CHAPTER 4

Mineral Cycles

I. INTRODUCTION

The cycling of minerals through forest ecosystems is closely linked with those of water and carbon. Precipitation washes minerals from the atmosphere and deposits them on leaves and other surfaces. Water carries dissolved minerals into the soil where they are taken up by roots and transported in the transpiration stream. Water also carries minerals out of the system through erosion and by leaching. Plants respire carbon obtained through photosynthesis to convert minerals from elemental to biochemical forms, and to recycle nutrients internally from older to newer tissues. Heterotrophic and symbiotic organisms rely on carbon supplied from roots and that extracted from detritus to acquire their energy supply and nutrients. Low molecular weight acids produced as metabolic products enhance the release of additional minerals from soil and rock. Other products of microbial decomposition contribute to the accumulation of soil humus.

A general picture of the processes involved in the cycling of minerals through forest ecosystems is presented in Fig. 4.1. In this chapter we start with a discussion of plant processes by identifying the essential elements for growth and then explain how these are acquired, stored, and internally recycled within vegetation before being returned through detritus production and leachate to the forest floor. Next, we consider the relative importance of atmospheric inputs, biological fixation, and geologic weathering for supplying various nutrients to forest ecosystems. We then focus on litter processes to appreciate the slow rate at which detritus is converted to soil humus and the environmental factors that affect this important soil component. A discussion of soil processes follows to explain how soil profiles form and how shifts in the relative availability of nutrients may occur seasonally. Finally, we discuss those processes that hold minerals and nutrients within the soil profile, buffering the system against losses, and those that enhance losses through volatilization and leaching. Much larger losses of nutrients occur through erosion, harvesting, and fire, but these subjects are related to disturbance and will be deferred for discussion until Chapters 6 and 8.

Direct measurement of all the variables important in mineral cycling requires a large investment in equipment and chemical analyses, as indicated in Fig. 4.2. Above the forest canopy, instruments must be installed to collect chemistry samples of atmospheric deposition in fog, precipitation, and dust along with the normal meteorological variables. To assess the exchange of minerals from the canopy, litterfall, throughfall, and stemflow must be measured. In the soil, solution chemistry needs to be monitored through extracts acquired from lysimeters (Johnson and Lindberg, 1992) or ion-exchange resin columns (Giblin *et al.,* 1994). To complete a balance sheet, some measurements of solution losses below the rooting zone and gaseous losses from the soil and canopy are also required. Although a network of installations now exist to monitor atmospheric inputs in some countries, our ability to predict changes in mineral cycling rates through a wide variety of ecosystems requires that we incorporate as much mechanistic understanding as possible into ecosystem simulation models.

In some cases we can derive estimates of chemical fluxes and turnover rates through the analyses of isotopes of nitrogen, carbon, and strontium (Sr, a surrogate for calcium). Stable isotope analyses, and those associated with radioactive decay of carbon-14, have the added advantage of providing a historical record of changes in the rates of chemical deposition, uptake by vegetation, and export into lake sediments, against which model assumptions and predictions can be compared (see Chapter 5).

II. PLANT PROCESSES AFFECTING NUTRIENT CYCLING

A. Essential Elements

In addition to C, H, and O, all plants require certain macronutrients. Nitrogen (N) is a major constituent of proteins, nucleic acids, and chlorophyll; phosphorus (P) is most

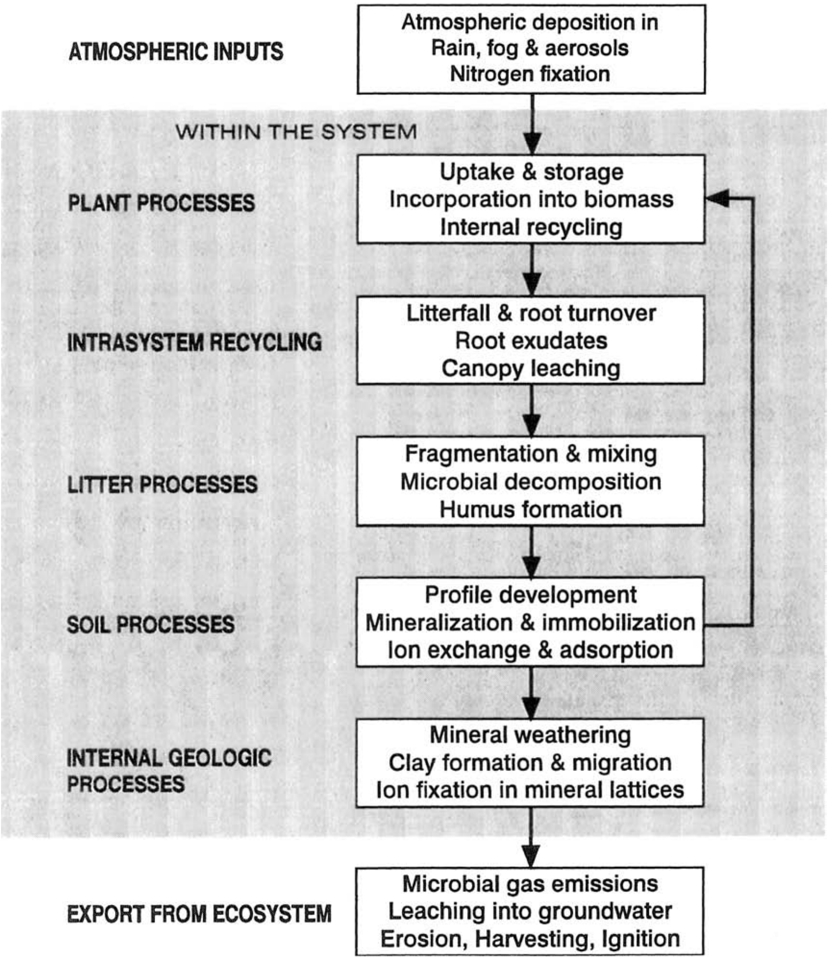

FIGURE 4.1. Minerals that cycle through a forest ecosystem have variable sources. Many are sequestered from the atmosphere; others are derived from geologic weathering of minerals. Plants modify the cycling of many elements through their selective uptake, internal redistribution, and the fraction returned annually to the forest floor. Litter on the forest floor is utilized by many soil organisms, but eventually a small fraction accumulates as soil humus. During the decomposition process, minerals are converted from organic to inorganic forms. Whether the elements are immobilized in microbial biomass, made available on soil exchange sites, adsorbed to clay surfaces, or fixed permanently into mineral lattices depends on a variety of soil and geologic processes that differ within the soil profile. Eventually some minerals are again taken up by plants and recycled through the system, while others may be lost as gases or in leachate. When disturbed, ecosystems may lose large amounts of elements through erosion, harvesting, and ignition, discussed in Chapter 6.

important as a component of the energy currency in biochemical reactions, and sulfur (S) is found in many amino acids. Specific roles are known for potassium (K) in controlling stomatal function and the charge balance across plant membranes, for calcium (Ca) as a constituent of cell walls, and for magnesium (Mg) in chlorophyll. These nutrients also stimulate the rate of various enzymatic reactions. The micronutrients iron (Fe), copper

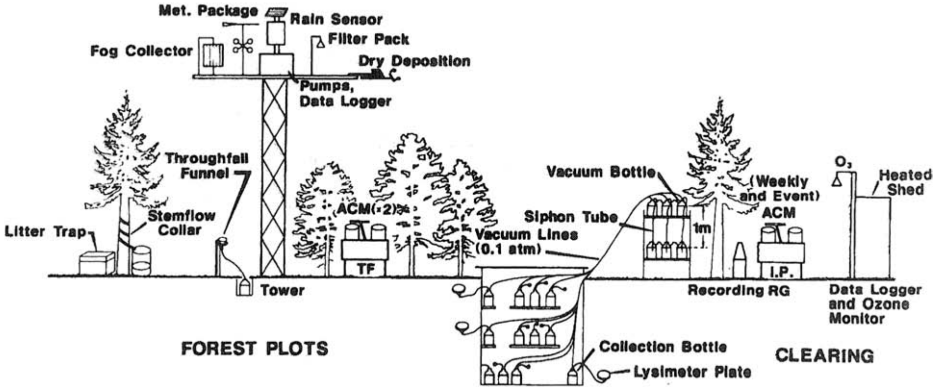

FIGURE 4.2. Schematic representation of equipment installed at 17 Integrated Forest Study (IFS) sites to evaluate the effects of atmospheric deposition and ozone levels on nutrient cycling. The IFS included a thorough analysis of air chemistry, hydrology, meteorology, and canopy, soil, and litter characteristics. Chemical changes in precipitation (with recording rain gauge, RG) and other forms of deposition were separately measured above and below the canopy, and at various depths in the soil. In addition, event and weekly accumulated measures of chemical (ACM) deposition as wet- and dryfall were collected as throughfall (TF) and precipitation intercepted by the canopy (I.P.). (Modified from *Atmospheric Deposition and Forest Nutrient Cycling,* Ecological Studies, Analysis and Synthesis, Volume 91, D. W. Johnson and S. E. Lindberg, eds., p. 3, Fig. 1.1, 1992, © 1992 by Springer-Verlag.)

(Cu), zinc (Zn), and manganese (Mn) are widely involved as coenzymes, whereas the essential roles of boron (B) and chlorine (Cl) are still poorly known. Grasses and some other plants accumulate silicon (Si) in cell walls, which provides strength and reduces tissue palatability to herbivores. Molybdenum (Mo) is essential for N metabolism in plant tissues, as well as for N fixation by symbiotic bacteria. Cobalt (Co) is essential for the microorganisms involved in N fixation. Although higher plants all require the same macronutrients, they differ in their selective accumulations, their microbial associations, and in the exudates and residues they produce. As a consequence, the amount and balance of nutrients sequestered in plant biomass affects soil fertility and forest productivity.

Nutrients must be available in appropriate forms and in sufficient amounts to meet growth requirements. Most plants exhibit rapid growth at the beginning of the growing season. To maintain a constant relative growth rate, even for a short period, requires that the flux of nutrients to growing points match the rate of expansion. Any reduction in the rate at which nutrients are supplied causes nutrient concentrations to drop in expanding tissue (Ingestad, 1982). A decrease in concentration may in turn alter carbon allocation patterns to roots, stem, and leaves (Chapter 3). To assess the nutrient balance of plants, four processes must be considered: uptake, storage, internal recycling, and return in litter. We will consider each in sequence.

B. Plant Uptake

Under field conditions, the concentration of nutrients in the soil solution is reduced during the period of exponential plant growth. Nutrients are supplied to plant root surfaces through three mechanisms: (1) the growth of roots and mycorrhizae into the soil; (2) the mass flow of ions with the movement of soil water as a result of transpiration; and (3) the diffusion of ions toward the root surface when uptake rates exceed supply (Eissenstat and Van Rees, 1994). The relative mobility and concentration of nutrients in soil solution and the rate of plant uptake determine which of these mechanisms predominates. Uptake of Ca is often the result of the interception of ions in newly exploited soil zones. Mass flow is important for Mg, SO_4^{2-}, and Fe. Plant demand for N, P, and K often exceeds delivery by mass flow, such that diffusion is the dominant process that supplies these macronutrients (Eissenstat and Van Rees, 1994).

Mycorrhizal fungi provide plants special advantages in accessing some forms of nutrients. Mycorrhizae can access films of water on soil particles not available to the smallest diameter roots because fungal hyphae have an average diameter of about 5 μm whereas the smaller diameter tree roots average 0.5 mm in diameter (Yanai *et al.,* 1995). Assuming the same construction cost, investment in a gram of mycelia provides 10^4 greater length than a gram invested in small-diameter roots and a hundredfold increase in surface area to extract water and nutrients. In temperate regions, many trees are infected by *ectotrophic mycorrhizae.* These form a hyphal sheath that surrounds the active fine roots of trees and many other plants and extend an additional network of hyphae into the soils. Most tree roots are infected by *endotrophic mycorrhizae* in which fungal hyphae penetrate the cells of the root cortex but do not form a sheath around the roots.

Mycorrhizal fungi, like other fungi, have their own extracellular enzymes, so they are able, with carbohydrates provided by plants, to extract at least some nitrogen and phosphorus directly from organic matter and convert and store these elements in forms available to plants (Martin *et al.,* 1983; Jayachandran *et al.,* 1992; Turnbull *et al.,* 1995). Mycorrhizae also produce organic acids that help aid in the breakdown of organic phosphorus. Mycorrhizae provide the greatest value to higher plants in the acquisition of nonmobile ions, particularly the least available forms of phosphorus and nitrogen (Bolan *et al.,* 1987; Northrup *et al.,* 1995). As the availability of nitrogen and other nutrients increases, mycorrhizal associations provide less competitive advantage and require twice as much carbon to maintain as nonmycorrhizal roots (Rygiewicz and Andersen, 1994).

Although some nutrients may enter the plant passively following the flow of water, many are actively transported with enzyme-mediated reactions across root membranes (Ingestad, 1982). Nonessential or toxic elements may similarly be metabolically excluded. One can easily imagine that plants from infertile habitats might possess adaptations to enhance nutrient uptake by root enzymes. However, little natural selection for enhanced enzymatic uptake among native species has occurred because diffusion limits the supply of most nutrients to root surfaces (Chapin, 1980; Chapin *et al.,* 1986). In conditions where nutrient deficiency slows plant growth, excess carbon is likely to be available to support additional investment in acquiring nutrients (Marx *et al.,* 1977). On the other hand, where nutrients are readily available, less exudates may be produced to stimulate mycorrhizal inoculation and development (Blaise and Garbaye, 1983).

C. Storage and Internal Recycling

Total nutrient demands are highly variable from species to species. Within a species, nutrient concentrations also vary depending on growth rates and the availability of nutrients.

When nutrients are added to deficient soils the growth rate of trees usually increases, often without inducing a change in foliar nutrient concentrations. When one nutrient or other factors limit growth, nutrients may be taken up in excess of immediate metabolic requirements. This results in high concentrations in foliage—a condition that is called *luxury consumption.* Differences in leaf nutrient concentrations form one basis for diagnosing deficiencies, but foliar analyses must be interpreted with care because much variation occurs with season, canopy position, and growth rate (Linder and Rook, 1984; Van den Driessche, 1984). More insight is gained when foliar composition is compared seasonally than judged from a single sampling and when account is taken for changes in carbohydrate reserves that alter the specific leaf weight over time (Linder, 1995; Fig. 4.3).

The optimum balance of nutrients is determined experimentally by varying nutrient concentrations in hydroponic solutions or sand cultures and observing the relative concentrations found in plants with maximum growth rates. At maximum growth rate the balance of nutrients in solution and those in leaf tissue are the same (Ingestad, 1979). The optimum nutrient balance differs only slightly among tree species when referenced to nitrogen content (Ingestad, 1979; Ericsson, 1994; Linder, 1995; Table 4.1). Because most of the nutrient demand in seedlings goes to foliage, these *nutrient balances* are optimum for that organ but not necessarily for other tissue such as wood or bark, which may be far higher in Ca and much lower in N and P (Table 4.2).

From data presented in Table 4.2, the foliar nutrient ratio calculated for Douglas-fir is N 100 : P 28 : K 62 : Ca 73. Calcium concentrations are nearly 10-fold higher than required (Table 4.1). Birch, with the ratio N 100 : P 5 : K 57 : Ca 51, also has acquired a surplus of Ca, but it is deficient in P. Although the concentration of N in the foliage of Douglas-fir is only one-third of that in birch, the total N content is one-third higher (102 compared to 76 kg ha^{-1}) because of the greater biomass (9180 compared to 2586 kg ha^{-1}). Assuming that not more than one-third of the conifer's needles are replaced each year, canopy requirements for N are about 35 kg ha^{-1} $year^{-1}$, less than half that required by the deciduous birch. For diagnostic purposes, departure from the optimum ratio during periods of rapid growth is indicative of nutritional problems. Beaufils (1973) developed a general index based on these principles which provides a statistical estimate of the degree to which each element is below or above the optimum value and assesses the implications on growth (Leech and Kim, 1981).

Physiological studies indicate that when plants are able to maintain good nutritional balance, a positive relation should exist between the total content of nitrogen in foliage and growth rates (Ågren and Ingestad, 1987; Cromer *et al.,* 1993a; Fig. 4.4). When an imbalance exists, growth may still increase linearly with nitrogen content, but at a reduced rate. These principles have been applied in Germany to separate nutrient-deficient spruce stands from healthy ones (Oren *et al.,* 1988a,b), as well as in New Zealand.

