.8
Pet food	2.7
Commercial fertilizer	24.3
Biological fixation	
Alfalfa	7.5
Desert plants	7.1
Fixation by combustion	36.3
Total inputs of fixed N	**98.4**
Outputs	
Surface water	2.6
Cows for slaughter	0.1
Milk	2.4
Atmospheric NO_x	17.1
Atmospheric NH_3	3.8
N_2O from denitrification	4.6
N_2 from denitrification	46.9
Total outputs	**77.5**
Accumulation (inputs-outputs)	20.9
Net subsurface storage	8.3
Landfills	8.6
Increase in human biomass	0.2

Source: Modified from Baker et al. 2001.

Many of the transformations in biochemistry involve oxidation and reduction reactions that generate or consume acidity (H^+). For instance, H^+ is produced during nitrification and consumed in the plant uptake and reduction of NO_3^-. Binkley and Richter (1987) review these processes and show how ecosystem budgets for H^+ may be useful as an index of net change in ecosystem function, particularly as soils acidify during ecosystem development (Chapter 4). H^+-ion budgets are also useful as an index of human impact, especially from acid

rain and excess nitrogen deposition (Driscoll and Likens 1982). For example, a net increase in acidity is expected when excess NH_4^+ deposition is subject to nitrification, with the subsequent loss of NO_3^- in stream water (van Breemen et al. 1982). H^+ budgets are analogous to measurements of human body temperature. When we see a change, we suspect that the ecosystem is stressed, but we must look carefully within the system for the actual diagnosis.

HUMAN IMPACTS ON TERRESTRIAL BIOGEOCHEMISTRY

Acid Rain

Forest growth has declined in many areas that are downwind of air pollution (Savva and Berninger 2010). In addition to the direct effects of ozone and other gaseous pollutants on their growth, plants in these areas are subject to "acid rain"—perhaps better named *acid deposition*, since some of the acidity is delivered as dryfall (Chapter 3). While all rain is naturally somewhat acidic (Chapter 13), human activities can produce rain of exceptional low pH as a result of NO_3^- and SO_4^{2-} that are derived from the dissolution of gaseous pollutants in raindrops (Eqs. 3.26–3.30). The chemical inputs in acid rain affect several aspects of soil chemistry and plant nutrition, leading to changes in plant growth rates.

Inputs of H^+ in acid rain increase the rate of weathering of soil minerals, the release of cations from cation exchange sites, and the movement of Al^{3+} into the soil solution (Chapter 4). At the Rothamsted Experimental Station in the United Kingdom, soil pH declined from 6.2 to 3.8 between 1883 and 1991, in association with acid rainfall (Blake et al. 1999). Depending on the underlying parent rocks, the forest floor and soil exchange capacity may be substantially depleted of Ca^{2+} in areas of acid deposition (Miller et al. 1993, Wright et al. 1994, Likens et al. 1996, Johnson et al. 2008a). Forests in the Adirondack Mountains of New York lost 64% of their soil Ca between 1930 and 2006 (Bedison and Johnson 2010).

Field experiments simulating acid rain show the depletion of cations on soil cation exchange sites and mobilization of Al^{+3} (Fernandez et al. 2003). Between 1984 and 2001 the loss of Ca from soils in the northeastern United States was closely balanced with an increase in Al on the cation exchange sites (Warby et al. 2009). High concentrations of Al^{3+} may reduce the plant uptake of Ca^{2+} and other cations (Godbold et al. 1988, Bondietti et al. 1989), and in the northeastern United States forest growth appears to decline as a result of a decreased Ca/Al ratio in the soil solution (Shortle and Smith 1988, Cronan and Grigal 1995). In a spruce forest of New England, Bullen and Bailey (2005) document decreasing Ca, Sr, and other cations and increasing Al in tree rings during the past century of acid inputs. Losses of Al from the mineral soil horizons are also associated with the mobilization of Al-bound phosphorus (SanClements et al. 2010).

Bernier and Brazeau (1988a, 1988b) link dieback of sugar maple to deficiencies of K on areas of low-K rocks and to deficiencies of Mg on low-Mg granites in southeastern Quebec. Magnesium deficiencies are also seen in the forests of central Europe, where forest decline is linked to an imbalance in the supply of Mg and N to plants (Oren et al. 1988, Berger and Glatzel 1994). Graveland et al. (1994) suggest that the effects of acid rain are also seen at higher trophic levels; in the Netherlands, birds showed poor reproduction in forests subject

to acid rain as a result of a decline in the abundance of snails, which are the main source of Ca for eggshell development. Similar effects are potentially related to the decline of the Wood Thrush in eastern North America (Hames et al. 2002).