Total plant nutrient contents reflect long-term nutrient uptake but tell us little about seasonal nutrient circulation. Mature foliage and other organs may exhibit relatively stable ratios of nitrogen with other elements, but this balance is often accomplished through internal reallocation. Reallocation of nutrients from twigs and older foliage helps sustain rapid shoot elongation when root uptake is inadequate to meet the demand. The actual flux, however, is difficult to estimate accurately unless isotopic tracers are used (Mead and Preston, 1994). Drought and other stresses reduce growth demand and the amount of

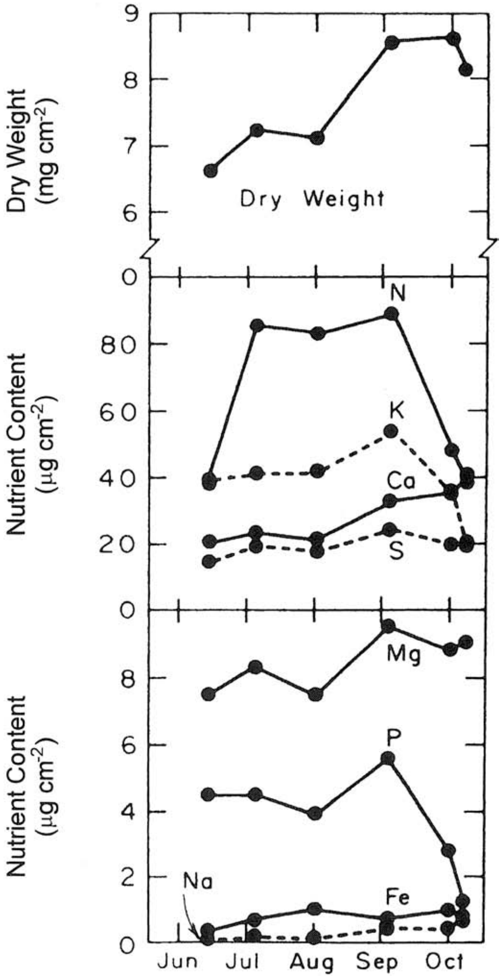

FIGURE 4.3. Seasonal changes in the dry weight and nutrient content of the leaves of scarlet oak (*Quercus coccinea*) in the Brookhaven Forest, Long Island, New York. (From Woodwell, 1974.)

nutrients reallocated (Nambiar and Fife, 1991). Ray parenchyma cells in sapwood store mobile nutrients such as N, P, and K, which can be transferred via the sap stream to meet growth demands until conversion to heartwood occurs (Van den Driessche, 1984; Van Bell, 1990). Small-diameter roots change little in their nutrient content over time (McClaugherty *et al.,* 1982; Nambiar and Fife, 1991; Aerts *et al.,* 1992). Large-diameter roots, however, store considerable reserves, which in some deciduous species are mobilized to support leaf expansion as well as new root growth (Van den Driessche, 1984; Wendler and Millard, 1996).

The reserves of nutrients available for export from a particular tissue can often best be measured by assessment of metabolically active forms (Attiwell and Adams, 1993). For

TABLE 4.1
Optimum Nutrient Weight Proportions in Leaves of Seedlings Grown in Solution Culture, Relative to N[a]

Species	N	P	K	Ca	Mg
Alnus incana	100	16	41	10	14
Betula pendula	100	14	55	6	10
Eucalyptus globulus	100	10	37	10	9
Picea abies[b]	100	16	50	5	5
Picea sitchensis[b]	100	16	55	4	4
Pinus sylvestris[b]	100	14	45	6	6
Populus simonii	100	11	48	7	7
Salix viminalis	100	14	45	7	7
Tsuga heterophylla[b]	100	16	70	8	5

[a] From Ingestad (1979) and Ericsson (1994).
[b] Expressed on basis of nutrient contents of entire seedlings.

phosphorus, the inorganic form best reflects its availability for allocation (Chapin and Kedrowski, 1983; Carlyle and Malcolm, 1986; Polglase *et al.,* 1992). For nitrogen, most reserves are in the form of proteins. Above a certain level, however, excess nitrogen begins to accumulate as free amino acids, which reflects a significant change in physiological status (Näsholm and Ericsson, 1990). The biochemical composition of plants becomes even more important when considering plant–animal interactions because the nutritional value of the vegetation to animals is largely dependent on the extent to which nitrogen is present in a digestible form (Chapter 6).

D. Return in Litter and Leachate

Large differences among species exist in the extent to which nutrients are concentrated in foliage, bark, and wood. Differences in litter quality affect decomposition rates, the availability of nutrients to other plants, and, potentially, the development of soils under different types of vegetation (Turner and Lambert, 1988; Gower and Son, 1992). Species adapted to disturbance often grow rapidly and have nutrient-rich tissues. Their high nutrient requirements, associated with high photosynthetic rates per unit leaf area and short leaf life spans, result in nutrient accumulations in biomass and litter that might otherwise be lost after forest cutting or fires (Pastor and Bockheim, 1984). Even within the same genus, large differences exist in the quality of litter produced from some components. Thus, although *Eucalyptus grandis* and *E. sieberi* have similar Ca concentrations in foliage (0.5%), their bark contents differ from ~2.0 to <0.05% (Turner and Gessel, 1990).

Small amounts of most nutrients are leached from living plant tissues. Potassium, an element which is highly soluble and concentrated in stomatal guard cells, is particularly easily removed through leaching. In general, K > P > N > Ca in regard to leaching losses from foliage. Differences in the rates at which nutrients are leached from foliage and bark may explain variation in epiphyte loads on forest species (Schlesinger and Marks, 1977). Fine roots also lose nitrogen and potassium through exudation and leaching.

TABLE 4.2

Comparison of Nutrient Distribution in Stands of Douglas-fir and Birch with Similar Total Biomass[a]

Species	Element or biomass	Foliage		Branches		Bole bark		Bole wood		Roots		Total content (kg ha^{-1})
		% Pool	% Weight	% Pool	% Weight	% Pool	% Weight	% Pool	% Weight	% Pool	% Weight	
Douglas-fir	N	32	1.13	19	0.28	15	0.26	24	0.06	10	0.1	320
Birch	N	14	3.04	31	0.59	—	—	27	0.11	28	0.3	543
Douglas-fir	P	44	0.32	19	0.06	14	0.05	14	0.01	9	0.02	66
Birch	P	12	0.16	35	0.04	—	—	32	0.01	21	0.01	34
Douglas-fir	K	28	0.68	17	0.17	20	0.24	24	0.04	11	0.07	220
Birch	K	22	1.76	23	0.16	—	—	32	0.05	23	0.09	200
Douglas-fir	Ca	22	0.81	32	0.48	21	0.37	14	0.04	11	0.11	333
Birch	Ca	6	1.56	28	0.68	—	—	42	0.20	24	0.31	651
Douglas-fir	Biomass	4.5	—	10.7		9.1	—	60	—	16	—	204,000
Birch	Biomass	1.2	—	13.3		—	—	62	—	23	—	215,500

[a] From Van den Driessche (1984). All values calculated on the basis of dry weight.

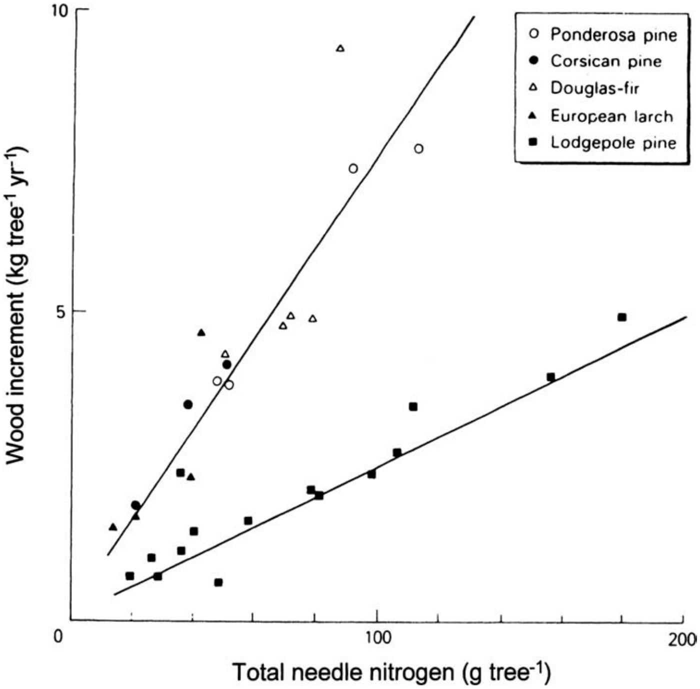

FIGURE 4.4. Conifer trees produce wood in proportion to the peak seasonal nitrogen content of their canopy. Wood increment is greater when nitrogen is in nutritional balance with other essential elements (upper line) than when it is not (lower line). Lodgepole pine performs similarly to other coniferous species on nutritionally well-balanced soils. (From Waring, 1989; after Benecke and Nordmeyer, 1982, and Nordmeyer *et al.,* 1987.)

Return of nutrients in litterfall is the major route of recycling from vegetation to soil. Aboveground litterfall can be measured through periodic collection, weighing, and chemical analysis of twigs, leaves, fruits, and other products that fall into nets or trays positioned just above the ground surface. Annual additions of coarse woody debris can be estimated by recording the amount that falls across string lines laid out annually in a large grid under a forest canopy. Nutrient return in litterfall can vary seasonally from year to year depending on forest composition and the leaf abscission process. In a temperate deciduous forest, Gosz *et al.* (1972) found that premature abscission of leaves in summer storms resulted in a small amount of litterfall with relatively high nutrient concentrations because nutrient reabsorption had not occurred.

In plant systems, nitrogen, phosphorus, and potassium are particularly mobile whereas calcium, which is bound within cell walls, is the least mobile nutrient. Calcium concentrations often increase as a percentage of dry weight in leaf litter because carbohydrate reserves are depleted before normal leaf abscission. For an absolute basis of comparison, nutrient concentrations should be expressed on a per unit of leaf area basis to take into account seasonal changes in specific leaf mass (Fig. 4.3). Although the fraction of nutrients withdrawn (or leached) from fresh foliage before abscission varies considerably among species (Table 4.3), the concentrations of nutrients in leaf litter are closely correlated with

TABLE 4.3
Nutrient Withdrawal and Leaching from Foliage before Abscission in Conifers and Broad-leaved Species, Expressed as Percent Change of Dry Weight[a]

Species	N	P	K	Ca	Mg
Conifers					
Picea abies	–7.5 to –22	–35 to –50	–68 to –72	–3 to +15	–9 to –26
Picea excelsa	—	–2	–17	+2	+35
Pinus sylvestris	–69	–81	–80	+18	—
Broad-leaved deciduous trees					
Alnus rubra	–30	–50	–6	+22	–5
Betula alleghaniensis	–55	–42	–59	0	—
Fagus sylvatica	–41	–77	–52	–13	–14
Populus tremuloides	–78	–67	–58	–23	+14
Broad-leaved evergreens					
Eucalyptus marginata	–64	–75	–54	+28	—
Eucalyptus regnans	–50	–58	–80	–3	–40
Nothofagus truncata	–45	–63	–81	+38	+26

[a] Selected from reviews by Ericsson (1994) and Van den Driessche (1984).

those in fresh foliage for a given species and site (Miller and Miller, 1976; Hunter *et al.,* 1985). Below ground, nutrients returned annually, as fine roots die, may match or exceed the amount contributed through leaf litter (Vogt *et al.,* 1986). This may seem surprising because nutrient concentrations in fine roots are often half that in fresh foliage; concentrations remain stable, however, and turnover rates and subsequent decomposition of fine roots are high.

E. Nutrient Use Efficiency

The absolute amount of nutrients returned in leaf litter tends to increase with soil fertility and total foliage production, as quantified in a series of fertilizer experiments in pine and eucalypt plantations (Crane and Banks, 1992; Cromer *et al.,* 1993a,b). Because the annual transfer of leaf biomass in litterfall mirrors aboveground production, as described by allometric relations introduced in Chapter 3, a measure of nutrient use efficiency can be derived by calculating the ratio of leaf litter production to its nutrient content. Vitousek (1982, 1984) used aboveground litterfall patterns to compare the relative nutrient use efficiency in world forests. He found that the ratios mass : N and mass : P in litterfall rapidly declined with increasing return of N and P to the forest floor, and that temperate and boreal forests were more likely to be N-limited whereas tropical forests were generally P-limited.

Bridgham *et al.* (1995) provide a thorough review of the nutrient use efficiency concept. They developed a general model that predicts the amount of nutrients returned in litterfall. Nutrient return should increase rapidly and then approach an asymptote with measured litterfall. They tested the model in a peat bog in North Carolina where productivity and species composition varied (Fig. 4.5a). They found general agreement with model predictions; the most nutrient-demanding species produced more litter but required a disproportionate

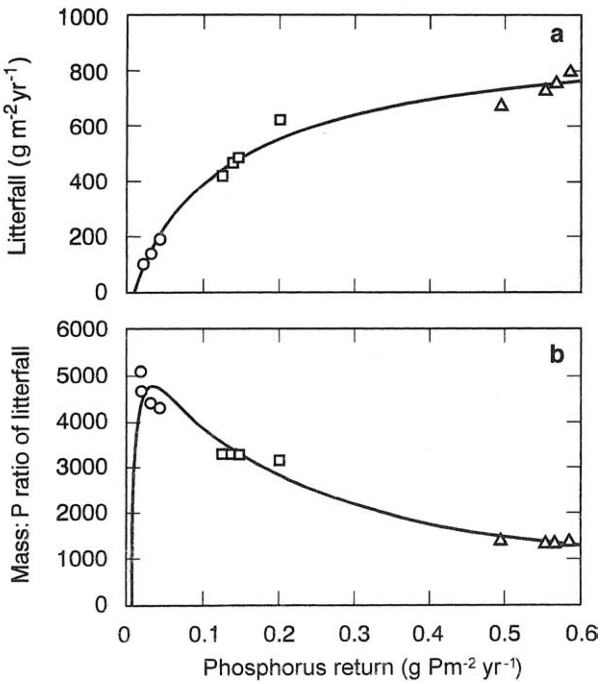

FIGURE 4.5. (a) Litterfall and nutrient return in litterfall in three peat-land communities in North Carolina illustrate that the least demanding species (○) increased production rapidly in response to an increment of phosphorus, whereas the more demanding (□) and most productive species (△) were progressively less nutrient efficient. Solid line represents model predictions. Similar responses were demonstrated for Ca and N. (b) The mass of litterfall : nutrient return ratio relative to phosphorus indicates from the model predictions that a rapid increase in nutrient use efficiency occurs above some minimum threshold and is followed by an exponential decrease with increasing litter return of phosphorus or other nutrients. (After Bridgham *et al., American Naturalist,* published by the University of Chicago Press. © 1995 by The University of Chicago.)

amount of nutrients compared with less demanding, less productive species. From values derived from the curves in Fig. 4.5a, they modeled and replotted the conventional relationship between nutrient return and the mass : nutrient ratio in litterfall (Fig. 4.5b). The analysis differs from earlier ones in that a minimum return of nutrients in litterfall (or uptake from the soil) is specified below which no production is predicted.

The nutrient use efficiency concept can be expanded to compare species differences in total aboveground production on equivalent sites. In Table 4.4, production efficiencies are compared for similar aged stands of *Pinus* and *Eucalyptus* growing on phosphorus-poor soils in Australia (Turner and Lambert, 1983; Baker and Attiwill, 1985). The two species have fairly similar production efficiencies in regard to gross annual demand for N and P (Efficiency I in Table 4.4), but the native eucalyptus extracts only about one-quarter of the P from soils demanded by pine for a comparable rate of production (Efficiency II). The native eucalypt requires only about half the P content in a kilogram of wood compared with the introduced pine. Lower leaf turnover and higher reabsorption of nutrients before leaf abscission are additional means by which species obtain high nutrient use efficiency.

TABLE 4.4
Comparison of *Pinus radiata* with *Eucalyptus grandis* for Several Measures of Production and Nutrient Efficiency[a]

Property	Component	*P. radiata*	*E. grandis*
Age, years		22	27
Mass, kg m^{-2}		27	39
Mean annual accumulation, kg m^{-2} year^{-1}	Total aboveground biomass	1.4	1.5
	Stem wood	1.1	1.2
Current annual production (C), kg m^{-2} year^{-1}	Total aboveground biomass	1.7	2.4
	Stem wood	1.0	1.5
Efficiency I: (C)/gross annual demand for nutrients, kg g^{-1}	N	0.28	0.24
	P	2.9	3.9
Efficiency II: (C)/annual uptake from soil, kg g^{-1}	N	1.3	1.8
	P	9.0	35
Efficiency III: Nutrient, cost of stem wood g kg^{-1}	N	0.57	0.85
	P	0.08	0.04

[a] From *Forest Ecology and Management,* Volume 6, J. Turner and M. J. Lambert, "Nutrient cycling within a 27-year-old *Eucalyptus grandis* plantation in New South Wales," pp. 155–168, 1983, and *Forest Ecology and Management,* Volume 13, T. G. Baker and P. M. Attiwill, "Above-ground nutrient distribution and cycling in *Pinus radiata* D. Don and *Eucalyptus obliqua* L'Herit. forests in southeastern Australia," pp. 41–52, 1985, with kind permission from Elsevier Science–NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

Evergreen species which display these attributes also tend to lose fewer nutrients through leaching. As a result, conifers are generally more efficient in nutrient use than deciduous species (Cole and Rapp, 1981). The efficient use of nutrients by trees, however, is not necessarily a desirable ecosystem property, because heterotrophic organisms are inhibited when carbon to nutrient ratios are high and, as a result, the release of nutrients from litter may be slowed to further limit productivity (Shaver and Melillo, 1984).