With an abatement of air pollution, the acidity of rainfall has declined in many areas of the eastern United States and Europe, commencing a slow recovery of soils and vegetation, especially in sites where Ca has been strongly depleted from the soil (Palmer et al. 2004). Soil pH increased in England and Wales between 1978 and 2003, presumably as a result of lower emissions of sulfur dioxide and lower levels of acid rain (Kirk et al. 2010). Atmospheric inputs of Ca in dryfall can assume special significance in the rejuvenation of soil cation exchange capacity (Drouet et al. 2005). When researchers added 1.2 tons Ca per hectare as the mineral wollastonite ($CaSiO_3$) to the forest at Hubbard Brook, New Hampshire, the addition restored soil Ca (Cho et al. 2010), ameliorated the effects of acidity on the growth of sugar maple (Juice et al. 2006), and reduced losses of nitrogen (Groffman and Fisk 2011).

It is important to note that soil acidity can derive from a number of causes. During forest growth, the accumulation of cations in biomass leads to greater soil acidity (Berthrong et al. 2009). For a U.S. forest in South Carolina, Markewitz et al. (1998) attribute 62% of soil acidity to plant uptake and 38% to atmospheric deposition. Permanent increases in soil acidity will result if the new inputs of cations during a forest growth cycle are less than the removals in harvest. Similarly, the use of NH_4^+ fertilizers, which generate H^+ during nitrification, appears responsible for the acidification of agricultural soils in China (Guo et al. 2010).

Nitrogen Saturation

Currently, the deposition of available nitrogen from the atmosphere in the northeastern United States and western Europe ($\sim$10 kg N ha^{-1} yr^{-1}) is about five times greater than that recorded under pristine conditions.[8] The excess nitrogen derives from combustion of fossil fuels (releasing NO_x) and agricultural activities (releasing NH_3) upwind (Fang et al. 2011). Many workers have speculated that excess nitrogen deposition may act as fertilizer—stimulating the growth of trees. Indeed, the added nitrogen could lead to significant enhanced growth and carbon storage in forests, enhancing the removal of CO_2 from the atmosphere (Thomas et al. 2010, Magnani et al. 2007; but see Sutton et al. 2008, Hogberg 2012). Fertilizer experiments show that some of the added nitrogen also accumulates in soil organic matter (Nave et al. 2009, Gardner and Drinkwater 2009), enhancing carbon storage in soils (Nadelhoffer et al. 2004, Pregitzer et al. 2008, Hyvonen et al. 2008, Liu and Greaver 2010). Surprisingly, even though most forests are nitrogen-limited, plant uptake of exogenous nitrogen is usually only 10 to 30% of that applied (Schlesinger 2009, Pregitzer et al. 2010).

In some areas of high nitrogen deposition, particularly at high elevations, forest decline is observed as the ecosystem becomes saturated with nitrogen (Aber et al. 1998, 2003; McNulty et al. 2005; Lovett and Goodale 2011). In these sites, nitrification rates increase dramatically, yielding higher losses of NO_3^- in stream waters (Peterjohn et al. 1996, Corre et al. 2003, Lu et al. 2010) and greater emissions of N_2O to the atmosphere (Brumme and Beese 1992, Peterjohn et al. 1998, Venterea et al. 2003). While the losses of nitrogen to stream waters

[8] See, for example, *http://nadp.sws.uiuc.edu/maplib/pdf/2010/TotalN_10.pdf*.

are normally dominated by dissolved organic nitrogen (DON) in areas of excessive nitrogen deposition, NO_3^- becomes increasingly dominant (Perakis and Hedin 2002, Lovett et al. 2000, Lutz et al. 2011). Forests receiving high nitrogen deposition show higher $\delta^{15}N$ in canopy foliage, indicative of a high rate of nitrification, and NO_3^- losses in streams increase (Pardo et al. 2007).