In summary, uptake of nutrients from the soil rarely meets demand during periods of rapid growth. In evergreen forests, reabsorption of nutrients from older and senescent foliage becomes increasingly important for maintaining growth as forests age and accumulate leaf area. Although the optimal balance of nutrients may not be maintained, aboveground growth is generally a linear function of the total N content in foliage. This relationship offers a simplification for the development of forest growth models designed to scale across landscapes (Chapter 8). The mass and nutrient content in leaf litterfall are integrating measures of ecosystem function that link not only to aboveground production but, as we shall see, to decomposition of organic matter and release of nutrients into the soil.

III. SOURCES OF NUTRIENTS

A. Atmospheric Deposition

We discussed earlier that carbon from atmospheric CO_2 is sequestered into forest ecosystems through photosynthesis (Chapter 2). In addition, nearly all of the nitrogen and sulfur pools in forest ecosystems is derived from the atmosphere (Placet *et al.,* 1990). The major transfer of nitrogen is through biological fixation, although lightning also produces nitrogen oxides that are transferred to the ground. The production of inorganic fertilizer and atmospheric transfers from agricultural fields, feedlots, and fossil fuel combustion now match or exceed N acquired from the atmosphere through natural processes (Vitousek and Matson, 1993). Volcanic eruptions release SO_2 (Schlesinger, 1991, 1997), but these contributions are relatively infrequent and small compared to those derived from current fossil fuel combustion (Johnson and Lindberg, 1992). Although Ca, Mg, and K are derived from mineral weathering, dust extracted from the atmosphere in precipitation and dryfall is a major source of these elements as well (Hedin and Likens, 1996).

Rainfall constituents are also derived from the ocean. As winds blow across the ocean surface, sea salt rich in Na, Mg, Cl, and S is injected into the atmosphere and carried over great distances as aerosols smaller than 1 µm. The ratio of Na to other ions in precipitation may provide an indication of the direction of storm fronts. For example, the calcium to sodium ratio in seawater is 0.04. For rainfall with Ca : Na ratios close to this value, one would deduce that most of the Ca was of marine origin (Schlesinger *et al.,* 1982). In the eastern continental United States, the typical Ca : Na ratio is 1.3 (Likens *et al.,* 1977) because the airflow that brings precipitation to this region carries calcium derived from soil dust and other inland sources.

The deposition of nutrients in precipitation is called *wetfall.* Clouds and fog may also provide an additional source of wet deposition. *Dryfall* is the result of gravitational deposition of particles and the absorption of gases during periods without rain. With the design of collectors that are electronically sensitive to rain, partitioning of nutrient deposition between wet and dry sources can be estimated (Fig. 4.2). Dryfall is the major atmospheric source in ecosystems with limited precipitation. Even in the humid temperate forests of the eastern United States, however, dryfall makes up an important fraction of the total annual atmospheric deposition of N, P, K, Ca, and Na (Lindberg *et al.,* 1986; Driscoll *et al.,* 1989). In mountain landscapes where forests are often immersed in clouds, sulfur deposited through fog condensation may represent as much as 50% of the total atmospheric deposition (Johnson and Lindberg, 1992).

Accurate estimates of atmospheric inputs are difficult to obtain over forests, in part because their large leaf area effectively captures fog droplets and aerosols from the airstream. Some reactive gases such as SO_2 and NO_2 are absorbed directly from the atmosphere by plant leaves and soil. Nearly one-third of the atmospheric S deposited in northern hardwood forests was estimated to be dependent on the presence of vegetation (Eaton *et al.,* 1978). Coniferous evergreen forests are two to three times as efficient as broadleaf deciduous forests in filtering wet- and dryfall from the atmosphere (Johnson and Lindberg, 1992). These differences are associated with tree leaf area, the seasonal duration of display, and aerodynamic properties of the canopy discussed in Chapter 2. A number of models predict canopy capture of aerosols in wet- and dryfall (Lovett *et al.,* 1982; Baldocchi, 1988; Lovett, 1994). Most of these models assume one-dimensional vertical transport, flat terrain, and homogeneous canopies. These assumptions make them less applicable to complex terrain and patchy vegetation (Lovett, 1994). More realistic models, however, are difficult to parameterize and cannot as yet be validated because of errors in measuring the various sources of deposition (Lovett, 1994).

B. Nitrogen Fixation

Over 78% of the atmosphere is composed of nitrogen as dinitrogen (N_2). Various gases, including oxygen, argon, carbon dioxide, and trace constituents, comprise the remainder. Gaseous N_2 is inert as far as biological processes are concerned. Thus, plants are bathed in a "sea of nitrogen" that they cannot use (Delwiche, 1970). Several types of bacteria and blue-green algae (cyanobacteria) possess the enzyme nitrogenase that converts atmospheric N_2 to NH_3 (ammonia), which is transformed into ammonium (NH_4^+), a form readily available to biota. The N-fixing organisms exist as free-living forms (*asymbiotic*), either on the surface or in soil (Woldendorp and Laanbroek, 1989), and in *symbiotic* association with fungi (*lichens*) and roots of some higher plants.

Symbiotic N fixation is an energy-consuming reaction, with a carbon cost between 4 and 10 g per g N fixed, averaging ~6 g C/g N (Vance and Heichel, 1991). Nitrogen fixation is highly dependent on the production and temporary storage of current photosynthate; thus, activity completely stops within a few days after the cessation of photosynthesis (Ekblak *et al.,* 1994). Because of the sensitivity of the photosynthetic process to light, symbiotic N fixation by shrubs and herbs is progressively limited as the forest canopy closes (Silvester *et al.,* 1979). Nitrogen fixation is also limited if N is freely available or when P, Mo, Co, and other trace nutrients required for the enzymatic reaction are in short supply. Linkage between primary production and soil fertility is thus a prerequisite for the development of any model of symbiotic nitrogen fixation.

Asymbiotic N fixation is generally higher in forest soils rich in organic matter (Granhall, 1981) and also occurs in coarse woody debris. Typical rates are 0.1 to 4 kg N ha^{-1} $year^{-1}$ in boreal forests, 0.1 to 5 kg N ha^{-1} $year^{-1}$ in temperate coniferous forests, 0.1 to 6 kg N ha^{-1} $year^{-1}$ in temperate deciduous forests, and 2 to 20 kg N ha^{-1} $year^{-1}$ in tropical forests (Boring *et al.,* 1988). Where rates of N accumulation are higher in ecosystems lacking symbiotic N fixers (Bormann *et al.,* 1993), asymbiotic N fixers may be obtaining energy from root exudates directly (Attiwill and Adams, 1993). This type of "associate-fixation" is more efficient than when bacteria are free-living, but it is probably less than 10% as efficient as the symbiotic arrangement (Marschner, 1995).

Biological nitrogen fixation is a major source of N in many types of ecosystems. In postfire development of Douglas-fir forests of Oregon, Youngberg and Wollum (1976) found that N fixation by the nodulated colonizing shrub *Ceanothus velutinus* contributed up to 100 kg ha^{-1} $year^{-1}$ of N for a number of decades on some sites. Similar rates of fixation have been reported for pure plantations of *Casuarina* in Puerto Rico (Parrotta *et al.,* 1994) and even higher rates for *Alnus* (Binkley *et al.,* 1994). For comparison, rainfall adds 1–2 kg ha^{-1} $year^{-1}$ in unpolluted forested regions (Hedin *et al.,* 1995) but more than 70 kg ha^{-1} $year^{-1}$ in some parts of heavily industrialized central Europe (Schulze, 1989).

Various methods have been developed to assess N fixation rates. Nitrogenase activity can be measured with the acetylene-reduction technique, which is based on the observation that the enzyme also converts acetylene to ethylene under experimental conditions. Plants or root nodules are placed in small chambers and the conversion of injected acetylene to ethylene is measured over a known time using gas chromatography. The conversion of acetylene in moles, however, is not always equivalent to the potential rate of fixation of

N_2 because the enzyme has different affinities for these substrates under varying conditions. As an absolute measure of N fixation, investigators have injected air enriched in $^{15}N_2$ into chambers and measured the increase in organic ^{15}N in test plants or soil through time. The direct approach to assessing N fixation is largely confined to small-scale studies of single plants or nodules (McNeill *et al.,* 1994).

As an alternative to direct measurements of N fixation, small amounts of ^{15}N-enriched fertilizer can be applied to the soil and the isotopic composition of leaves of a potential symbiotic N-fixing species compared against a nonfixing species. Nonfixing species do not have direct access to the atmospheric N supply, and thus the resulting $^{15}N/^{14}N$ ratio of tissue N will differ between the two species in proportion to the nitrogen fixed, with the absolute amount related to total N incorporated annually in biomass (Parrotta *et al.,* 1994). At times it is difficult to find a suitable nonfixing species with comparable rooting depth and affinity for a particular form of nitrogen; in such cases the δ^{15} N of extractable soil N may serve as a reference (Handley and Raven, 1992; Handley *et al.,* 1994).

The abundance of ^{15}N relative to ^{14}N in plant tissue or xylem sap may also serve to document the relative importance of N fixation to the available nitrogen pool (Shearer and Kohl, 1986). Dinitrogen fixed from the atmosphere has a similar isotopic composition to its source, which is the standard of reference ($\delta^{15}N = 0.0 \pm 2.0‰$). As nitrogen is mineralized from organic matter in soils, the heavier ^{15}N accumulates as the lighter ^{14}N is volatilized or leached. As a result, both soil nitrogen content and the fraction of ^{14}N decrease with depth, and they can be predicted on the basis of Rayleigh distillation kinetics (Mariotti *et al.,* 1981; Schulze *et al.,* 1994b). Evans and Ehleringer (1993) applied this approach in a semidesert ecosystem where N-fixing lichens and related forms cover undisturbed soil surfaces. Soils collected beneath trees and shrubs and between canopies showed lower N concentrations and proportionally higher $\delta^{15}N$ values, which implied from the model that essentially all of the N present in the system was derived through fixation rather than from other sources.

In most ecosystems, our understanding of the importance of N fixation is still incomplete. There are few studies of N fixation among the leguminous species of tropical forests. Collectively, these might not only provide an important source of N in these ecosystems, but also account for the abundant N circulation in many tropical forests. In other systems, N fixation is highly variable seasonally and also changes with stand development. Symbiotic N fixation, which depends directly on carbon assimilation by the host plant, is limited by the same set of factors that control photosynthesis but, in addition, is significantly reduced when N is too readily available and when other critical nutrients are in short supply (Liu and Deng, 1991).

C. Weathering

Except for nitrogen, most nutrients have their origin from the mineral composition of rocks. The inherent fertility of forest soils, their texture, and their buffering capacity to acid precipitation are all related to the type and age of the parent material from which the soil is derived. Nearly all rocks contain primary minerals that were formed under conditions of greater temperature and pressure than found at Earth's surface. On uplift and exposure, the rocks undergo *weathering,* a general term that encompasses a variety of geological processes by which parent rocks are broken down. Mechanical weathering is fragmentation of materials without chemical change. Chemical weathering occurs when parent rock materials react with water and mineral constituents are released as dissolved ions. Chemical weathering also includes the formation of new, secondary minerals that are more stable under the physical conditions at Earth's surface. Weathering is closely involved with the formation of soils, because the bulk of the physical structure of soils is composed of fragmented and weathered rock materials.

Chemical weathering is the main process by which nutrients are released from rock. From 80 to 100% of the inputs of Ca, Mg, K, and P is derived from weathering in many forest ecosystems (but see review on dust inputs by Hedin and Likens, 1996). Only in unusual conditions does the parent rock contain measurable amounts of N (Dahlgren, 1994). The release of ions occurs most rapidly under warm temperatures and with large amounts of precipitation. Thus, on a worldwide basis, climate is the major determinant of weathering rates. Chemical weathering is more rapid in tropical forests than in temperate or boreal forests and, likewise, progresses more rapidly in forests than in grasslands or deserts.

It is traditional to think of weathering of the underlying bedrock as the source of nutrients and soil development in forest ecosystems. Over large areas, however, soil profiles are developed from materials that have been transported and not weathered in place. For example, many forests in the northeastern United States occur on glacial deposits. In other areas, volcanic ash, wind-borne material (loess), or stream-water alluvium have resulted in deep and fertile soils. In all these cases, weathering may largely be from minerals in the deposited horizons and not from parent bedrock.

Rates of chemical weathering and nutrient release are dependent on rock type. Metamorphic rocks (e.g., gneiss, schist, quartzite) and many igneous rocks (e.g., granite, gabbro) formed deep in the Earth consist of primary silicate minerals that are crystalline in structure. Quartz is the simplest silicate mineral, consisting of only silicon and oxygen in a tetrahedral crystal. Quartz is extremely resistant to chemical weathering. Other primary minerals are silicates in which various *cation* (positively charged ion) components (e.g., Al^{3+}, Ca^{2+}, Na^{+}, K^{+}, and Mg^{2+}) and ions of trace metals (Fe, Mn, etc.) are substituted in the crystal lattice. These minerals include feldspars, mica, olivines, and hornblende. The elemental substitutions make these primary minerals less stable and more prone to chemical attack. In rocks of mixed composition, such as granite, chemical weathering may be concentrated on the relatively labile minerals, while others such as quartz are left unchanged. In the process of chemical weathering, primary minerals are altered to more stable forms, ions are released, and secondary minerals are formed.

Sedimentary rocks underlie 75% of the land area and include shales, sandstones, and limestones. These rocks were formed relatively close to Earth's surface, usually as sediment under water. Shales and sandstones may consist largely of secondary minerals eroded during earlier weathering epochs, and they are often rather weakly cemented rocks. In many instances, sedimentary rocks are prone to erosion, but the component minerals may be stable end products and not subject to further chemical attack. Rapid erosion, thus, does not necessarily imply abundant nutrient availability in the soil profile.

The most important chemical weathering process in forest ecosystems is that of *carbonation.* The reaction is driven by the formation of carbonic acid, H_2CO_3, in the soil solution:

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2CO_3. \tag{4.la}$$

Because plant roots and decomposing soil organic matter release CO_2 to the soil air, the concentration of H_2CO_3 is often much greater than that in equilibrium with atmospheric CO_2 at 0.035% concentration. Carbonation reactions are dominant in the weathering of limestone and yield soluble Ca:

$$CaCO_3 + H^+ + HCO_3^- \Rightarrow Ca^{2+} + 2HCO_3^-. \tag{4.1b}$$

Silicate minerals also weather by carbonation, for example,

$$\text{K-Al-silicate} + H^+ + HCO_3^- \Rightarrow K^+ + H_4SiO_4 + \text{Al-silicate} + HCO_3^-. \tag{4.lc}$$

This simplified reaction represents the weathering of potassium feldspar. During the process, a primary mineral is converted to a secondary mineral by removal of K and soluble silica. Except in unusual circumstances, the dominant *anion* (negatively charged ion) in seepage or runoff water is bicarbonate ion, HCO_3^-.

Other abiotic weathering reactions include simple dissolution of minerals, oxidations, and hydrolysis. Biotic weathering may involve organic acids released by plant roots that can weather biotite mica, a primary mineral that contains K. Lichens are important in rock weathering through the release of phenolic acids (Ascaso *et al.,* 1982). Fungi release oxalic acid and other organic acids which weather soil minerals and affect the concentration of phosphorus and other nutrients in solution (Comerford and Skinner, 1989).

Weathering of silicate rocks yields positively charged nutrient cations (e.g., K^+, Ca^{2+}, Mg^{2+}, and Fe^{3+}) in varying proportions depending on the initial rock composition and the environmental conditions for weathering reactions. Weathering of carbonates is more rapid and yields soils and stream waters that are dominated by Ca and Mg. In these neutral to alkaline soils, the availability of other soil nutrients, particularly P, may be limited. Weathering of ultrabasic igneous rock (peridotite) or its metamorphic derivative (serpentine) yields soils with unusually high concentrations of Mg, Fe, and trace minerals relative to Ca. On soils derived from such rocks, forest growth is stunted or impossible (Proctor and Woodell, 1975).