Along three gradients of increasing air pollution in southern California, Zinke (1980) showed that N content in the foliage of Douglas fir increased from 1% to more than 2%, while P content decreased abruptly, changing the ratios of N to P from about 7 in relatively pristine areas to 20 to 30 in polluted areas. Such an imbalance in leaf N/P ratios is also seen in the Netherlands, in areas of excessive inputs of NH_4^+ from the atmosphere (Mohren et al. 1986). Historical collections show increasing nitrogen concentrations in some plants during the past century (Peñuelas and Filella 2001), perhaps indicating a shift of the terrestrial biosphere away from N deficiency (Elser et al. 2007). Nevertheless, in areas of high N deposition, forests show only scattered evidence of P deficiency (Gress et al. 2007, Finzi et al. 2009, Weand et al. 2010).

The symptoms of nitrogen saturation vary as a function of underlying site fertility, species composition, and other factors. Lovett and Goodale (2011) stress the importance of the rate of N input to the rate of N uptake by plants and soil microbes in controlling the appearance of nitrogen saturation and enhanced N loss. Low fertility sites may show only small changes in nitrification because plants take up the excess N deposition from the atmosphere (Fenn et al. 1998, Lovett et al. 2000). Without specific field experiments, it is often difficult to separate the effects of acid rain from those of excess nitrogen, since a large fraction of the nitrogen deposited from the atmosphere arrives as nitric acid, and inputs of NH_4^+ generate acidity if they are nitrified (Stevens et al. 2011). Temperate forests have been studied most extensively, but it is likely that these effects will be increasingly found in tropical regions, where P limitation predominates (Hall and Matson 1999, Koehler et al. 2009, Corre et al. 2010, Cusack et al. 2011, Hietz et al. 2011).

Nitrogen saturation is reversible. With experimental reductions of nitrogen inputs in areas of high deposition, the rates of nitrification and the loss of NO_3^- to stream waters decline (Quist et al. 1999, Corre and Lamerdorf 2004, Lutz et al. 2012b).

Rising CO_2 and Global Warming

Rising concentrations of CO_2 in Earth's atmosphere appear to stimulate the growth and carbon storage of land plants by enhancing plant photosynthesis (Chapter 5). Early greenhouse studies suggested that this response might be short-lived because of soil nutrient limitations (Thomas et al. 1994a). Several workers postulated a progressive nutrient limitation of field plants grown at high CO_2 (Luo and Reynolds 1999, Luo et al. 2004); however, some experiments that exposed intact forests to high CO_2 show a positive response to CO_2 that lasts up to a decade (Finzi et al. 2006). Some of the greater nutrient demand by faster growing plants is met by greater nutrient-use efficiency in photosynthesis (Springer et al. 2005), greater nutrient reabsorption before leaf abscission (Finzi et al. 2002, Norby et al. 2001), and greater allocation of carbon to root exudates that stimulate the decomposition of soil organic matter and nutrient mineralization (Drake et al. 2011, Phillips et al. 2011b).

Plants also respond to elevated CO_2 with greater root growth, which appears to explore the soil nutrient pool more fully (Norby and Iversen 2006, Hungate et al. 2006, Pritchard et al. 2008b, Finzi et al. 2007, Jackson et al. 2009). The duration of the positive growth response

of plants to high CO_2 in field experiments is surprising; eventually, stoichiometric constraints, such as the C/N ratio in plant biomass, will limit the amount of carbon that can be sequestered in woody biomass and soils in the absence of exogenous inputs of N (Johnson 2006, van Groenigen et al. 2006). Indeed, nitrogen appears to constrain long-term growth response at the FACE experiment at Oak Ridge, Tennessee (Norby et al. 2010, Garten et al. 2011).

Soil-warming experiments, designed to simulate ongoing climate change, typically show an increase in soil nitrogen mineralization (Van Cleve et al. 1990, Rustad et al. 2001, Shaw et al. 2001, Melillo et al. 2002). The change in soil microbial activity mobilizes nitrogen for plant uptake, potentially enhancing plant growth and carbon uptake. In wet tundra, soil warming stimulated the rate of decomposition, but caused only a small increase in plant growth in field experiments (Johnson et al. 2000b, Mack et al. 2004, Shaver et al. 2006). In contrast, in temperate forest ecosystems, soil warming stimulates nitrogen mineralization, plant carbon uptake, and net carbon sequestration in aboveground tissues (Melillo et al. 2011). In some areas, where the loss of the insulating effect of a winter snow pack results in frozen soils, nitrogen mineralization rates are likely to decline under warmer, future climatic conditions (Groffman et al. 2009).