Many types of secondary minerals can form in soils through weathering processes. Temperate forest soils are dominated by layered silicate or clay minerals. These exist as small particles (<0.002 mm) that provide a great deal of structural and chemical properties of soil. In general, two types of layers characterize the crystalline structure of these minerals: Si layers and layers dominated by Al, Fe, and Mg. These layers are held together by oxygen atoms. Clay minerals and the size of their crystal units are recognized by the number, order, and ratio of these layers. Moderately weathered soils are often dominated by secondary minerals, such as montmorillonite, which have a 2:1 ratio of Si- to Al-dominated layers. More strongly weathered soils, such as in the southeastern United States, are dominated by kaolinite clays with a 1:1 ratio of layers. Some of the secondary minerals formed in soils can incorporate other elements such as K and P into their crystalline structure. When this happens, those nutrients are locked in a form unavailable to plants

(Walker and Syers, 1976; April and Newton, 1992). In tropical rain forests, high temperatures and rainfall cause most of the silica to be leached from soils. The highly weathered soils of tropical forests are dominated by crystalline oxide minerals and hydrous oxides of Fe and Al. Removal of Ca, K, and other basic elements is nearly complete as a result of long periods of intense leaching through the soil profile. At the other extreme, recently glaciated lands have soils enriched with powdered fragments of freshly exposed mineral surfaces, which provides a buffer against acid precipitation often lacking in nonglaciated areas (Johnson and Lindberg, 1992).

Weathering rates cannot be measured directly. Within the soil profile, however, much can be inferred from changes in the solution chemistry collected with porous-plate lysimeters installed at various depths (as shown in Fig. 4.2). Table 4.5 presents lysimeter analyses that demonstrate changes in the weathering processes throughout a soil profile developed under a subalpine forest in the central Cascades of Washington. By the time rain enters the soil it has become acidic as a result of organic acids leached from vegetation and decaying organic matter in the forest floor. This solution mobilizes Fe, Al, and other cations from weathering at 15 cm. These are largely precipitated in a lower soil layer (30 cm), but carbonation weathering commences again at 60 cm, resulting in losses of cations and silica to groundwater.

In undisturbed ecosystems, gross weathering rates from the soil and underlying material are often estimated from the difference between measured atmospheric additions and losses of the elements in stream water (Likens *et al.,* 1977). The approach overestimates weathering rates in the portion of the soil tapped by roots and ignores exchange processes in the riparian zone (Waring and Schlesinger, 1985). Alternatively, the natural abundance of strontium ($^{87}Sr/^{86}Sr$) has been used to quantify rates of weathering associated with different soil horizons and from bedrock (Miller *et al.,* 1993; Bailey *et al.,* 1996). Strontium is an element that reacts chemically similarly to Ca and, by inference, other cations.

TABLE 4.5

Chemical Composition of Precipitation, Soil Solution, and Groundwater in a 175-year-old *Abies amabilis* Stand in Cascade Range of Northern Washington[a]

			Soluble ions, mg liter^{-1}			Total, mg liter^{-1}	
Solution	pH	Total cations, meq liter^{-1}	Fe	Si	Al	N	P
Precipitation							
Above canopy	5.8	0.03	<0.01	0.09	0.03	0.60	0.01
Below canopy	5.0	0.10	0.02	0.09	0.06	0.40	0.05
Forest floor	4.7	0.14	0.14	3.50	0.79	0.54	0.04
Soil solution							
15 cm	4.6	0.12	0.12	3.55	0.50	0.41	0.02
30 cm	5.0	0.08	0.08	3.87	0.27	0.20	0.02
60 cm	5.6	0.25	0.25	2.90	0.58	0.37	0.03
Groundwater	6.2	0.26	0.26	4.29	0.02	0.14	0.01

[a] From Schlesinger (1991). Data from Ugolini *et al.* (1977b), *Soil Science* **124**, 291–302. Copyright (1977) Williams & Wilkins.

Aerosols from the atmosphere have δ^{87}Sr values in coastal regions that mirror that of oceans, and the δ^{87}Sr values change predictably as continental sources of dust are added. Rocks develop characteristic δ^{87}Sr values based on initial rubidium/strontium ratios and rock age. Strontium-87 is produced by the radioactive decay of ^{87}Rb (half-life, 49 Gyear), whereas ^{86}Sr is stable and does not decay radiogenically. By determining the Sr isotopic composition of vegetation, various soil horizons, underlying till and bedrock, as well as stream water flowing from a spruce–fir forest in northeastern United States, Miller *et al.* (1993) estimated the weathering contributions, cation reservoirs, and atmospheric contributions with a simple isotopic mixture model which specified the δ^{87}Sr of the two extremes: atmospheric inputs and underlying glacial till (Fig. 4.6).

Most models of weathering assume a long-term stable climate and lack responses to changes in atmospheric inputs. With concerns about acid rain deposition on forests, however, more refined models are being developed and applied to interpret the contribution

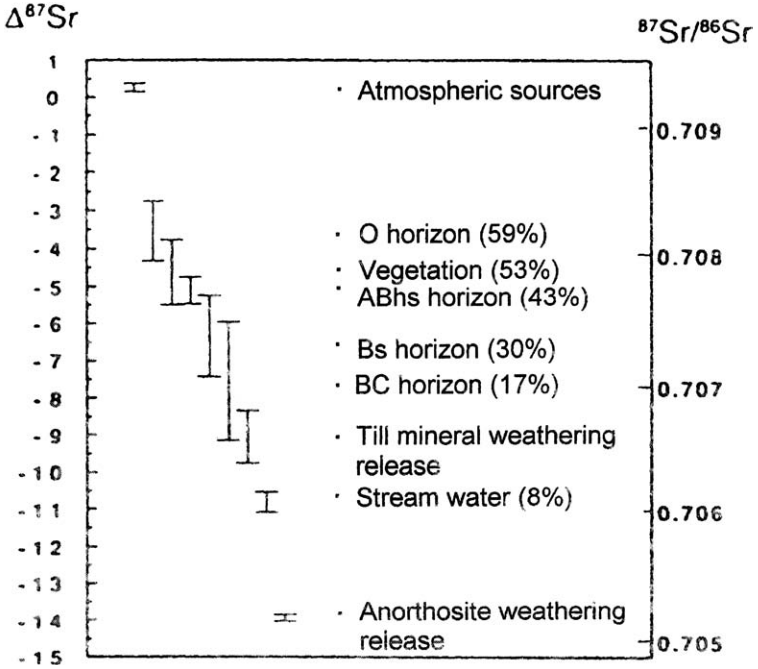

FIGURE 4.6. Weighted averages (dots) and one standard deviation (range bars) of the ^{87}Sr/^{86}Sr ratio of cation reservoirs in spruce–fir forests in New Hampshire. Shown in parentheses are percentages of Sr derived from atmospheric sources, the local comparative reference ($\delta^{87}\mathrm{Sr} = 0‰$ versus glacial till at $-9‰$). The δ^{87}Sr of stream water is lower than that released from till, which indicates weathering from anorthosite bedrock. Mineral weathering, according to this analysis, contributed about 20% of the Sr incorporated into vegetation annually. The cation-exchange reactions contributed an average of 30% and new mineral weathering an average of 70% of the Sr exported in stream water. The pool of exchangeable cations in the organic soil horizon represents <1% of net annual losses, and the soil is accumulating cations from the atmospheric inputs equivalent to about 0.5 kmol ha^{-1} year^{-1}. (From Miller *et al.,* 1993. Reprinted with permission from *Nature.* Copyright 1993 Macmillan Magazines Limited.)

of mineral weathering toward buffering cation losses on an annual basis (Liu *et al.,* 1991; April and Newton, 1992; Arthur and Fahey, 1993).

IV. SOIL AND LITTER PROCESSES

The soil in forest ecosystems usually consists of a number of layers, or horizons, that collectively comprise the complete soil profile. Recognition of the processes that occur in these horizons is an essential part of understanding nutrient cycling in forest ecosystems. A characteristic property of forest soils is a nearly permanent cover of leaf litter and woody debris. Beneath this surface organic layer, distinct soil horizons usually develop with different chemical, physical, and biological properties. Humans have altered the development of soil horizons by changing the natural sequence of disturbance, the kinds of plants, animals, and microbes present, and the nutrient capital in forest soils. The basic processes, however, remain the same by which nutrients are made available in the soil, taken up by plants, and eventually returned in organic residues.

In this section we first describe patterns of soil development in temperate-zone forests and then briefly contrast these to boreal and tropical regions. We then consider the decomposition process by which detritus is converted to humus and inorganic forms of minerals are released. Once nutrients are in solution they may be transformed, held on soil exchange sites, immobilized in plant and microbial biomass, or adsorbed and made unavailable to plants. All of these processes interact in complicated but, as our knowledge grows, increasingly predictable ways.

A. Soil Profile Development

The forest floor is often easy to separate from the underlying layers of mineral soil, but these two major categories may be further subdivided. The forest floor often consists of L, F, and H layers (Fig. 4.7). The L layer consists of fresh, undecomposed litter. The F layer lies immediately below the L layer and consists of fragmented organic materials in a stage of partial decomposition. This layer is dominated by organic materials in cellular form, and fungi and bacteria are common. Beneath the F layer lies the H or humus layer, primarily consisting of amorphous, resistant products of decomposition and with lower proportions of organic matter in cellular form. The lower portion of the H layer often shows an increasing proportion of inorganic mineral soil constituents, but organic components still dominate.

The upper mineral soil is designated as the A horizon. It may vary in thickness from several centimeters to 1 m. The A horizon is recognized as a zone of removal or *eluvial* processes. Soil water percolating through the forest floor contains organic acids derived from the humic materials. These waters remove iron, aluminum, and other cations by weathering of the mineral components of the A horizon. Iron and aluminum are complexed with the water-soluble fluvic acids in the soil solution and percolate to the lower horizons. Clay minerals are also removed from the A horizon. When the removal is extreme, a whitish A_2 horizon is easily recognized and may consist of nearly pure silica, which is relatively insoluble in acid conditions (Pedro *et al.,* 1978).

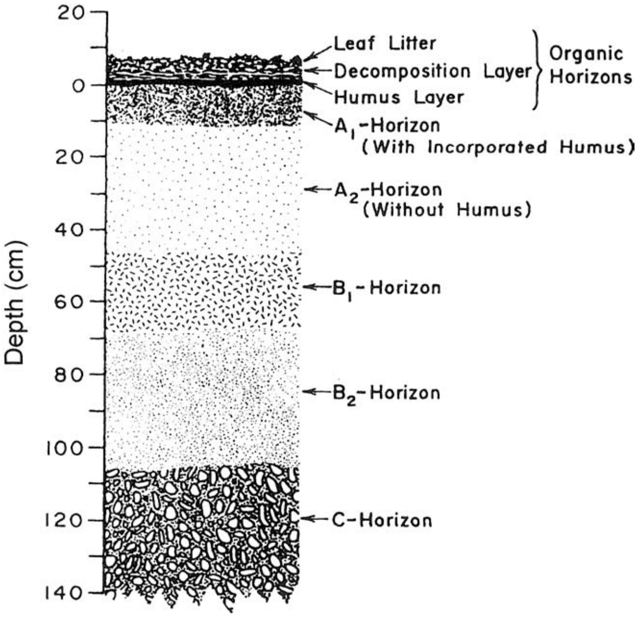

FIGURE 4.7. Diagram of the profile of a podzolic soil under an old stand of shortleaf pine (*Pinus echinata*) in North Carolina showing the three organic horizons over the A, B, and C horizons of the mineral soil. (From *Plants and the Ecosystem,* Third Edition, by W. D. Billings. © 1978 by Wadsworth Publishing Company, Inc. Reprinted by permission of Wadsworth Publishing Company, Belmont, California 94002.)

Substances leached from the A horizons are deposited in the underlying B horizon. This is defined as the zone of deposition or *illuvial* horizon. Iron and aluminum precipitate in the B horizon, and secondary clay minerals are formed (Ugolini *et al.,* 1977a). Soluble humic materials are complexed with the clay from the A horizon, and their deposition in the B horizon is known as *podzolization.* Below the B horizon, the C horizon consists of coarsely fragmented soil material with little organic content. When the soil has developed from local materials, the C horizon shows mineralogical similarity to the underlying parent rock.

The distribution of forest floor and soil groups forms a continuous gradient over broad geographic regions, in response to parent materials, topography, climate, vegetation, and time (Jenny, 1980). In the more extreme latitudes, decomposition in the forest floor is very slow as a result of cold and waterlogged conditions. Thick forest floor accumulations may comprise the entire rooting zone. In these areas the underlying mineral soil may be effectively isolated from the nutrient cycling processes in the forest ecosystem, particularly where peat bogs and permafrost occur. In much of the boreal region, the mineral soil is derived from glacial deposits. Weathering of primary minerals is slow in cold conditions, and there is little leaching of the soil profile when it is frozen much of the year; thus, the A and B horizons are poorly differentiated.

Within the general description of temperate forest soils, ecologists have long differentiated between mor and mull forest floors. In broad geographic terms, mors develop in cooler climates, often characterized by coniferous vegetation. Decomposition in the forest floor is slow and incomplete, resulting in a thick organic layer. Moreover, the litter of coniferous species contains high concentrations of phenolic substances and lignin that yield acid decomposition residues. As a result, the soil solution often has a pH as low as 4.0. In these conditions, fungi predominate over bacteria. Earthworm populations are low in mor forest floors, which results in little fragmentation and mixing with the underlying soil (Phillipson *et al.,* 1978).

Mull forest floors are typically found under deciduous forests in warm temperate climates. Most of the characteristics of mulls are in contrast to those of mors. Decomposition is more rapid, residues are less acidic, and earthworms are more abundant. Bacteria play a greater role in decomposition processes in mull forest floor, and the pH is higher. Fragmentation and mixing often make differentiation of the forest floor difficult and obscure sharp boundaries between the mineral horizons. Under pH 5.0–7.0, which are typical of these soils, Si is relatively soluble. Thus Si, Fe, and Al are removed in relatively equal proportions from the A horizon minerals, and there is no sharply defined A_2 horizon (Pedro *et al.,* 1978).

As one travels from the temperate zone to the lowland tropics, decomposition is progressively more rapid and complete. There is little forest floor mass, and there are lower concentrations of humic acids in the percolating soil waters. In this environment, Si is more soluble than Fe and Al. Long periods of weathering under high rainfall have removed Si and cations from the entire soil profile. Resistant soil materials are hydroxides of Fe and Al. Aluminum hydroxides may produce acidity (H^+) in soil waters, depending on the state of hydration, and P forms highly stable complexes with Fe and is unavailable. Thus, over large portions of the lowland tropical rain forest region, soils are infertile and show P deficiency (Sanchez *et al.,* 1982a).

Soils in tropical forests may be many meters in depth, because in many areas they have developed over millions of years without disturbances such as glaciation. In the absence of clear zones of eluviation and illuviation, distinction of the A and B horizons is difficult. The profiles are also well mixed by earthworms. The absence of a thick forest floor does not imply that these soils are low in soil organic content. Throughout the lower profile, light-colored fluvic acids are complexed with the mineral soil materials and represent a significant storage of soil C in organic form (Sanchez *et al.,* 1982b).

A useful chemical index of the regime of soil formation and the degree of weathering is seen in the ratio of Si to sesquioxides (Fe and Al) in the soil profile (Table 4.6). In boreal forest soils, Si is relatively immobile and Fe and Al are removed, which results in high values for this ratio in the A horizon. The accumulation of the secondary mineral montmorillonite in the moderately weathered soils of the glaciated portions of the United States yields Si : sesquioxide ratios of 2 to 4, as a result of the ratio of Si to Al in the crystal lattice. Silicon : sesquioxide ratios are lower in more highly weathered soils. In the southeastern United States, lower ratios characterize soils in which kaolinite has accumulated as a secondary mineral. Tropical soils show very low values for this ratio in all horizons: they are dominated by iron and aluminum hydroxides, and in highly weathered conditions relatively little Si remains.

Differences in soil profile development locally and regionally have long served as a convenient way to classify and map local and regional variation. Today, models that

TABLE 4.6

Silicon : Sesquioxide ($Al_2O_3 + Fe_2O_3$) Ratios for A and B Horizons of Some Soils in Different Climatic Regions[a]

		Mean Si : sesquioxide ratio		
Region	Number of sites	A-horizon	B-horizon	Reference
Boreal	1	9.3	6.7	Leahey (1947)
Cool temperate	4	4.1	2.3	MacKney (1961)
Warm temperate	6	3.8	3.2	Tan and Troth (1982)
Tropical	5	1.5	1.6	Tan and Troth (1982)

[a] Note that the removal of Al and Fe results in high values in boreal and cool temperate soils, especially in the A horizon. Lower values characterize tropical soils, and there is little differentiation between horizons as a result of the removal of Si from the entire profile in long periods of weathering.

attempt to expand estimates of NPP, trace gas emissions, and other ecosystem processes depend heavily on landscape delineation of major soil groups (Melillo *et al.,* 1993; Potter *et al.,* 1996).

B. Fragmentation and Mixing

In many forests, leaf litter is fragmented and mixed into the lower layers of the soil within 1 year of abscission. The physical breakage of logs, after fungal attack has weakened the original cellular structure of wood, may largely determine the rate of their disappearance from the forest floor. The physical reduction and mixing of litter is largely carried out by an abundance of soil animals, ranging from microscopic nematodes to large earthworms (Hole, 1981). The result is an increased surface area for microbial attack and the movement of litter to more constant conditions of temperature and moisture in the lower profile.

There is an enormous diversity of soil invertebrates involved in the fragmentation or comminution of litter (Fig. 4.8). The functional roles of each are poorly known, partly because of the interactions between these organisms. For example, destruction of wood cellulose by termites is due to the action of symbiotic protozoa and bacteria contained in their lower digestive tracts. In the forest floor, some litter microarthropods are primarily predators on species that feed directly on fresh litter. Others feed on fungal hyphae that invade the forest floor layers. Dead soil animals and their fecal materials may be eaten by other animals, which, in turn, may be consumed by predators. Such interactions are an important aspect of the animal community in soil detritus in contrast to the more linear trophic relationships among the animals that feed above ground. The result is a rapid reduction in the size of litter material and a corresponding increase in area for microbial attack (Waring and Schlesinger, 1985).

Nematodes are among the smallest soil animals. Their populations range from 1,700,000 to 6,300,000 m^{+2} among various forest types, and nematodes tend to be particularly

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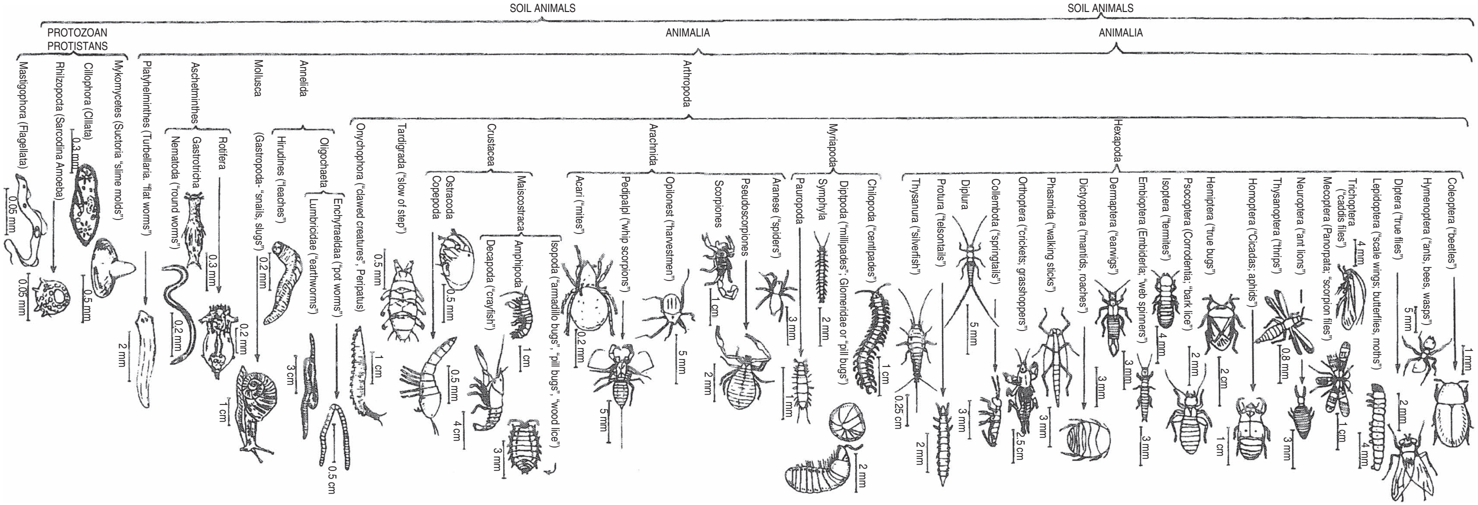

FIGURE 4.8. Classification of some of the groups of small soil animals important in processing forest litter. (From Hole, 1981.)

abundant in coniferous forests (Sohlenius, 1980). Springtails (Collembola) and mites (Acari) are also prevalent in coniferous forests, ranging up to $400{,}000\,\mathrm{m}^{-2}$ (Hole, 1981). Earthworms, on the other hand, are intolerant of coniferous litter and more abundant in temperate and tropical forests. Earthworms shift their activity downward in the soil profile moving from boreal to tropical regions (Lavelle *et al.,* 1993). Despite the large number of soil organisms in boreal and coniferous forests, the total biomass of soil animals increases by a factor of 6 from boreal to tropical forests. The biomass of earthworms is sometimes as high as 250 g fresh weight m^2 (Witkamp, 1971). Earthworms are especially effective in mixing the litter material through the soil profile; their movements leave open channels for air and water transport in the soil, while their decay-resistant casts preserve soil organic matter (Lavelle *et al.,* 1993). Termites are also most abundant in warm temperate and tropical forests, where their wood-tunneling activities cause a relatively rapid disappearance of fallen logs, as they can consume more than 50 times their weight per year in biomass (Wood, 1976).

Soil organisms have been classified by body size and trophic structure in attempts to understand their function. For the ecosystem ecologist, however, the most practical approach often is to look for the net effect of these organisms on the rates of energy flow and nutrient cycling in the detritus layers. In such studies, the decomposition of freshly abscised litter has been monitored under experimental conditions that either allow or exclude the normal activity of soil animals. The presence of soil organisms often allows a significantly greater overall rate of decomposition, largely through a more rapid fragmentation of litter (Witkamp and Ausmus, 1976).

Soil animals utilize the carbon-containing compounds of detritus as an energy source, respiring CO_2. Collectively these animals can respire up to 7% of the mass of litterfall in forest ecosystems (Witkamp and Ausmus, 1976). Because the biomass of soil animals is never a significant fraction of the forest floor, nutrient retention in these organisms does not slow nutrient cycling through the ecosystem (Seastedt and Tate, 1981). Compared to fresh litter, their fecal matter is often slightly higher in concentrations of N and P, as well as in lignified compounds that are difficult to digest. If litter material is first processed by soil animals, the resulting substrate is different both physically and chemically from fresh litter.

C. Microbial Decomposition

Although inorganic forms of nutrients are supplied through atmospheric inputs and mineral weathering, and conserved by plants through internal recycling, much, if not most, of the annual nutrient requirement of trees and other plants is supplied from the decomposition of dead materials in the soil. Decomposition of detritus completes the intrasystem cycle by releasing nutrient elements for plant uptake. *Decomposition* is the general term for the breakdown of organic matter by which soil bacteria and fungi obtain metabolic energy. *Mineralization* is a more specific term that refers to the processes that release carbon as CO_2 and nutrients in an inorganic, more oxidized form, such as sulfur in SO_4^{2-}. The decomposition process proceeds by the release of extracellular degradative enzymes (Burns, 1982). Often a sequence of decomposers is involved in the breakdown of organically bound nutrients with the release of inorganic forms.

During decomposition, significant loss in mass may occur through leaching of low molecular weight sugars, polyphenols, and amino acids, a process we all observe in making tea. Some of these compounds are also readily decomposed. Cell-wall materials, cellulose, hemicellulose, and lignin, which make up the majority of nonsoluble material in litter, are differentially attacked by microbes. Lignin is most resistant to attack, but it is so intimately entwined with cellulose strands in most materials that some must be degraded to allow microbial access to the more easily processed cellulose and hemicellulose. In the decomposition process, some degradation byproducts are formed that are "ligninlike," which may cause an increase in the total amount of lignin in the decaying material (Aber and Melillo, 1991; Johnson, 1992).

The rate at which different components in litter decompose is therefore not identical. Nevertheless, a general index of decomposition is often obtained by assuming comparable rates for all materials in broad categories. For example, the mean residence time (MRT, defined as the ratio of pool size to the rate at which material is added or removed from it, per unit of time) of all nonwoody forest floor material can be estimated from the ratio of forest floor mass to annual litterfall once forest floor accumulation stabilizes. The MRT decreases exponentially with increasing annual litterfall across biomes, varying from more than 40 years in some boreal needle-leaved evergreen forests to less than 1 year in some wet tropical forests (Landsberg and Gower, 1997; Fig. 4.9). A prediction of MRT, under steady-state conditions, can be derived Eq. (4.2), purely as a function of the dry mass of annual litterfall (x), in Mg ha^{-1} year^{-1}, where

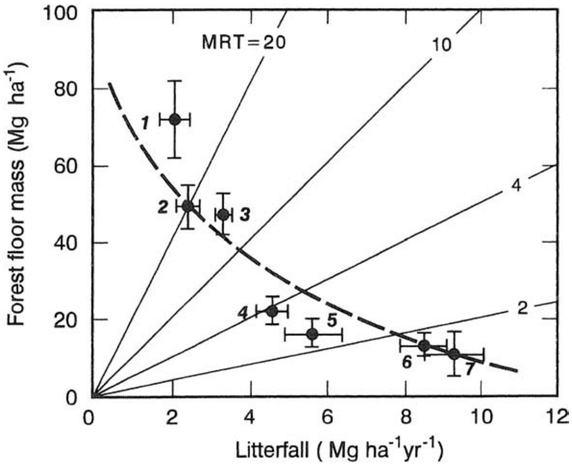

FIGURE 4.9. Average forest floor mass plotted against litterfall for (*1*) boreal needle-leaved evergreen, ($n = 16$), (*2*) boreal broad-leaved deciduous ($n = 7$), (*3*) temperate needle-leaved evergreen ($n = 73$), (*4*) temperate broad-leaved evergreen ($n = 11$), (*5*) temperate broad-leaved deciduous ($n = 40$), (*6*) tropical broad-leaved evergreen ($n = 31$), and (*7*) tropical broad-leaved deciduous forests ($n = 2$). Assuming the forest floor is in steady state, the average mean residence time (MRT, years) can be calculated as forest floor mass/litterfall mass. The straight lines indicate these values. The dashed curve is fit to the mean values and is the basis for deriving a related equation [Eq. (4.2)] that predicts MRT from equilibrium annual litterfall. (From Landsberg and Gower, 1997.)

$$\text{MRT (year)} = 55.4\,e^{-0.443x} \qquad r^2 = 0.93. \tag{4.2}$$

The mean residence time of forest floor litter is an important ecosystem property that is likely to change substantially with climatic variation and with the type of vegetation present. Through remote sensing, the maximum seasonal change in leaf area index can be monitored from space (Spanner *et al.*, 1994), which, with supplemental data on specific leaf mass (Pierce *et al.*, 1994), provides an opportunity to assess MRT across a wide range of spatial and temporal scales (Chapter 7). This estimate of forest floor MRT, however, excludes the turnover of roots and coarse woody debris (Harmon *et al.*, 1986; Vogt *et al.*, 1986).

Alternatively, decomposition rates can be determined using the litterbag technique, in which fresh litter is confined in a large number of mesh bags and placed on the forest floor or buried in the soil. At periodic intervals, some of the bags are retrieved and the loss in mass of litter measured. Simple models are based on an exponential pattern of loss where the fractional weight loss (m_1) over time (t, in days, months, or years) is given by

$$m_1(t) = c_1 e^{-kt} \tag{4.3}$$

Here, k is the decomposition (or decay) constant, which is determined from the plot of ln m_1 against t, from which $k = -(\ln m_1 + \ln c_1)/t$, where ln is the natural logarithm and c_1 is the intercept; when c_1 is set to unity to correspond with the initial weight, then $k = -(\ln m_1)/t$. The MRT and the time required to achieve 63, 95, and 99% of loss in mass (under steady-state conditions) can be calculated as $1/k$, $3/k$, and $4.6/k$, respectively (Olson, 1963). Thus, a litter sample that has a mass of 0.50 of its original after 200 days (0.55 of a year) would have a k value of 0.0035 day^{-1} or 1.26 year^{-1}, with a MRT of 0.8 year and 1% of its original mass present after 3.65 years.

The range in decomposition constants for deciduous and evergreen foliage, as well as fine and coarse woody debris, is variable within a biome (Table 4.7). In general, k values are higher in tropical forests than in other biomes, but there is no simple function with temperature or moisture, for the chemical composition of litter influences decomposition

TABLE 4.7
Decomposition Coefficients (k, years) for Foliage and Fine and Coarse Wood for Deciduous and Evergreen Forests in Contrasting Environments[a]

		Tissue component		
Biome	Leaf habit	Foliage	Fine wood	Coarse wood
Boreal	Deciduous	0.39–0.70	0.06–0.12	0.02–0.30
	Evergreen	0.22–0.45	—	—
Cold temperate	Deciduous	0.28–0.85	0.10–0.38	—
	Evergreen	0.14–0.69	—	0.01–0.06
Warm temperate	Deciduous	0.44–2.46	—	0.03–0.27
	Evergreen	0.16–0.75	—	0.04
Tropical	Deciduous	0.62–4.16	—	—
	Evergreen	0.16–2.81	—	0.12–0.46

[a] After Landsberg and Gower (1997).

rates as much as do climatic variables (Berg *et al.*, 1993). If the chemical composition of the litter is indexed by its initial lignin : nitrogen ratio, weight loss is more predictable within a particular climatic zone (Melillo *et al.*, 1982; Nadelhoffer *et al.*, 1983; Fig. 4.10). This chemical index of litter quality, which is widely applied in models of decomposition, reflects the fact that protein and amino acids are high in nitrogen and easily assimilated by microorganisms, whereas lignin, a complex polymer of aromatic rings, is exceedingly difficult for most microorganisms to attack and decompose. For a given quality of substrate, the decomposition rate increases exponentially with temperature with a respiration quotient (Q_{10}) between 1.5 and 2.5, assuming similar moisture conditions (see Chapter 3, Fig. 3.7).

We have obtained most of our understanding of the effects of temperature and other factors on decomposition from short-term studies of forest floor materials. The larger pool of organic matter stored as humus in soils has a much longer turnover time than the forest floor. This pool has grown in importance with the concern about climatic warming (Chapter 9). The net ecosystem exchange to the atmosphere is likely to increase, because decomposition increases exponentially with temperature, whereas photosynthesis is likely to be less responsive, ignoring change in species composition and the rise in atmospheric CO_2 (Chapters 3 and 5). To address these concerns, ecosystem models designed for longer term analyses separate soil organic matter (SOM) pools into at least three categories: (a) a small fraction (such as microbial biomass) that is extremely labile (5%), (b) an

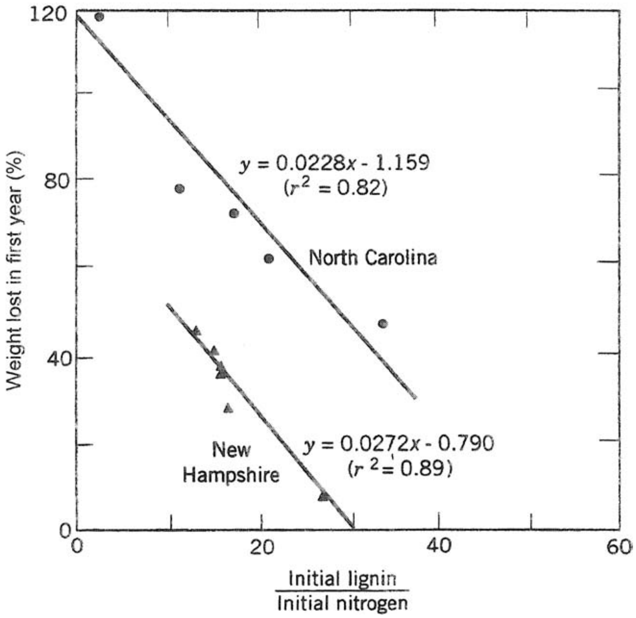

FIGURE 4.10. Decomposition of forest leaf litter as a function of lignin : nitrogen ratio in fresh litterfall of various species in New Hampshire and North Carolina forests. The warmer climate typical of North Carolina allows litter there with a lignin : nitrogen ratio below 10 to be decomposed in less than 1 year. (From Melillo *et al.*, 1982.)

intermediate pool (60–85% of the total), and (c) a passive SOM pool with turnover times of thousands of years (Parton *et al.*, 1987; Comins and McMurtrie, 1993).