SUMMARY

Interactions between plants, animals, and soil microbes link the internal biogeochemistry of terrestrial ecosystems. Plants adapted to low nutrient availability have low nutrient contents and higher nutrient reabsorption before leaf-fall, yielding higher nutrient-use efficiency (Figure 6.22). In some cases these characteristics can be induced by experimental treatments that reduce nutrient availability. For instance, when Douglas fir were fertilized with sugar, which increases the C/N ratio of the soil and the immobilization of N by microbes, reabsorption of foliar N increased, implying greater nutrient-use efficiency by the trees (Turner and

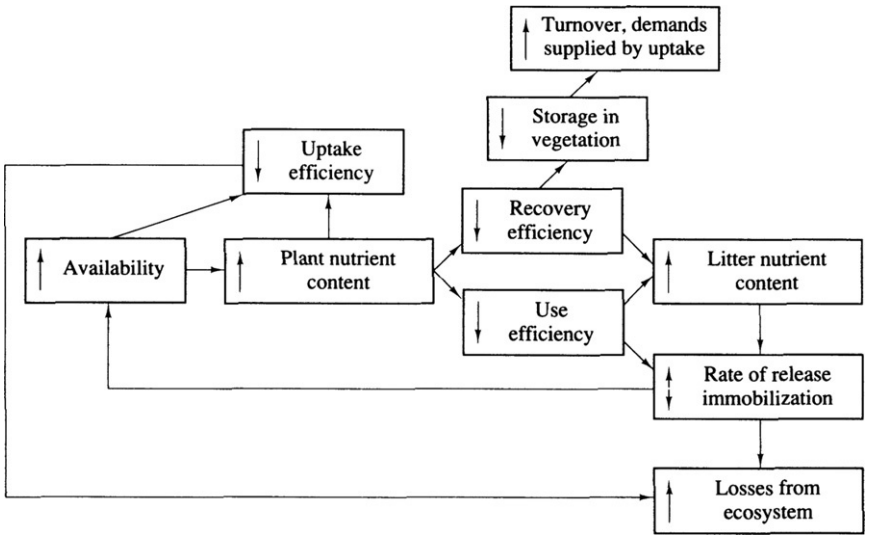

FIGURE 6.22 Changes in internal nutrient cycling that are expected with changes in nutrient availability. *Source: From Shaver and Melillo (1984). Used with permission of the Ecological Society of America.*

Olson 1976). Internal cycling by the vegetation may partially alleviate nutrient deficiencies, but decomposition of nutrient-poor litterfall is slow, further exacerbating the low availability of nutrients in the soil (Hobbie 1992, Lovett et al. 2004). Thus, nutrient-poor sites are likely to be occupied by vegetation that is specially adapted for long-term persistence under such conditions (Chapin et al. 1986b). In turn, the vegetation leaves its imprint on microbial activity and soil properties (Lovett et al. 2004, Reich et al. 2005).

Biogeochemistry controls the distribution and characteristics of vegetation at varying scales. Continental distributions of vegetation, such as the widespread dominance of conifers in the boreal regions, are likely to be related to the higher nutrient-use efficiency of evergreen vegetation under conditions of limited nutrient turnover in the soil. The effect of soil properties on the regional distribution of vegetation is seen in the occurrence of evergreen vegetation on nutrient-poor, hydrothermally altered soils in arid and semiarid climates (Figure 6.23). Fine-scale spatial heterogeneity of soil properties, as recorded by Robertson et al. (1988) for a field in Michigan, has been linked to the maintenance of diversity in land plant communities (Tilman 1985), and several studies show the importance of local soil conditions to the distribution and abundance of forest and grassland herbs (Snaydon 1962, Pigott and Taylor 1964, Lechowicz and Bell 1991, John et al. 2007). Additions of fertilizer tend to reduce the species diversity of plant communities (Huenneke et al. 1990, Wedin and Tilman 1996, Stevens et al. 2006, Cleland and Harpole 2010).

Linkages among components of the intrasystem cycle suggest that an integrative index of terrestrial biogeochemistry might be derived from the measure of a single component, such as the chemical characteristics of the leaf canopy (Matson et al. 1994). Wessman et al. (1988b) analyzed the spectral reflectance of leaf tissues in the laboratory as a first step toward developing an index of forest canopies by remote sensing. Their data show a strong correlation between nitrogen and lignin measured by infrared reflectance and by traditional laboratory analyses. Several workers now use satellite measurements of reflectance to characterize canopy properties (Martin and Aber 1997, Asner and Vitousek 2005, Kokaly et al. 2009, Ollinger 2011).