The fraction of SOM in each of the various pools can be determined as a result of nuclear bomb testing in the early 1960s which nearly doubled the radiocarbon concentration of atmospheric CO_2. Eventually, the increased radioactive ^{14}C was incorporated into plant and soil organic matter and now serves as a basis on which the residence times of various categories of soil organic matter may be determined. Fractions are separated by differences in density and resistance to treatment with acids and bases. The low density fraction contains relatively undecomposed vascular plant material and sometimes a fairly large component of charcoal. The higher density fraction is associated with the mineral soil and increases with clay content (Trumbore *et al.*, 1996).

How rapidly the intermediate pool turns over is of particular concern because it represents a major fraction of total SOM and is most likely to affect net ecosystem exchange in the twenty-first century. Trumbore *et al.* (1996) showed from a ^{14}C analysis of archived (pre-1963) and contemporary soils taken from undisturbed forest ecosystems in California that 50 to 90% of the carbon in the upper 20 cm of soil (A horizon soil carbon) was in the intermediate category. The estimated turnover time of the intermediate SOM component ranged from 7 to 65 years, increasing exponentially with current mean annual temperature. Townsend *et al.* (1995) conducted a similar study across an elevation gradient in Hawaii using ^{14}C analyses and made additional comparisons of changes in $\delta^{13}C$ composition of soil organic matter following the conversion of forests (C_3 plants) to C_4 pasture grasses. The long-term implications of changing rates on the decomposition of soil organic matter are discussed in more detail in Chapter 5.

D. Humus Formation

As decomposition proceeds, there is an increasing content of amorphous organic matter, humus, that is produced from microbial activity associated with lignin degradation. The structure of humus is poorly known, but it appears to contain aromatic rings with phenolic (-OH) and organic acid (-COOH) groups. Molecules have no consistent molecular mass (range 5000 to >1,000,000) or repeating units. Humus accumulates in the lower horizons of forest soils. Although most humus has a high concentration of nitrogen in amino ($-NH_2$) groups, it is highly resistant to microbial attack. A long turnover time may apply even in tropical climates, when humus molecules acquire a random coil shape that facilitates protection in micropores of clay structures. Minerals with high specific surface areas and high ion-charge densities such as allophane and some iron oxides are particularly good at complexing large amounts of organic material in a form inaccessible to microbes; in contrast, kaolinite and other 1 : 1 layer-lattice minerals are much less efficient (Lavelle *et al.*, 1993).

Annual increments in the humus pool are small but continuous during soil profile development. Schlesinger (1991) summarized carbon accumulation rates measured in numerous soil chronosequence studies and reported average rates of 8.7, 5.6, and 2.4 $g\,C\,m^{-2}\,year^{-1}$ for boreal, temperate, and tropical forests, respectively. If we assume that NPP might average 5 $Mg\,C\,ha^{-1}\,year^{-1}$ (Chapter 3), then humus production is generally <1% of annual NPP. Because both the accumulation and turnover of humus are so slow, it is unlikely that this important carbon pool is ever really in steady state. Nevertheless, the dynamics are important to quantify because of the size of the organic and mineral pool involved.

Although the structure and formation of humus substances remain elusive, the importance of humus in forest ecosystems is clear. Humus contains an overwhelming proportion of the total N, P, and S in forest soils. In coarse-textured soils, humus greatly increases the water holding capacity; in fine-textured soils, humus reduces the bulk density, which improves conditions for drainage, root growth, and soil organisms. In most forests, humus in the soil profile exceeds the combined content of organic matter in the forest floor and aboveground biomass (Waring and Schlesinger, 1985).

E. Mineralization and Immobilization

The release of nutrients from decomposing organic matter does not proceed at the same rate as decomposition, because microbes, like plants, are growth-limited if either their energy source or nutrient supply is restricted. The rate at which litter loses mass is only a rough measure of the amount of carbon available to decomposing organisms. Nutrients present in excess of microbial requirements will be released (mineralized) as decomposition progresses, while those limiting growth will be preferentially retained (immobilized) in live microbial biomass. For example, during the decomposition of pine needles in Sweden, microbial growth is more limited by N, P, and S, which are shown to increase in reference to their initial litter content over time, compared with other nutrients that are lost at rates equal to or greater than that at which decomposition proceeds (Berg and Staaf, 1981; Fig. 4.11).

The rate of nutrient immobilization is highest in the first stages of decomposition of fresh litter, when the most easily decomposed compounds are available as an energy source. As the carbon and energy yield from decomposition declines, microbial growth slows, and there is little further nutrient immobilization. It is the death of the microbial populations (<5% of SOM) that accounts for most nutrients released in their inorganic form from litter (Marumoto *et al.*, 1982; Diaz-Ravina *et al.*, 1995). After a year or so, the concentrations of N and P in the partially decayed litter increase substantially. As a general rule, initial net mineralization will occur at C : N ratios below 20 : 1, C : P ratios less than 200 : 1, and C : S ratios less than 200 : 1. In contrast, net immobilization will begin to occur at C : N ratios of 30 : 1, C : P ratios exceeding 300 : 1, and C : S ratios over 400 : 1 (Stevenson, 1986). Immobilization is most significant for N and P, which are generally limiting to microbial growth, and much less significant for Mg, K, Ca, and Mn. The critical carbon to nutrient ratios vary slightly, depending on the substrate and assimilation efficiency of the decomposer (Paul and Clark, 1996).

A total reduction in the absolute amount of nutrients in the litter represents net mineralization and increased availability to plants. On the other hand, a net immobilization of nutrients may also occur through the incorporation by microbes of nutrients taken from older decaying material, captured in throughfall and soil solution, or derived from free-living nitrogen fixers. Asymbiotic N fixation is particularly important in the decay of coarse woody debris, which often has initial C : N ratios between 200 : 1 and 500 : 1. Immobilization of nutrients predominates in the layer of fresh litter on the soil surface, whereas mineralization of N, P, and S is usually greatest in the lower forest floor. During soil

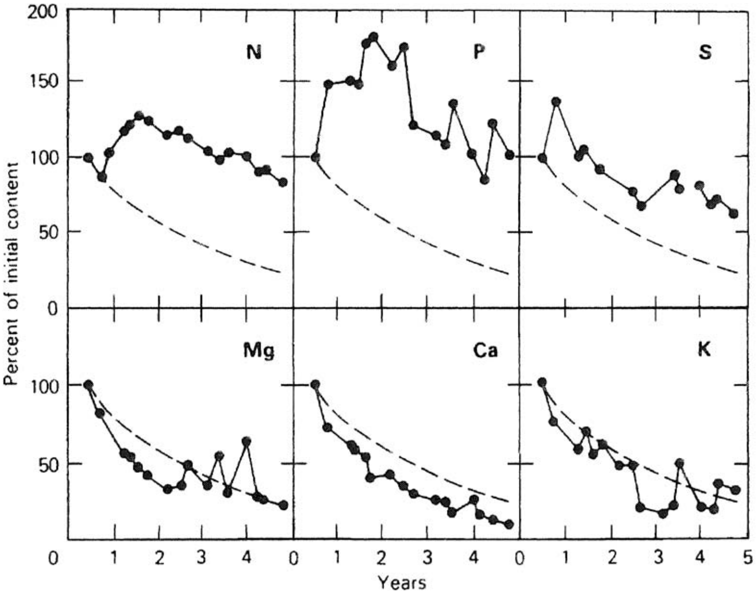

FIGURE 4.11. Loss of nutrient elements from the litter of Scots pine (*Pinus sylvestris*) during the first 5 years of decomposition in Sweden. For each nutrient, the solid line indicates the percentage of the initial content remaining at various intervals. Note that loss of Mg, Ca, and K is more rapid than the disappearance of the organic mass of litter (dashed line), whereas N, P, and S are retained during the period of litter decay. (From Staaf and Berg, 1982.)

development, nutrient-rich fulvic acids with low C : N, C : P, and C : S ratios are transported to the lower soil horizons where the nutrients may be quickly mineralized and made available to plants. Sollins *et al.* (1984) also found that the lighter density fraction of soil organic matter, representing fresh plant residues, generally has a higher C : N ratio and lower mineralization than the heavier density fraction comprising humic substances. Across biomes, N is likely to be most immobilized in temperate and boreal forests, whereas P is likely to be immobilized more commonly in tropical forests (Vogt *et al.*, 1986).

Seasonal fluctuations of soil temperature and moisture can stimulate microbial activity more than in constant favorable conditions (Biederbeck and Campbell, 1973). These variations cause greater turnover of the microbial populations and mobilization of nutrients (Diaz-Ravina *et al.*, 1995). Similarly, the periodic addition of fresh litter materials high in degradable carbon can sometimes stimulate the degradation of resistant substrates in the soil (Sørenson, 1974; Janzen *et al.*, 1995). The balance between mineralization and immobilization thus shifts continually from season to season through a soil profile. This variation can be modeled and measured, but it requires detailed knowledge of spatial variation in environmental conditions and substrate quality (White *et al.*, 1988).

The mineralization of nitrogen is a particularly good example of a dynamic process (Fig. 4.12). It begins with the release of ammonium (NH_4^+) from decomposing material. Some NH_4^+ may undergo nitrification, in which oxidation of NH_4^+ to nitrate (NO_3^-) is coupled to the fixation of carbon by chemoautotrophic bacteria in the genera *Nitrosomonas*

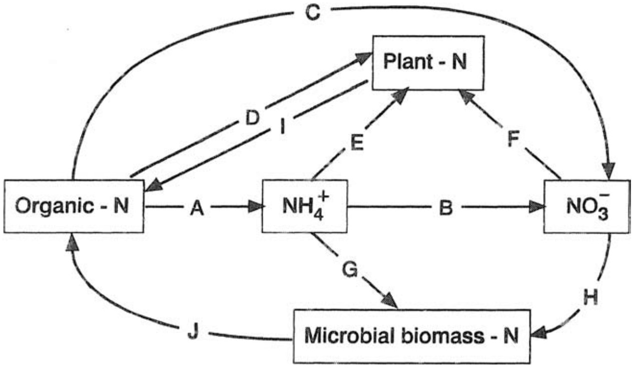

FIGURE 4.12. Schematic diagram of important transformations of N within the soil and forest floor. A, Gross mineralization; B, gross nitrification with NH_4^+ as the substrate; C, gross nitrification with organic N as the substrate; D, mineralization of organic substrate through mycorrhizal fungi directly into plants; E and F, plant uptake of NH_4^+ and NO_3^-, respectively; G and H, gross immobilization (microbial assimilation) of NH_4^+ and NO_3^-, respectively; I and J, organic N inputs from plants and microorganisms, respectively, via death, sloughing, and exudation. Note that net mineralization measured by laboratory incubations and buried litterbags is $(A + C) - (G + H)$. Similarly, net nitrification is $B + C - H$. (From Davidson *et al.*, 1992.)

and *Nitrobacter.* These autotrophic nitrifying bacteria obtain their carbon directly from CO_2 rather than from plant material. Some heterotrophic organisms can also convert organic N directly to NO_3^-. In addition, it is recognized that some mycorrhizal fungi can shortcut the mineralization process by acquiring N directly from dissolved organic nitrogen (DON) associated with humic compounds in extremely N-poor soils (Northup *et al.*, 1995; Ruess *et al.*, 1996). Gross mineralization and gross immobilization, as shown with ^{15}N studies, can occur in a matter of days, so that net mineralization may represent less than 10% of the total N released in a 30-day period (Davidson *et al.*, 1992). Gross mineralization is therefore a preferred measure of N available to plants and microbes (Myrold, 1987).

Stable isotopes of nitrogen offer a means of assessing the relative availability of nitrogen to plants. During each step in the process of converting organic N to NH_4^+, and to NO_3^-, the heavier isotope (^{15}N) is discriminated against, which results in the product of each transformation being less enriched in ^{15}N than its substrate (and exhibiting a lower $\delta^{15}N$). The difference between the natural abundance of ^{15}N found in foliage and that in soil may thus serve as an integrative measure of N availability to a particular tree species. Garten and Van Miegroet (1994) applied this principle in the Great Smoky Mountains of eastern Tennessee, where atmospheric deposition of N has been documented to increase with elevation. They demonstrated that $\Delta^{15}N$ values (between foliage and surface soils) progressively narrowed as coniferous species encountered soils with higher amounts of available N (Fig. 4.13). The correlation was also good for deciduous hardwood species, but varied more because of differential preferences for NH_4^+ and NO_3^- (Garten and Van Miegroet, 1994). Differences in rooting depth and in the form that N is acquired increase the variation in $\delta^{15}N$ observed among species growing on infertile sites. Once N becomes readily available, however, species tend to show similar $\delta^{15}N$ values (Schulze *et al.*, 1994b).

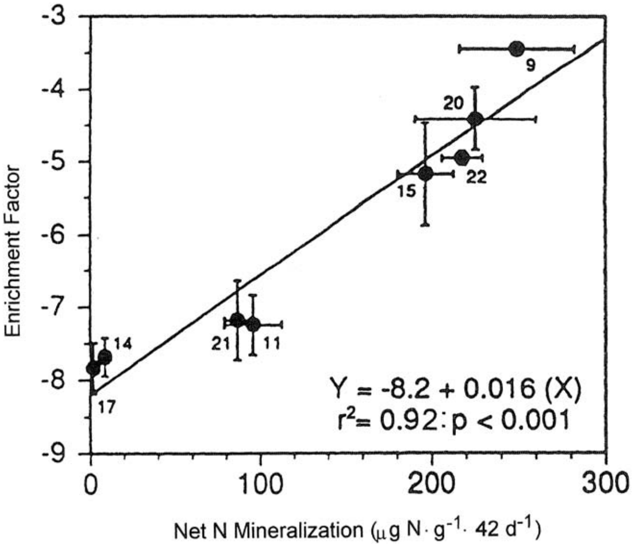

FIGURE 4.13. Atmospheric deposition of nitrogen increases across an elevation gradient in the Great Smoky Mountains National Park in Tennessee. As a result, assays of net mineralization of N in the surface mineral soil show a parallel increase (plots 17 to 9). Stable isotope composition was determined on foliage samples from coniferous species and from the soil on which they grew. The difference in isotopic composition (enrichment factor) decreased proportionally as net mineralization of N in the soil increased. Data are means ($n = 6$), and error bars represent ± SE. (From Garten and Van Miegroet, 1994.)

Forest composition and nutrient availability are often closely interlinked, as we inferred from the earlier discussion on nutrient use efficiency. In the case of nitrogen, tree species with extremely low requirements are adapted to soils where DON is the major form present (Northrup *et al.*, 1995); most conifers are adapted to intermediate conditions where NH_4^+ is the dominant form, whereas riparian zone species are particularly suited to high levels of NO_3^- through their ability to induce the formation of nitrate-reducing enzymes in their foliage (Smirnoff *et al.*, 1984; Smirnoff and Stewart, 1985). Ecosystem retention of N, as we shall see, is also progressively reduced with increasing availability, so that high losses of NO_3^- usually indicate an excess availability while a dominance of DON in leachate reflects extreme scarcity of N.

The following summarizes some key points and implications from the last three sections:

- Fragmentation and mixing are essential steps that a host of small soil animals perform on litter before it is subjected to microbial decomposition. The introduction of pesticides or other toxic chemicals may reduce the efficiency of various groups of animals and could substantially alter the normal rates of decomposition and mineralization.
- Decomposition of woody debris, leaf litter, and belowground components of detritus proceeds at significantly different rates. For this reason, it is generally recommended that these organic pools be separately recognized.

- Moisture and temperature conditions strongly affect decomposition and mineralization rates. The hydrologic and energy balance models introduced in earlier chapters provide a means of defining these environmental variables without requiring direct measurements in the litter and soil.
- The chemical quality of the organic substrate, which can he quantified by C : N ratios and other related indices, strongly affects the mineralization and immobilization processes.
- As a scaling principle, a decreasing amount of detail is required to estimate process rates at progressively longer time intervals. Thus, on an annual basis, decomposition rates can be relatively easily assessed, on the basis of decomposition constants acquired from litterbag studies, forest floor/litterfall mass comparisons, and even from satellites by monitoring the annual transfer of leaf litter from the canopy to the ground. The general reliability of these annual estimates, however, rests on an understanding of key variables and interactions acquired at much shorter time steps.

F. Cation and Anion Exchange

Ion exchange in soils is a process based on the surface charge of clays and organic particles. By virtue of this charge, ions released from weathering or decaying organic matter, or those added through atmospheric deposition, are held on the particle surfaces and resist leaching. The ions, however, are not held with such force that they cannot exchange rapidly with other ions from the soil solution nor be taken up by plant roots.