In the White Mountains of New Hampshire, forest productivity appears related to canopy nitrogen content, as measured by remote sensing (Figure 6.24; Ollinger and Smith 2005,

FIGURE 6.23 Occurrence of *Pinus ponderosa* and *Pinus jeffreyi* on acid, nutrient-poor hydrothermally altered andesites in the Great Basin Desert of Nevada, with *Artemisia tridentata* occurring on adjacent desert soils, of higher pH and phosphorus availability. *Sources: Schlesinger et al. (1989) and Gallardo and Schlesinger (1996).*

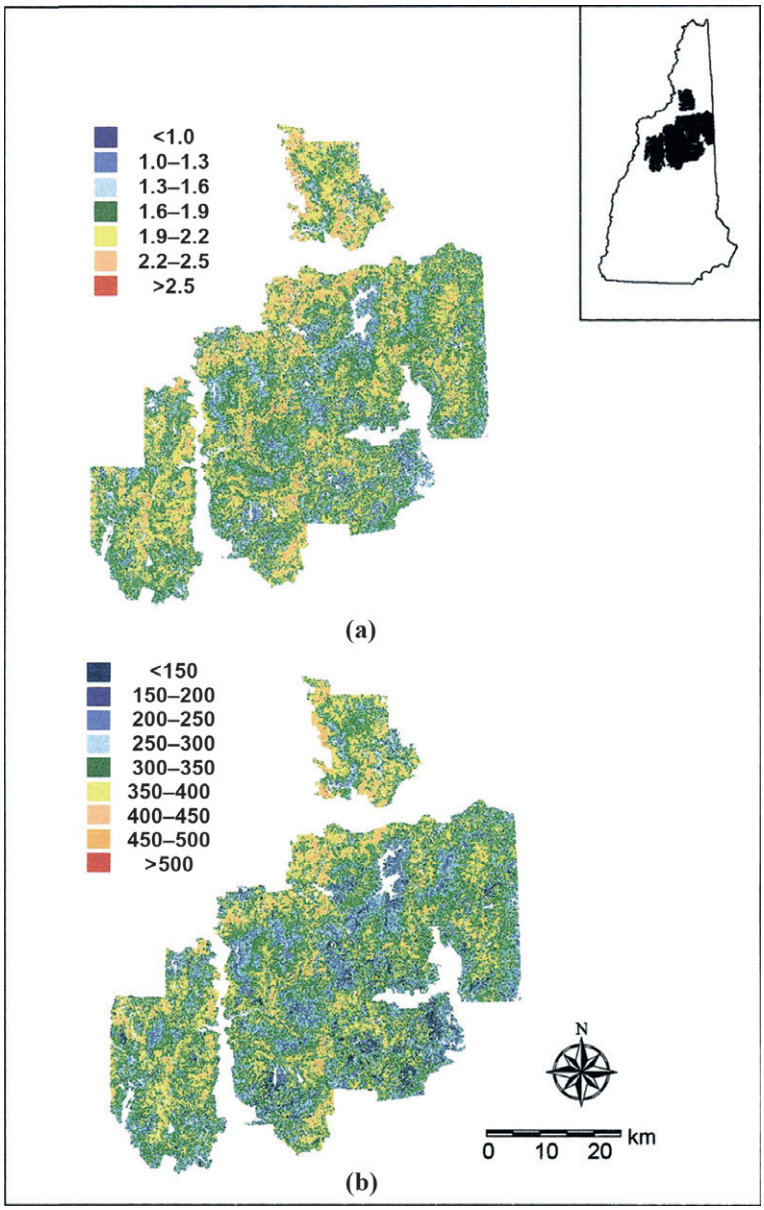

FIGURE 6.24 Spatial variation of canopy nitrogen and forest wood production in central New Hampshire, as estimated from the AVIRIS satellite. (a) Whole-canopy nitrogen concentration (%). (b) Aboverground woody biomass production ($g \cdot M^{-2} \cdot yr^{-1}$). *Source: From Smith et al. (2002). Used with permission of the Ecological Society of America.*

Ollinger et al. 2008), and variations of leaf C/N ratio across sites provide a convenient index of the intrasystem cycle of nutrients (Ollinger et al. 2002). Recognizing that decomposition is frequently controlled by the lignin and nitrogen content of litter (refer to Figure 6.11), remote sensing of canopy characteristics has potential for comparative regional studies of nutrient cycling in different plant communities (Myrold et al. 1989). Canopy lignin, measured by aircraft remote sensing, was highly correlated to soil nitrogen mineralization in Wisconsin forests (Wessman et al. 1988b, Pastor et al. 1984). These studies reinforce our appreciation of the linkage between vegetation and soil characteristics, as outlined in Figure 6.22.

Various models demonstrate other linkages between plant and soil processes in terrestrial biogeochemistry. Walker and Adams (1958) suggested that the level of available phosphorus during soil development was the primary determinant of terrestrial net primary production, since nitrogen-fixing bacteria depend on a supply of organic carbon and available phosphorus. They use the level of organic carbon in the soil as an index of terrestrial productivity and suggest that organic carbon peaks midway during soil development and then declines as an increasing fraction of the phosphorus is rendered unavailable by precipitation with secondary minerals (Figure 4.11). The model is consistent with observations of the increasing limitation of NPP by phosphorus during soil development (Chadwick et al. 1999, Richardson et al. 2004).

Numerous workers have examined the Walker and Adams (1958) hypothesis in various ecosystems. Tiessen et al. (1984) found that available phosphorus explained 24% of the variability of organic carbon in a collection of 168 soils from eight different soil orders. Roberts et al. (1985) found a similar relationship between bicarbonate-extractable P and organic carbon in several grassland soils of Saskatchewan. Raghubanshi (1992) found that phosphorus was well correlated to soil organic matter, soil nitrogen, and nitrogen mineralization rates in dry tropical forests of India. Thus, available phosphorus explains some, but not all, of the variation in soil organic carbon, which is ultimately derived from the production of vegetation. The linkage of phosphorus and carbon is likely to be strongest during early soil development, when both organic phosphorus and carbon are accumulating. The importance of organic phosphorus increases during soil development, and through the release of phosphatase enzymes, vegetation interacts with the soil pool to control the mineralization of P.

Parton et al. (1988) present a model linking the cycling of C, N, P, and S in grassland ecosystems. The flow of carbon is shown in Figure 6.25. The nitrogen cycling submodel has a similar structure, since the model assumes that most nitrogen is bonded directly to carbon in amino groups (McGill and Cole 1981). Lignin controls decomposition rates and nitrogen is mineralized from soil pools when critical C/N ratios are achieved during the respiration of carbon. Phosphorus availability is controlled by a modification of a model first presented by Cole et al. (1977), which includes C/P control over mineralization of organic pools and geochemical control over the availability of inorganic forms as in Figure 6.19. However, unlike N, C/P ratios in plant tissues and soil organic matter are allowed to vary widely as a function of P availability.

The complete model was used to predict patterns of primary production and nutrient mineralizations during 10,000 years of soil development (Figure 6.26). Net primary production and accumulations of soil organic matter are strongly linked to P availability during the