The layered silicate clay minerals that dominate temperate zone soils possess net negative charge that attracts and holds cations dissolved in the soil solutions. Silicate clay minerals possess several types of negative charges which contribute to soil cation-exchange capacity (CEC). Exchange capacity is defined in *relative equivalent mass:* the amount of the substance, in grams, that will supply the same total charge as is supplied by 1 g of H^+. Equivalent mass is then computed by dividing the mass of the ion by the valence. Thus a solution that contains 1 g of H^+, 23 g of Na^+, or 20 g of Ca^{2+} contains 1 equivalent of each ion. Exchange capacity is usually expressed in milliequivalents (meq) per 100 g or, with standard international (SI) units, cmol (+) per kilogram of soil.

At the edges of clay particles, hydroxide radicals (-OH) are often exposed to the soil solution. As the pH of the solution increases (i.e., becomes less acidic), H^+ ions become less strongly bound to oxygen in the -OH radicals, increasing the negative charges on clays. In addition, there is another source of negative charge that arises from ionic substitutions within silicate clays. For example, when Mg^{2+} substitutes for $A1^{3+}$, there is an unsatisfied negative charge in the internal crystal lattice. Unlike the first source of negative charge, this second source is permanent because it originates inside the crystal structure and cannot be neutralized by covalent bonding of H^+ from the soil solution. Organic compounds in soils also create cation-exchange sites on phenolic (-OH) and organic acid radicals. Organic matter is the only source of cation-exchange sites in coarse-textured sandy soils and in peat bogs.

Cation-exchange capacity and base saturation, the percentage of the exchange sites occupied by nutrient cations (Ca^{2+}, Mg^{2+}, K^+, NH_4^+, Mn^{2+}), increase during initial soil development on newly exposed parent materials. As weathering of soil minerals continues, cation-exchange capacity and base saturation decline (Bockheim, 1980). Temperate forest soils dominated by 2:1 clay minerals have much higher cation exchange capacity (100–150 meq/100 g) than soils dominated by 1:1 clay minerals (5–40 meq/100 g). Most fertile temperate forest soils have high cation-exchange capacity, which allows more nutrient cations to be held on clay particles and reduces losses by leaching. A high base-exchange capacity in the surface soil and subsoil also provides a buffer against pH changes associated with acid precipitation, and thus is a critical ecosystem property throughout the temperate forest region in the northern hemisphere (Johnson and Lindberg, 1992). Tropical forest soils are general poorly buffered, first because they are dominated by iron and aluminum oxides which provide extremely low cation-exchange capacity (2–4 meq/100 g) and, second, because most of the base cations have been leached as a result of long periods of intense weathering and leaching.

In contrast to the permanent negative charge in soils of the temperate zone, tropical soils dominated by oxides and hydrous oxides of iron and aluminum show variable charge on soil exchange sites, depending on soil pH (Johnson and Cole, 1980; Schlesinger, 1991, 1997). At low pH, soil surfaces absorb H^+ from solution and become positively charged (attracting anions). At some intermediate pH, the previously absorbed H^+ dissociates into solution, which leaves no net charge (zero point charge) on the exchange complex. At extremely high pH (i.e., above pH 9), an additional H^+ dissociates, leaving the surface negatively charged (attracting cations).

The pH at which zero point charge (ZPC) occurs varies. Anion-exchange capacity is typically greater in soils where the crystalline surfaces of Fe and Al minerals are highly fractured, exposing a large surface area. Anion-exchange capacity is also present in the soils of warm temperate forests where iron and aluminum hydroxides are abundant in the soil profile (Johnson *et al.*, 1979). This anion-exchange capacity helps explain how much of the sulfate in acid rain does not readily leach through Fe- and Al-rich weathered soils in the southeastern United States (Johnson *et al.*, 1986).

Similarly, tropical forest soils with high anion-exchange capacities are able to adsorb a fair proportion of NO_3^- in their lower profile. Following a forest clearing, the mineralization of fresh litter may add an additional 300–600 kg N ha^{-1} to that normally produced. Once perennial vegetation with deep root systems is reestablished the adsorbed nitrate is again accessible and may be recycled through the ecosystem (Matson *et al.*, 1987).

Exchange of cations and negatively charged anions from the surface of secondary soil minerals and organic matter occurs as a function of chemical mass balance with the soil solution. Elaborate models of ion exchange have been developed by soil chemists (Tan, 1982). In general, cations are held and displace one another in the following sequence on cation-exchange sites:

$$Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+.$$

Anion exchange follows the sequence

$$PO_4^{3-} > SO_4^{2-} > Cl^- > NO_3^-$$

Either sequence can be altered by the presence of large quantities of the more weakly held ions in the soil solution. Liming to reduce the effects of acid rain, for example, displaces and neutralizes H^+ from the exchange sites by providing an excess of Ca^{2+}. In addition, acidic conditions mobilize Al^{3+}, the cation most likely to displace others from exchange sites. Hydrogen ions affect the solubility of most other ions in soil solution; thus, pH is often considered the master variable that controls soil nutrient availability.

In time, most forest soils become more acid because plant roots selectively absorb more nutrient cations than anions, releasing H^+ in organic acids to maintain an internal balance of charge. In addition, root respiration releases CO_2, forming carbonic acid in the soil solution (Fig. 4.14). The increase in H^+ ions in solution reduces base saturation through time and increases nutrient losses by leaching to lower parts of the soil profile and into the groundwater. Conventional measurements of nutrient availability on exchange sites are performed on small samples of soils collected from various parts of the soil profile. Alternatively, sampling the chemistry of solutions collected from above the canopy to below the rooting zone can provide much additional insight (Table 4.5). The information provided from such detailed analysis of soil solution chemistry is often required to assess the longer term implications of various management policies regarding slash disposal, fire control, fertilization, and the manipulation of species composition in an effective manner.

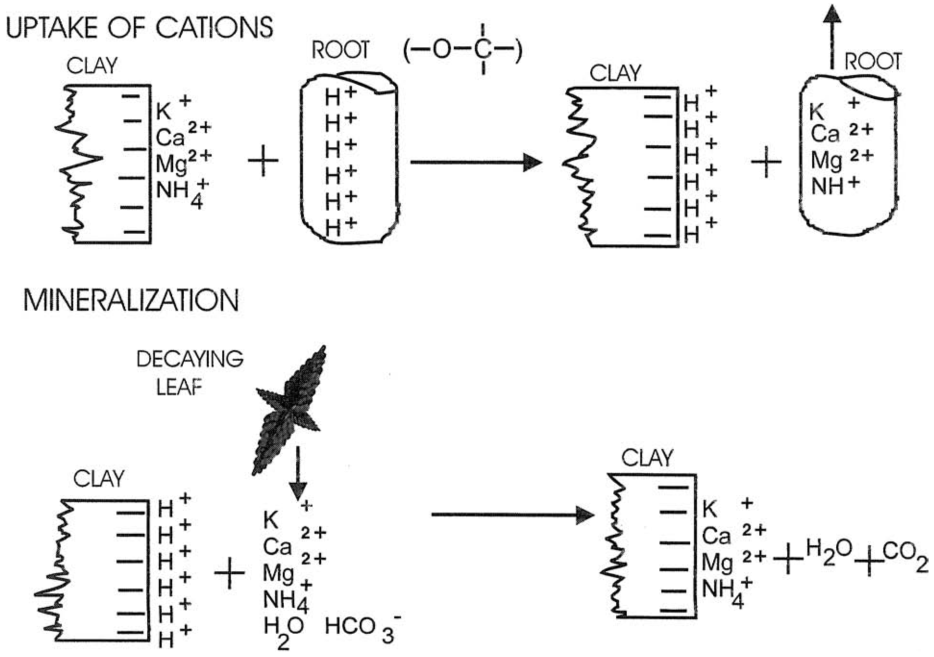

FIGURE 4.14. The cation cycle begins with positively charged nutrient ions held on negatively charged clay particles. The cations are exchanged for hydrogen ions released as organic acids by plants. Roots take up the nutrients and leaf litter returns them annually to the soil. Through decomposition, nutrient cations are released to return again to the soil exchange sites. (From Glatzel, 1991.)

G. Adsorption and Fixation

There is a gradation in nutrient availability between ions held weakly on exchange sites, those absorbed onto surfaces of clay and humus, and those fixed more permanently through substitution directly into the layer lattice of a clay. As previously noted, iron and aluminum hydroxides have a surface positive charge at normal soil pH. Nutrient anions, especially PO_4^{3-} and SO_4^{2-}, are often held under these conditions much more tightly than in normal exchange reactions. This stronger chemical bonding is termed *adsorption.* Because the reaction is sensitive to the concentration of ions in solution, the process may be reversed and *desorption* can occur. Starting at low ion concentrations in solution, the adsorption process increases rapidly, then plateaus as the soil approaches its maximum capacity to adsorb ions (Schlesinger, 1991). Under acidic conditions, a large total amount of anions of phosphate and sulfate may be permanently held on the surfaces of iron sesquioxides through the release of -OH or H_2O to the soil solution (Binkley, 1986).

The cations NH_4^+ and K^+ may also be fixed so strongly on clays that they cannot be recovered by exchange reactions. Both of these cations can be entrapped in the intermicellar regions of expanding lattice clays. On closure of the space, NH_4^+ and K^+ are fixed. The total amount of these ions that can be fixed can be quite high, but the fixation capacity is limiting; thus, above a certain concentration, ions will be kept in solution (Tan, 1982). Ammonia (NH_3) and amino acids can also be fixed through physical condensation reactions of phenolic by-products from partly degraded lignin (reviewed by Johnson, 1992). Nonbiological incorporation of ammonia into humus is enhanced by high pH and high concentrations of NH_3 and NH_4^+. Thus adding nitrogen as urea (CON_2H_4), a condensation product of NH_3 and CO_2, often results in >40% being bound in a fixed form (Preston *et al.*, 1990; Nason and Myrold, 1992).

Biological activity affects adsorption–desorption and even the fixation process by modifying pH through the release of organic acids and by the selective extraction of ions from solution. Graustein *et al.* (1977) suggested that the production of oxalate compounds by fungal hyphae increases PO_4^{3-} availability by complexing iron in the soil solution. Soluble organic compounds, including polyphenols and humic acids, also mobilize or complex ions in solution. In general the adsorption and fixation potential of a soil horizon is increased by the presence of hydrous oxides of iron and aluminum and decreased by the presence of organic matter (Ae *et al.*, 1990). Adsorption and fixation of anions are generally highest in lower soil horizons where iron and aluminum oxides accumulate and organic content is low. Fixation of ammonia and ammonium is more likely in the upper profile where organic content is high. The speed at which adsorption–desorption reactions occur is relatively rapid (hours), in contrast to mineral weathering which requires centuries to convert primary to secondary minerals and to transfer clays, Si, Al, and Fe from one horizon to another.

Models of the adsorption–desorption process are useful in explaining differences observed in nutrient availability and in losses in solution associated with both upland and bottomland soils (Kafkafi *et al.*, 1988; Yanai, 1991; Masscheleyn *et al.*, 1992; Prenzel and Meiwes, 1994). Principles derived from these detailed models provide a basis for judging what soils are most sensitive to disturbance from logging or to chronically high additions of sulfur and nitrogen from anthropogenic sources (Chapter 6).

H. Volatilization and Leaching

In undisturbed forests, losses of nutrients and organic carbon occur mainly through microbially induced volatilization and through leaching. On an annual basis, these losses are small and often in near balance with inputs from weathering, atmospheric deposition, and fixation of N and C. Methane (CH_4), nitrous oxide (N_2O), dinitrogen (N_2), and hydrogen sulfide (H_2S) are examples of gases volatilized from anaerobic soils. Leaching is important in carrying dissolved organic carbon, nitrogen, and other elements downward through the soil and subsoil to the groundwater, where it may seep into adjacent ecosystems, and again become available to plants, or flow directly into streams and lakes.

Nitrogen is one of the nutrients most subject to loss by volatilization, particularly when added as urea fertilizer which can be quickly converted to NH_3 gas when soils are warm and moist (Nason and Myrold, 1992). Some fraction of the volatilized NH_3 may be captured on foliage and incorporated into organic compounds, so the net loss from the ecosystem may be less than that estimated from the soil (Pang, 1984; Nason and Myrold, 1992). During the process of nitrification, some NO and N_2O gas may be released, but the loss from upland temperate and boreal forest soils is usually small, $<2\,\text{kg N ha}^{-1}\,\text{year}^{-1}$ (Robertson and Tiedje, 1984). In some recently disturbed tropical soils, rates may be much higher (Matson *et al.*, 1987). Often, the net N exchange from undisturbed upland forest is negative, as microbes take up more N from the atmosphere than they release (Aber and Mellilo, 1991).

Nitrogen is also volatilized through *denitrification*, the reverse process that converts nitrate to N_2O and N_2:

$$NO_3^- \rightleftharpoons NO_2^- \rightleftharpoons NO \rightleftharpoons N_2O \rightleftharpoons N_2. \tag{4.4}$$

Denitrification is performed by soil bacteria that are aerobic heterotrophs in the presence of O_2, but it also operates under anaerobic conditions (Schlesinger, 1991). The ratio of N_2O to N_2 produced during denitrification is not constant; increased concentrations of nitrate, nitrite, molecular O_2, and soil acidity in the presence of NO_3^- stimulate the production of N_2O relative to molecular N (Schlesinger, 1991). For a long time, denitrification was thought to occur only in flooded, anaerobic soils; however, soil scientists have shown that oxygen diffusion to the center of soil aggregates is sufficiently slow that anaerobic microsites are present even on upland sites (Tiedje *et al.*, 1984).

In a closely related process, SO_4^{2-} can also be converted to sulfur dioxide (SO_2) or hydrogen sulfide (H_2S), which occurs commonly in marshes and other types of wetlands but rarely in forests. Again, heavy deposition of sulfate on forests may increase sulfur volatilization losses, but leaching losses are more important because they contribute to the removal of other cation nutrients in solution and the acidification of soils (Mitchell *et al.*, 1996). Trace gas emissions are a particular concern in wet tropical climates where, following forest clearing or windthrow, uptake of water and nutrients by vegetation is reduced while soil temperature and the pore space filled with water increase (Keller and Reiners, 1994). Under these conditions large amounts of NO, N_2O, and other trace gases may be released until the available C and N pools are fully utilized (Steudler *et al.*, 1991; Chapter 6).

All heterotrophic microbial activity is highly dependent on the availability of an adequate labile carbon source, the appropriate substrate, and the temperature. Trace gas emission is particularly sensitive to free oxygen levels, which are highly correlated with the fraction of water-filled pores and the soil texture. In the case of CH_4 production, tropical wetlands and boreal peat bogs are the major contributors, while most upland forest soils are net sinks (Schlesinger, 1991). Generalized models for predicting N_2 and N_2O production from nitrification and denitrification, as well as methane production and consumption, are now available with monthly or finer resolution (Crill, 1991; Peterjohn *et al.*, 1994; Parton *et al.*, 1996). Because these generalized models were based on extensive laboratory and field experiments, they may be widely applied across landscapes. Through remote sensing, seasonal estimates of surface moisture and temperature conditions can be acquired that are closely correlated with trace gas production from specified vegetation units (Waring *et al.*, 1995b).

Leaching losses from forests are usually much higher than those associated with trace gas emissions. In previous sections, we have identified those forms of nutrients and organic matter that are highly soluble and not held strongly on clay exchange sites, or otherwise adsorbed or fixed. These include dissolved organic carbon (DOC), DON, NO_3^-, K^+, Cl^-, H^+, and HCO_3^-. Not surprisingly, these forms are among those most likely to be leached from forest ecosystems, even in undisturbed conditions. The total flux of elements carried in solution can be derived by combining models that predict water flow (discussed in Chapter 2) with those that predict ionic concentrations in solution (referenced in this chapter).

In most undisturbed temperate and boreal forest systems, concentrations follow the order DON > NH_4^+ > NO_3^- in the soil solution, and the total export of N in any form is low (Northrup *et al.*, 1995; Currie *et al.*, 1996). In temperate deciduous forests, conditions favor nitrification in the spring before budbreak; however, once leaves begin to expand, demand for nitrogen usually exceeds the available supply, so again leaching losses are minimum. In autumn, on the other hand, fresh litter has a high C : N ratio, so most nitrogen is immobilized during early phases of decomposition before soil temperatures become limiting. Flooding, of course, removes nitrate from the soil, but anaerobic conditions also halt NO_3^- production. When nitrate appears in seepage and stream water, particularly in temperate and boreal forests, it is often indicative of ecosystem disturbance associated with an outbreak of defoliating insects, root disease, blowdown, or chronically high rates of atmospheric deposition (Chapter 6). In the wet tropics, nitrification is a dominant process, but even there disturbance favors an increased rate of nitrification and losses through leaching (Matson *et al.*, 1987).

V. MASS BALANCE AND MODELS OF MINERAL CYCLES

Mineral cycling through an ecosystem includes transfers in and out, as well as the internal cycles through the vegetation and soil. One approach to account for these transfers is to perform a mass balance analysis. We provide examples of mass balance analyses from an isotope-tracer study and from a more conventional approach. Both studies rely on calculations of primary production and estimates of annual litterfall.