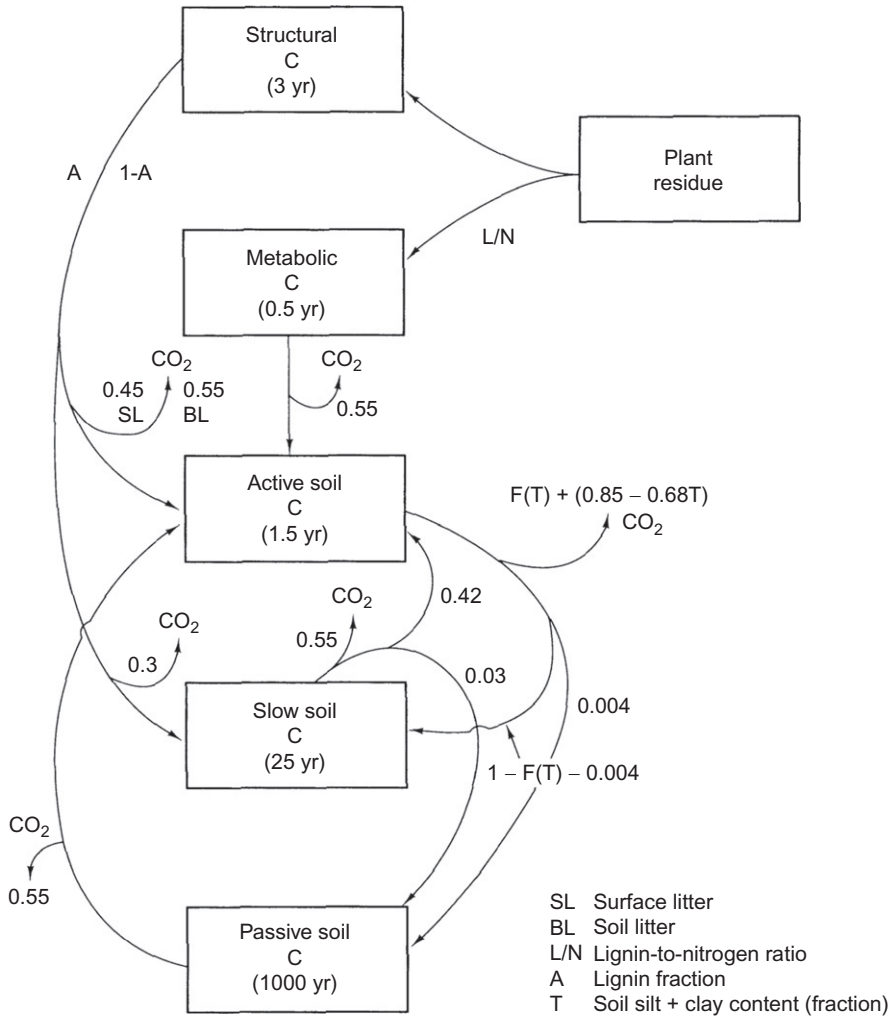

FIGURE 6.25 Flow diagram for carbon in the CENTURY model. The proportion of carbon moving along each flowpath is shown as a fraction, and turnover times for reservoirs are shown in parentheses. *Source: From Parton et al. (1988). Used with permission of Springer.*

first 800 years, after which increases in plant production are related to increases in soil N mineralization. Organic P increases throughout the 10,000-year sequence. In simulations of the response of native soils to cultivation, the model predicted a correlated decline in the native levels of organic carbon and nitrogen in the soil, but a relatively small decline in P. Validation of the model is seen in the data of Tiessen et al. (1982), who found declines of 51% for C and 44% for N, but only 30% for P in a silt loam soil cultivated for 90 years in Saskatchewan.