A second approach to account for the movement and transformation of element through forest ecosystems is through the application of detailed mineral cycling models. Unlike ecosystem models presented in Chapter 3, mineral cycling models must incorporate more soil processes, and often this requires separation of the surface and subsoil into many layers. By reviewing one mineral cycling model, we provide an example of the kind of process information incorporated in these types of simulation models.

A. Mass Balance Analysis

The annual circulation of nutrients may be assessed with a mass balance approach. Because annual changes in the soil nutrient pool are small, and difficult to measure, most mass balance analyses exclude belowground measurement, beyond quantifying the total pool of nutrients in the rooting zone. The first mass balance analysis we present was obtained by adding small amounts of isotopically enriched fertilizer to a spruce forest in Germany. Buchmann *et al.* (1996) demonstrated that less than 1 kg ha^{-1} of $^{15}NH_4^+$ and $^{15}NO_3^-$ was required to obtain a quantitative measure of the circulation of these two forms of N from the soil, through the vegetation, and back in the litterfall. Table 4.8 presents the total amounts and percentages of labeled N recovered from each identified ecosystem component 8 months after initiation of the experiment. From these analyses, which account within <1 to 3.7% for all of the labeled ^{15}N applied, we see that >80% of labeled N was retained in the soil, with more than two-thirds in the organic horizon. Although spruce trees represented over 5 times the biomass of the understory vegetation, they acquired only one-third (3.4 versus 9.1%) of the ammonium and less than half (6.5 versus 14.8%) of the nitrate ^{15}N tracer.

The estimated retention of ^{15}N additions into different ecosystem components was determined with the following mass balance equation:

$$m_{\text{label}} \approx m_{\text{f}}(\delta^{15}\text{N}_{\text{f}} - \delta^{15}\text{N}_{\text{i}})/(\delta^{15}\text{N}_{\text{label}} - \delta^{15}\text{N}_{\text{i}}) \tag{4.5}$$

TABLE 4.8

Total Nitrogen Budget and Percent ^{15}N Label Recovered from Major Ecosystem Components after Application of 0.6 kg ha^{-1} of Isotopically Enriched NH_4^+ and NO_3^- to a German Spruce Forest[a]

	Nitrogen in biomass		^{15}N retained, % of total	
Ecosystem component	g m^{-2}	% of total	$^{15}NH_4^+$	$^{15}NO_3^-$
Picea abies	10.5	0.65	3.4	6.5
Understory plants	10.0	0.63	9.1	14.8
Litter	0.2	0.01	0.03	0.04
Roots	3.0	0.18	1.0	3.5
Plant totals	23.7	1.47	13.5	24.8
Soil organic horizon	164	10.2	62.6	46.3
Mineral soil, 0–65 cm	1412	88.3	24.5	32.6
Total ecosystem	1600	100	100.6	103.7

[a] After Buchmann *et al.* (1996) with kind permission from Kluwer Academic Publishers.

where m_{label} is the mass of ^{15}N-labebed compound incorporated into the component, m_{f} is the final mass of N in the component, $\delta^{15}\mathrm{N}_{\mathrm{f}}$ is the final δ^{15}N abundance in the component, $\delta^{15}\mathrm{N}_{\mathrm{i}}$ is the initial δ^{15}N abundance in the component, and $\delta^{15}\mathrm{N}_{\mathrm{label}}$ is the δ^{15}N abundance in the labeled compound. Similar mass balance analyses have been derived with the natural abundance of Sr isotopes used as a surrogate for Ca to separate the contribution of atmospheric deposition from mineral weathering and quantified that acid precipitation is causing a net depletion in the available Ca pool in a 53-ha forested watershed in New Hampshire (Bailey *et al.*, 1996).

A more conventional and complete nutrient analysis is illustrated for an 80-year-old beech forest in Germany (Table 4.9). As with the isotopic analyses, measurements of total biomass and its mineral content were required to estimate internal storage and the annual transfer of nutrients. Mineral uptake is equivalent to the annual storage in wood plus the replacement of losses in litterfall and leaching, minus that added from atmospheric deposition or through N fixation. Note that >90% of the annual requirement of N is allocated to foliage, whereas <10% is allocated to wood. The annually recycled nutrient capital returned to the soil in litterfall or leachate was a relatively small percentage of the pool in tree biomass (N, 5%; P, 3%; K, 9%; Ca, 10%; and Mg, 9%). The short-lived organs, however, store a smaller percentage of total nutrients accumulated in biomass. For most nutrients, storage in wood increased by about 1% each year.

TABLE 4.9

Storage (kg ha^{-1}) and Annual Circulation of Nutrients in (kg ha^{-1} year^{-1}) in a Beech Forest, Solling, Germany[a]

Ecosystem components	N	P	K	Ca	Mg
Annual storage					
Foliage	96	6	31	18	3
Wood and branches	309	30	171	285	24
Roots	580	11	32	26	6
Forest litter layer	1050	72	123	118	44
Soil–root zone	9452	2310	550	280	45
Total storage kg ha^{-1}	11,487	2429	907	727	122
Annual demand					
Foliage (A)	96	6	31	18	3
Wood and branches	11	1	7	11	1
Roots	2	0.5	1	1	0.5
Total demand (B), kg ha^{-1} year^{-1}	109	7.5	39	30	4.5
Annual return in solution					
Throughfall and stemflow (C)	22	0.5	23	18	4
Precipitation (D)	22	7	4	13	3
Net loss from canopy leaching (C – D)	0	–6.5	19	5	1
Net uptake (B + C – D), kg ha^{-1} year^{-1}	109	1	58	35	5.5
Return in litterfall (E)	54	4	18	18	2
Total return (E + C – D)	54	–2.5	22	23	3
Reabsorption (A – E)	42	2	13	–7	1
Demand from soil (B + C – E – D), kg ha^{-1} year^{-1}	55	–3	40	17	0.5

[a] From Cole and Rapp (1981).

The beech forest received 22 kg N ha^{-1} $year^{-1}$ in precipitation, with additional unmeasured contributions in dryfall. This excess N was derived from pollution, which may help explain the excessive amounts of N and Ca recorded in throughfall and stemflow, as well as the apparent lack of P required from the soil. In any case, excess N has accumulated in the foliage to the extent that other nutrients, with the exception of Ca, are suboptimal in relative abundance (Table 4.1). Nutrient budgets for nearly 40 sites were summarized by Cole and Rapp (1981) as part of the International Biological Program during the 1970s. These analyses serve as benchmarks against which to measure the effects of changes in atmospheric deposition since the 1970s (Chapter 6).

B. Mineral Cycling Simulation Models

The need for extrapolation to conditions where atmospheric inputs, vegetation, litter, and soil conditions may all have changed has encouraged the development of ecosystem simulation models that attempt to couple water, carbon, and mineral cycles (see Chapter 3). Most ecosystem simulation models consider nitrogen as it affects decomposition, net primary production, and soil organic matter accumulation but generally disregard other elements and processes that involve exchange, adsorption, fixation, and weathering. Soil scientists have developed detailed models of weathering and ion exchange, but most are not linked to changes in forest composition or to litter quality. Concern about the long-term implications of acid precipitation has fostered a collaborative effort to produce more comprehensive nutrient cycling models that include the necessary interactions to predict changes in Al : Ca ratios in soil solution, acidity, and base saturation that affect nutrient uptake and primary production (Kros and Warfvinge, 1995).

Although a large number of nutrient cycling models exists, only a few are well balanced, in the sense that they describe all aspects of the forest ecosystem with a comparable level of detail. Tiktak and van Grinsven (1995) in their review of 16 models also found little consistency in the manner in which nutrient uptake and reallocation within vegetation were treated. In fact, the biggest challenge to modeling nutrient cycling appears to lie in predicting how roots respond to changes in soil chemistry and the subsequent effects on tree growth and nutrient use efficiency (Mohren and Ilvesniemi, 1995). Less than a third of the models reviewed were well documented and available for independent testing; only three were designed to consider forests with a mixture of species (Tiktak and van Grinsven, 1995). Even in estimating the water balance of a pure spruce forest, models differed substantially in partitioning evaporation, transpiration, and interception (Bouten and Jannson, 1995).

We briefly review a mineral cycling model described by Liu *et al.* (1991) to encapsulate the components and interactions that must be considered in a complete mineral cycling model. This particular model was applied to compare intensively monitored ecosystems in an acid rain study (Johnson and Lindberg, 1992). The model explicitly tracks mineral fluxes between the vegetation and soil and also considers interactions with atmospheric deposition and mineral weathering. These latter components were essential to assess changes in solution chemistry, soil fertility, and transfers into groundwater and streams. The model routes precipitation through the canopy and soil layers and simulates evaporation, transpiration, and deep seepage, as well as lateral flow out of the soil. The model allows soils to be separated into up to 10 strata, each of which may have different physical and chemical characteristics. The movement of water through the system is simulated with appropriate equations that take into account continuity between strata, saturated and unsaturated flow, and surface runoff. Percolation occurs between layers as a function of differences in soil permeability and water content. Lateral flow occurs when a stratum becomes saturated (Chapter 2).

Canopy chemistry is the first component associated with deposition. The model allows for separate interception of wet- and dryfall and stores a fraction of the precipitation on leaf surfaces up to a defined capacity. Chemical reactions that occur on canopy surfaces allow for direct uptake, increase in surface concentrations by evaporation, and foliar leaching in proportion to LAI. The products of dry- and wetfall interact with the surface canopy to produce throughfall that may be markedly different chemically from incident precipitation. Nutrient reabsorption is simulated as partial withdrawal of nutrients from leaves before leaf fall.

Within the soil, nutrient pools associated with soil solution, the ion-exchange complex, mineral, and soil organic matter are separately tracked. Interactions among these pools include mineralization, nitrification, anion adsorption, cation exchange, and mineral weathering. Release of nutrients from leaf litter that accumulates on the forest floor is primarily dependent on the C : N ratio of that substrate. Other decay products include nutrient and organic constituents, both solid (e.g., humus) and solution phase (e.g., organic acids). The nutrients released enter the solution phase where they are available for uptake by vegetation or the exchange complex, and for transport through the litter and soil horizons by percolation and lateral flow. The dissolved organic matter, which has a preponderance of acidic functional groups, generally depresses solution pH but also serves as a buffer by minimizing subsequent changes in pH. Organic acid concentrations are modeled to decrease with depth as the dissolved material is adsorbed, precipitated, and mineralized from upper to lower horizons.

Nitrogen is tracked as it is mineralized as ammonium through its possible conversion to nitrate. The series of reactions results in the loss of acid-neutralizing capacity. The movement of mobile nitrate ion through the profile as a strong acid accelerates cation leaching. Because the model allows for seasonal variations, it accounts for uptake of nitrogen during the growing season and the possible accumulation of nitrate in surface horizons during the winter under a protective snowpack. Snowmelt may flush some of the nitrate through the soil, although plant uptake may shortly thereafter deplete the same horizons.

Anion adsorption of sulfate, phosphate, and organic acids is also modeled. Sulfate adsorption is particularly important in altering acid–base chemistry when present in large amounts. Adsorption of sulfate increases the acid-neutralizing capacity of the soil solution, thereby reducing hydrogen ion exchange with base cations and the dissolution of base cations through weathering. Much of the sulfate is adsorbed into lower soil horizons, depending on the concentrations of aluminum and iron oxides and hydroxides present. Adsorption increases with decreasing pH.

High base cation exchange serves as an effective solution-phase buffer by limiting changes in soil solution pH through exchange with hydrogen and aluminum ions. If excess base cations are introduced, they are absorbed and hydrogen and aluminum ions released.

Released hydrogen ions are neutralized by reactions with bicarbonate and carbonate, and the aluminum is precipitated as aluminum hydroxide. The cation-exchange process proceeds rapidly and provides effective short-term buffering. Without weathering, however, many soils lose their buffering capacity within 50 to 200 years (Schnoor and Stumm, 1984).

Mineral weathering is normally a slow process, but one which releases base cations and silica into solution. The model predicts these reactions as a function of the mass of minerals present and the solution-phase hydrogen ion concentration, largely buffered through base-exchange processes against the direct impact of acid rain. In soils with low cation-exchange capacities, weathering rates are particularly important in assessing long-term nutrient status (Chapter 5).

In the uppermost soil layers, seasonal variation in soil solution chemistry is likely where atmospheric inputs are high (Fig. 4.15), whereas in the lower soil profile, buffering is sufficient so that decades are required before significant changes can be perceived (Liu *et al.*, 1991; Johnson and Lindberg, 1992). Once confidence is acquired in the model assumptions by monitoring seasonal variation in solution chemistry, the effort can be shifted toward predicting longer trends on the basis of annually integrated estimates of nutrient and organic matter loss or accumulations, changes in soil profile features, and other subjects considered in later chapters.

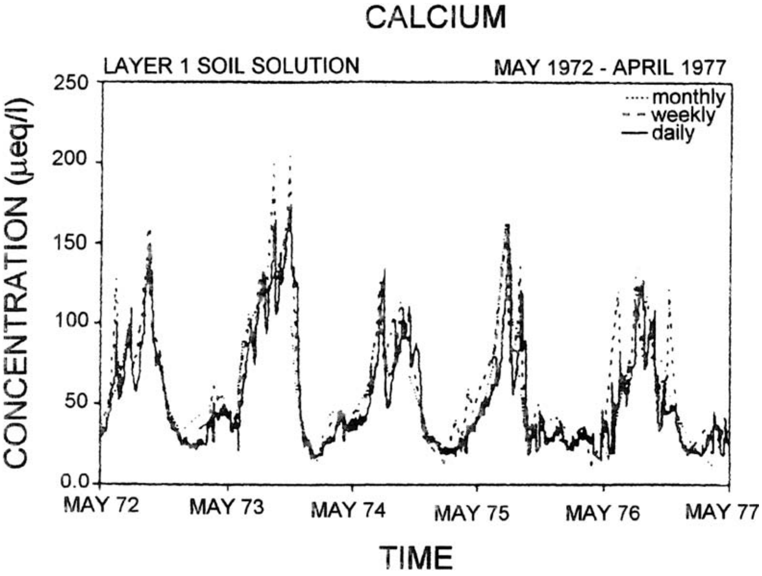

FIGURE 4.15. Mineral cycling models are able to predict changes in soil solution chemistry at frequent intervals in response to changes in the flux of nutrients in precipitation or from snowmelt. In this example, a sensitivity test shows that calcium concentrations in the uppermost horizon of a heavily leached soil can be predicted nearly as well at monthly intervals as at daily or weekly time steps. (From Liu *et al.*, 1991.)

VI. SUMMARY

The extent to which plants are able to acquire and maintain a balance of nutrients strongly controls their growth rate and ultimately the composition of forests. Nutrient balance can conveniently be defined in reference to the mineral nitrogen content in leaves. Imbalances in the availability of nutrients lead to a decrease in nutrient use efficiency. In some cases, the form in which a nutrient appears is also significant because species differ in their selective acquisition and in the way that surplus nutrients are stored. Moreover, in the soil, some forms of phosphate (organic) and nitrogen (NH_4^+) are more available to plants than others that are adsorbed, fixed, or more easily leached. The extent to which a nutrient is derived from soil, recycled within the vegetation, or is dependent on atmospheric inputs is an important consideration in the long-term management of forests. Likewise, the species composition of a forest is important because evergreen and deciduous species differ in their ability to capture nutrients from the atmosphere, extract them from the soil, and maintain a litter substrate with a favorable nutrient balance and rapid turnover.

Throughout this chapter we have illustrated how various stable isotopes (and ^{14}C) provide a quantitative basis to separate the sources of some nutrients, and to follow differential uptake and cycling of selected nutrients through the ecosystem. We advocate broader application of this methodology in testing models and in evaluating historical and future changes in ecosystem responses.

From a scaling standpoint, the distribution of broad soil groups associated with different climates and parent materials serves as a first-order stratification of the mineral cycling potential of forest ecosystems. The ratios forest floor litter mass : annual litterfall and mass of litter : nutrient content have special value because these are easily obtained and closely coupled to primary production, decomposition, and general nutrient availability. Broader generalizations may be possible through various satellite-derived measures of canopy nitrogen and lignin content, and through the annual turnover that may be compared against predictions from a range of increasingly mechanistic simulation models.

Models that combine all the relevant processes involved in mineral cycling are by necessity complicated, but they present an important advancement in our ability to evaluate the implications of various policies. Because they can be run at a variety of time steps with varying amounts of internal detail, mineral cycling models provide a means of testing simplifying assumptions and assessing the degree of error introduced by integrating at progressively longer time steps. They deserve, therefore, to be well documented and made more widely available for scientific and practical use.