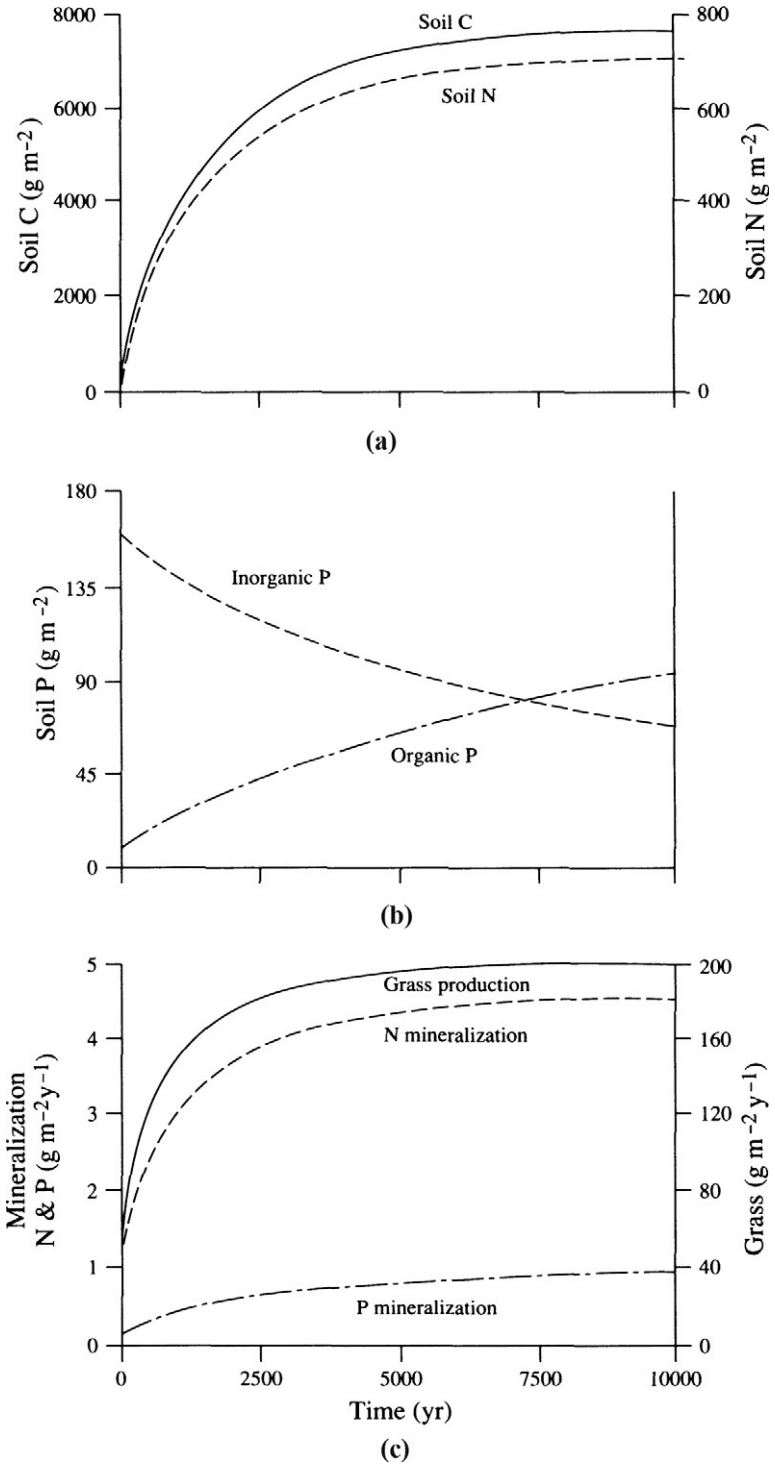

FIGURE 6.26 Simulated changes in soil C, N, and P during 10,000 years of soil development in a grassland, using the CENTURY model. *Source: Parton et al. (1988). Used with permission of Springer.*

Recommended Readings

Aber, J.D., and J.M. Melillo. 2001. *Terrestrial Ecosystems*. Academic Press/Elsevier.
Agren, G.L. and F.G. Andersson. 2011. *Terrestrial Ecosystem Ecology*. Cambridge University Press.
Dobrovolsky, V.V. 1994. *Biogeochemistry of the World's Land*. CRC Press.
Johnson, D.W., and S.E. Lindberg (Eds.). 1992. *Atmospheric Deposition and Nutrient Cycling*. Springer-Verlag.
Likens, G.E., and F.H. Bormann. 1995. *Biogeochemistry of a Forested Ecosystem*, second ed. Springer-Verlag.
Marschner, P., and Z. Rengel (Eds.). 2007. *Soil Biology: Nutrient Cycling in Terrestrial Ecosystems*. Springer-Verlag.
Paul, E.A. 2007. *Soil Microbiology, Ecology and Biochemistry*, third ed. Academic Press/Elsevier.
Sterner, R.W., and J.J. Elser. 2002. *Ecological Stoichiometry*. Princeton University Press.
Vitousek, P.M. 2004. *Nutrient Cycling and Limitation*. Princeton University Press.
Wolfe, D.W. 2001. *Tales from the Underground*. Perseus.

PROBLEMS

1. For ryegrass (Table 6.2), what ratio of plant uptake of NH_4 and NO_3 will produce no change in the acidity of soil in the rooting zone?
2. Using data for the chaparral shrubland (Table 6.4), calculate nutrient-use efficiency (NPP/unit nutrient uptake) for each element. Speculate on why nutrient-use efficiency in this shrubland differs from that in the forests listed in Table 6.6.
3. What is the C/N ratio of carbonaceous chondrites, the Earth's crust, land plants, and terrestrial animals? What does this suggest about nitrogen availability to the biosphere?
4. If global net primary productivity on land is 60×10^{15} g C/yr, and the average C/N ratio of plant biomass is 100, what is the upper limit (i.e., maximum estimate) of oxygen used every year in microbial nitrification?
5. Assume that a forest soil contains 8000 kg N/ha and that each year 80 kg N/ha/yr are mineralized and half of those are nitrified and lost. There is very little isotopic fractionation during mineralization, but during nitrification ^{14}N molecules react up to $1.035\times$ faster than ^{15}N molecules. Assuming no new inputs to the soil, what is the change in $\delta^{15}N$ in the soil pool after one year? (Do not round the numbers as you perform this calculation.)